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# THE EVALUATION OF CARBOTRAP-B AND CARBOSIEVE SIII FOR VOLATILE ORGANIC COMPOUNDS SAMPLING APPLICATIONS THAT USE THERMAL DESORPTION-GAS CHROMATOGRAPHY AS THE ANALYTICAL TECHNIQUE

**A Thesis Submitted to**

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**by**

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**for the degree of**

**Doctor of Philosophy**

**Based on research carried out under the direction of**
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**June 2002**

## DECLARATION

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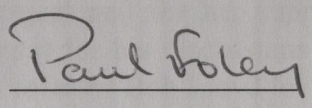

Paul J. Foley

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## Summary

The effects of concentration, temperature and humidity on the value of breakthrough volumes ($V_b$) for forty-four volatile organic compounds (VOC) on Carbotrap-B have been determined using the frontal chromatography method. The same method was used to determine the effects of concentration and humidity on the values of $V_b$ for 19 VOC on Carbosieve SIII. Carbotrap-B is a Graphetised Carbon Black that is reported to be a Class I adsorbent as defined by the Kislev classification of adsorbents. Carbosieve SIII is a Carbon Molecular Sieve that is reported to be a weak Class III adsorbent. Experimental data for both confirm that Carbosieve SIII behaves as a weak Class III adsorbent and exhibits specific adsorbent effects with adsorbates such as ethyne. Carbotrap-B is shown not to behave as an ideal Class I adsorbent as it exhibits specific adsorption effects with benzene. Of the forty-four VOC adsorbed onto Carbotrap-B only one, propan-1-ol, had values of $V_b$ of less than 1L/g (instant breakthrough) at $mg/m^3$ concentrations. This suggests it to be an ideal adsorbent for VOC sampling applications for the range of VOC the adsorption of which was investigated. Carbosieve SIII was shown to be a stronger adsorbent than Carbotrap-B for the VOC studied. However, care needs to be taken to avoid saturation of the adsorbent as this may affect its reusability. There were problems with sampling ethyne on Carbosieve SIII.

From the measured $V_b$, original isotherms have been produced and adsorption parameters based on the Langmuir, Freundlich and Dubinin-Polyani adsorption models have been calculated. The calculated adsorption parameters describe the behaviour of these VOC on both Carbotrap-B and Carbosieve SIII under the experimental conditions and are useful data for VOC sampling applications including modelling of pumped and diffusive sampling. An example of how some of the calculated parameters were successfully applied to modelling diffusive sampler behaviour of Carbotrap-B will be given. Each of the adsorption models give similar results and gives good agreement with the experimental data in the $mg/m^3$ concentration range. It will be shown that contrary to previous assumptions the Langmuir adsorption parameters obtained at $mg/m^3$ concentrations cannot be used to predict $V_b$ at $\mu g/m^3$ concentrations and the calculated Langmuir parameter $m_{max}$ does

not represent the maximum adsorbent capacity. The Freundlich and Dubinin-Polyani models are shown to be more successful in describing the adsorption behaviour of the VOC at $\mu g/m^3$ levels where $V_b$ is independent of concentration. Experimentally measured values of $V_b$ for several VOC at $\mu g/m^3$ concentrations provide a simple relationship that makes it possible to use the $mg/m^3$ adsorption parameters to calculate values of $V_b$ for other VOC at $\mu g/m^3$ levels without having to extrapolate data from one concentration region to another.

Temperature is shown to have an inverse effect on the measured values of $V_b$ for several VOC on Carbotrap-B. The measured values of $V_b$ are used to calculate the isosteric heats of adsorption ($-\Delta H^{st}$) for some of the compounds using the Van't Hoff equation. The calculated values of $-\Delta H^{st}$ are shown to be of the same magnitude as those typically recorded for physisorption processes. The experimentally measured values of $V_b$ provide a simple relationship from which the change in measured $V_b$ due to a change in the temperature of adsorption can be calculated.

The effect of humidity has no effect on the measured values of $V_b$ for VOC on the hydrophobic Carbotrap-B. Carbosieve SIII on the other hand is a hydrophilic adsorbent and this property of the adsorbent affects the measured values of $V_b$ in two ways. There is a negative effect for the values of $V_b$ for the adsorption of non-polar VOC. The values of measured $V_b$ of polar VOC such as ethanol increase as the humidity content of the atmosphere from which it is been sampled increases.

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# CHAPTER 1

## INTRODUCTION

## 1.1 Introduction and aims

Organic compounds that evaporate readily and with a vapour pressure greater than 0.1mmHg (0.0133kPa) at 298K belong to the group known as Volatile Organic Compounds (VOC) (Harper 2000). They contribute to air pollution directly, or through chemical or photochemical reaction forming secondary air pollutants (Komenda *et al* 2001). They are ubiquitous atmospheric species that can be attributed to both biogenic and anthropogenic emissions (Hester and Harrison 1995). VOC are emitted in large quantities from biogenic sources such as vegetation and natural processes. Anthropogenic sources of VOC include the agricultural, construction, manufacturing, and transport industries, as well as electricity generating stations. VOC pollution from anthropogenic sources is an unfortunate side effect of modern economic and social activity (EU Publication 1998). With estimated global emission rates of 1150 Terra g $yr^{-1}$, biogenic emissions dominate over those from anthropogenic sources by one order of magnitude (Guenther *et al* 1995). VOC comprise a wide range of compounds including hydrocarbons, oxygenates and halogen containing compounds. Many of these compounds cause adverse health effects in humans after short term and/or chronic exposure and they account for a large proportion of the 189 hazardous air pollutants (HAP) listed in the 1990 US EPA Clean Air Amendment Act (USEPA 1994, WHO Document 1999). Several VOC have been shown in laboratory trials to exhibit carcinogenic or mutagenic properties (Ott and Roberts 1998, Clicquot de Mentque 1998).

Historically the monitoring of these compounds has concentrated on short-term exposure to VOC in the workplace (Woolfenden and Graham 1996). It is only recently that the effects of chronic exposure to ambient atmospheric levels of these compounds have been taken into consideration. In 1996 the World Health Organisation (WHO) published air quality guidelines for Europe (WHO, 1996) that along with those for the classical pollutants also contained guidelines for VOC such as benzene, toluene and styrene. As the demands of modern society increase and knowledge of the toxicity of VOC improves, the effective control of the emission of these compounds to the atmosphere is becoming a primary objective for many worldwide regulatory bodies (EU Publication 1998). Exposure limits need to be set to control the exposure of the population to VOC, whether it be workplace exposure or

exposure at ambient concentrations. The concentration of VOC is a vital parameter in the establishment of exposure limits. Unfortunately it is difficult to quantify actual population exposure to ambient levels of VOC. Although urban background concentrations of compounds such as benzene, toluene and xylenes (BTX) are often continuously monitored, recent work has shown that the levels measured by fixed stations do not reflect those to which the population is actually exposed (Gonzalez-Flesca *et al* 1999). In order to determine the real exposure of the population, widespread multi-site sampling campaigns, incorporating both indoor and outdoor monitoring as well as personal exposure monitoring, are necessary. These campaigns can also be used to validate pollutant dispersion models in addition to providing realistic population exposure models (Cocheo *et al* 2000). These kinds of accurate measurements of population exposure will become even more important as the European Ambient Air Framework directive is put in place (EU Directive 1996).

The European Ambient Air Framework directive is the European Commisions accepted strategy that will be used to regulate the emissions of pollutants, improving air quality and monitoring the exposure of the population to ambient air pollutants. The Framework sets binding air quality objectives for a range of specific pollutants. It requires each member state to carry out an assessment of the quality of ambient air and to devise plans and programmes of action to be initiated where ambient air quality fails to meet the specified criteria. It also lays down provisions for a complete and coherent system for gathering, reporting and the publication of information. It provides for the adoption of daughter directives for each of the following key ambient air pollutants.

- Sulphur Dioxide
- Nitrogen Dioxide
- Particulate matter
- Carbon Monoxide
- Ozone
- Polyaromatic Hydrocarbons
- Lead
- Mercury
- Arsenic
- Nickel
- Cadmium
- Benzene

The daughter directives will set the limit values and alert thresholds for each of these pollutants. The limit value is defined as the level of a particular pollutant in the air below which, according to current scientific knowledge, there are no significant

detrimental effects on human health or the environment. It comprises both concentration and time components. The margins of tolerance and deadlines for reaching the respective limit values will be specified in the directives. Each directive will also lay down the criteria and techniques for the measurement of pollution concentrations and define reference measurement and sampling techniques. In order to define these reference methods and successfully implement the directives a large volume of relevant data is required. The directive of interest to this thesis is the benzene daughter directive that establishes exposure limits for benzene in ambient air to $5\mu g/m^3$ (EU Directive 1998). Daughter directives for other VOC are also likely to be proposed and adopted in the future. Reference methods chosen for the benzene directive have been based on data obtained using an "indirect" measurement technique. A "direct" technique was used to obtain the experimental results reported in chapter 4 of this thesis. The data obtained by the "direct" technique are more relevant to the chosen reference methods and so it is hoped that the data reported in this thesis will add to the ever growing volume of data required to implement the directives. The following discussion describes the reference methods as well as defining both the "indirect" and "direct" techniques and the relevancy of both to the reference methods and the directive.

Various measurement techniques have been developed for monitoring VOC concentrations in air (Fox 1997, Groves *et al* 1998, Dewulf and Langenhove 1999, Fox 1999, Harper 2000). Concentrations may vary with both space and time and the measurement techniques need to take account of these fluctuations to provide a result that will be useful for the intended purpose. Measurements may be designed to detect maximum concentrations or concentrations that exceed limit values, or concentrations averaged over a certain sampling period. One method of measuring VOC concentration involves on-site analysis using direct-reading instruments with fast response times (Harper 1994). Infrared spectrometers or portable on-line samplers and analysers have been used for this purpose (Fox 1997 and 1999). This method has the disadvantage of being very costly and this reduces the actual number of operational sites at any one time. Also many instruments are neither sufficiently sensitive nor selective in their measurements to give useful data. Other limitations also exist, such as stability, the provision of a secure and safe power supply, and field calibration.

Another approach is to take a sample in the field and send the sample for analysis to a specialised laboratory. This is a more common approach and in most cases more practical as VOC are normally found in trace concentrations and most of the analytical techniques require an enrichment step. Several sampling techniques have been used and these include:

- Cryogenic sampling, which involves passing the sample through a loop immersed in liquid nitrogen or argon in order to trap the VOC. The storage of samples and the provision of the cryogenic fluids may pose some problems (Dewulf and van Langenhove 1997, Kivi-Etelatalo *et al* 1997, Moschonas and Glavas 1997).

- Absorption of the VOC into a liquid using an impinger. A known volume of air is passed through the liquid that either reacts chemically with or physically dissolves the analyte of interest. This method is not a preferred technique because liquids may leak or spill and the liquids that must be used are often corrosive or poisonous (Harper 1994, Baya and Siskos 1996).

- Chemical collection involving collection of the analyte through reaction with a liquid coated onto a solid support. The reaction can be made very specific and the chemical derivative is more often than not easier to analyse than the original analyte. This technique is very practical, particularly when specificity is required during the sampling step (Harper 1994).

- Sampling of the atmosphere into a passivated canister involves the sampling of the whole air matrix into a pre-cleaned evacuated canister. The disadvantages of this method are mainly logistical, as the canisters require relatively complex sampling apparatus and stringent clean-up procedures between samples. The canisters themselves are bulky to transport and are relatively expensive (Dewulf and van Langenhove 1997)

- Adsorption onto solid adsorbents by either dynamic or passive sampling. This is a popular sampling technique. Dynamic sampling involves drawing a

volume of air through a tube containing a bed of solid adsorbent. Passive involves diffusion of the molecules onto the adsorbent surface. Analysis normally involves a chromatographic technique. Both dynamic and passive sampling have been chosen as standard reference methods for the daughter directive for benzene (Harper 1994, Allen *et al* 1996, Bates *et al* 1997, McClenny and Colon 1998).

The principal aim of this thesis is to study the use of solid adsorbents for VOC sampling applications. The method to be used involves dynamic sampling onto solid adsorbents.

For dynamic sampling applications, the suitability of an adsorbent for VOC sampling applications depends on the physical and chemical nature of both the adsorbent and the adsorbate. The adsorbent should have a high adsorption capacity for the adsorbate of interest (Crisp 1980). The efficiency of an adsorbent for adsorbing any particular adsorbate is determined by many factors but as yet, no one physical characteristic (e.g. boiling point, vapour pressure, molecular weight, polarisability etc.), of the adsorbate or the adsorbent has been identified that consistently correlates with adsorption capacity (Moyer 1983). The perfect adsorbent is one that will reversibly collect all compounds efficiently over the full concentration range of interest and under all environmental conditions and which facilitates the subsequent use of an easy analytical technique at the lowest possible cost (Harper 1994). In reality this is not easy to achieve. Commercial adsorbents should possess the same adsorption characteristics from batch to batch and because they are packed into tubes and used several times they should have sufficient mechanical strength to retain their shapes and sizes. A number of important parameters define the suitability of an adsorbent for use in the sampling of VOC.

- ***Desorption or recovery efficiency*** is defined as the ratio of the mass of analyte recovered by the desorption step to the mass of adsorbate sampled onto the adsorbent. The surface of the adsorbent should be chemically inert to allow complete recovery. Also the adsorbent should have a good thermal stability to ensure efficient desorption and that no undesired changes or

reactions should occur during the desorption step (Ciccioli *et al* 1976, Bertoni *et al* 1981, van den Hoed and Halmans 1987, Bishop and Vallis 1990, Cao and Hewitt 1993, Mastrogiacomo *et al* 1995).

• ***Storage stability*** which is defined as the ability of the adsorbent to retain an adsorbed species over a period of time, under normal storage conditions, without loss of the adsorbed species through desorption or reaction. Solvent spiking and gas phase spiking of the adsorbent are two techniques used in the determination of the storage stability of an adsorbent. Stability measurements are carried out by sampling atmospheres of known VOC concentrations and storing the samples under predetermined conditions for certain fixed periods of time before analysis (Moyer 1983, Peters and Bakkeren 1994, Helmig D 1996, Dewulf and van Langenhove 1997, Dettmer and Knobloch 2000)

• ***Safe Sample Volume***. To be analytically useful the sampling of VOC should be as quantitative as possible. The Safe Sampling Volume ($V_s$) is defined as the volume of air that can be drawn through the sampler without appreciable sample loss in the effluent. When such loss occurs then there is said to be breakthrough. The volume at which breakthrough occurs is known as the breakthrough volume $V_b$. $V_s$ is calculated as a predefined fraction of $V_b$ (Coppi *et al* 1987, Harper 1993, Peters and Bakkeren 1994, Baya and Siskos 1996).

• ***The affinity of the adsorbent for water***. If the affinity of the adsorbent for water is too large it may result in possible interferences with the GC-analysis. In cryogenic sampling this can cause blockage of a cryogenic trap due to the formation of ice (Helmig and Vierling 1995, Dewulf and van Langenhove 1997).

In addition to the above physico chemical properties of the adsorbent, a number of several environmental factors such as temperature, adsorptive concentration and the relative humidity of the air may also influence the effectiveness of the adsorbent (Moyer 1983, Dewulf and van Langenhove 1997).

The breakthrough volume, $V_b$, is defined as the volume of a gaseous sample that passes through an adsorbent bed before a given fraction of the analyte is eluted from the adsorbent. It is an important parameter in defining the suitability of a solid adsorbent for active sampling. In the early applications of solid adsorbents this parameter was determined by means of elution chromatography and was calculated as a function of the retention volume and the number of theoretical plates in a chromatographic system using the adsorbent as the stationary phase (Raymond and Guiochon 1975, van der Straeten et al 1985). As a result, extensive accounts of retention volumes have appeared as guidelines in the use of adsorption systems (HSE Method 1993, ISO/DIS Method 1999). An implicit assumption of this retention volume model was that the retention volume did not depend on the concentration of the VOC. Breakthrough volumes can also be determined by the frontal chromatography method (Harper 1993). This method involves continuously passing a flow of air with a known VOC concentration through an adsorbent bed. The concentration of VOC in the effluent at the exit of the adsorbent bed is monitored. $V_b$ is determined to be the volume of air that has passed through the adsorbent bed just up to the point where VOC is detected in the effluent stream. Parameters of the airflow such as temperature, humidity, VOC concentration and number of adsorbing species can be all studied using this method. The results obtained from the frontal chromatography method are therefore more appropriate for VOC sampling applications because the actual sampling conditions can be reproduced during measurements of $V_b$ (Harper 1995, Bertoni and Tappa 1997).

As mentioned above both dynamic sampling and passive sampling of VOC onto an adsorbent bed have been chosen as reference sampling methods for the daughter directive for benzene. Consequently a full knowledge of solid adsorbents with regard to VOC adsorption at a wide range of concentrations and environmental conditions will be necessary to fully implement this directive. Although a considerable amount of information in this area can be found in the literature (Pankow *et al* 1998), hardly any information dealing with breakthrough volumes of complex atmospheres under various environmental conditions is available (Comes *et al* 1993). Much work has been carried out on $V_b$ determinations by the retention volume method (Harper 1993). This method only allows for a qualitative comparison of different adsorbents (Bertoni and Tappa 1997). Also, $V_b$ measurements made by this method are not suitable for the

investigation of the effects of various environmental parameters on the values of $V_b$ itself. There have been several studies carried out to determine the effect of competitive effects, temperature, concentration, relative humidity and flow rates on values of $V_b$ (Harper 1993, Helmig and Vierling 1995, Simon *et al* 1995, McClenny and Colon 1998). The majority of these studies, however, have concentrated on the effects that these parameters have on the storage stability (Peters and Bakkeren 1994, Helmig 1996, Dettmer and Knobloch 2000) and thermal desorption efficiencies (Bertoni *et al* 1981, van den Hoed and Halmans 1987, Cao and Hewitt 1993) of the adsorbents, i.e., the application of the adsorbents to the analytical techniques and not to the actual sampling applications of the adsorbents.

Several models have been developed to describe mathematically the process of the adsorption of gaseous molecules onto a solid adsorbent. Among the earliest developed were the Langmuir, Freundlich and Dubinin-Polyani models of adsorption and each of these will be discussed in more detail in Chapter 2. From experimentally measured values of $V_b$, isotherms based on each of these models can be drawn (Azou *et al* 1992, Comes *et al* 1993, Cal *et al* 1994). Adsorption parameters for each model can then be calculated from these isotherms. The adsorption parameters describe the adsorption behaviour of the VOC studied on the adsorbent over the range of concentrations studied assuming that the model accurately describes the adsorption process involved. By calculating the adsorption parameters for a range of compounds over a range of different environmental conditions, the adsorption behaviour of similar compounds can be predicted. These parameters can be used practically as an efficient tool for optimising and developing an effective sampling strategy for monitoring VOC concentrations in the ambient atmosphere over a wide range of environmental conditions.

There have been some studies, using the frontal chromatography method, in which experimentally derived isotherms have been compared to model isotherms and adsorption parameters calculated for the adsorption systems involved, but so far these have involved only the adsorbents Tenax GC and activated charcoal (Azou *et al* 1992, Comes *et al* 1993, Cal *et al* 1994, Comes *et al* 1998a and 1998b). In previous studies, Langmuir adsorption isotherms for the adsorption of VOC, in the $mgm^{-3}$ concentration range, on Tenax at ambient temperatures were determined using

breakthrough volumes determined by the frontal chromatography method (Comes *et al* 1993 and 1998a and 1998b). This work showed that breakthrough volumes, in this concentration range, depended on the VOC concentration, a fact that was not possible to measure using the retention volume method. Langmuir equations for the prediction of solid adsorbent breakthrough volumes for single and multi-component mixtures were also derived. An assumption, not tested at the time, was made that these equations could be used to determine breakthrough volumes in the $\mu gm^{-3}$ range by simple extrapolation of the $mgm^{-3}$ range isotherm to lower concentrations.

Gas Chromatography (GC) is the most commonly used technique for the analysis of sampled VOC. Most modern analytical apparatus incorporates a pre-concentration step in the analytical chain. Solid adsorbents have been extensively employed and one can expect further expansion and development of their use. The integrity of the sample must be observed during the sampling, transport and analysis stages. When GC is used as the analytical technique the sampled VOC need to be desorbed from the adsorbent and injected into the GC column. Two methods normally used for desorbing VOC from the adsorbent are solvent extraction and thermal desorption. Although both methods boast advantages and disadvantages, thermal desorption is now becoming more widely accepted. An important reason for this is that solvent extraction usually involves the use of toxic solvents, so that as laboratory regulations on chemical exposure limits become more stringent, thermal desorption is becoming the more environmentally friendly of the two methods. An excellent review of adsorbents used for both methods has recently been published (Harper 2000). The two adsorbents to be used in this project were chosen not only for their applicability in the sampling of VOC but also for their suitability to thermal desorption.

The two adsorbents selected, Carbotrap-B and Carbosieve SIII, are both commercially available adsorbents, supplied by Supelco (Bellefonte, PA, US). Both are carbon adsorbents and the characteristics of each are described in Section 2.2 of this thesis. There are many other commercially available adsorbents and some, like Tenax, have been studied more thoroughly than the two chosen here. The main criteria for choosing both Carbotrap-B and Carbosieve SIII were their applicability to thermal desorption-gas chromatography as they are thermally stable up to 673K. They also

have good desorption efficiencies and storage stabilities. These adsorbents are reported by the manufacturer to cover the range of VOC of interest to this work, (Carbotrap B: $C_5$ - $C_{12}$ aliphatic hydrocarbons, halogenated hydrocarbons and BTX compounds, Carbosieve SIII: $C_1$ - $C_5$ hydrocarbons and halogenated hydrocarbons).

The work that will be reported in this thesis involved the study and characterisation of the two solid adsorbents, Carbotrap-B and Carbosieve SIII, for VOC sampling applications. The measurement of the values of $V_b$ for sixty-three VOC on these adsorbents was carried out using the frontal chromatography method. This method is a dynamic technique. The VOC were chosen from the list of 189 hazardous air pollutants (HAP) listed in the 1990 US EPA Clean Air Amendment Act (USEPA, 1994). The effects of the following environmental parameters:

- Adsorptive concentration
- Temperature
- Humidity

on the measured values of $V_b$ of the VOC of interest were studied. The measured $V_b$ were used to determine isotherms based on the Langmuir, Freundlich and Dubinin-Polyani adsorption models. From these isotherms adsorption parameters were calculated. The adsorption parameters characterised the adsorption behaviour of the VOC on the adsorbents under the environmental conditions employed during the $V_b$ determinations. The overall aims of the research work described in this thesis are:

- To provide experimental data on the breakthrough volumes of the VOC of interest on the chosen adsorbents during dynamic sampling,

- To study the effects of changes in environmental conditions on these data for $V_b$.

- To calculate adsorption parameters for the systems using the Langmuir, Freundlich and Dubinin-Polyani models.

The isotherms and adsorption parameters that will be reported will be useful data for pumped tube sampling applications as well as for adsorption modelling applications for diffusive samplers. As will be evident they provide calculated values of $V_b$ that are very close to experimental results and allow the effects of concentration, humidity and temperature to be taken into account. As new regulations and sampling methods for VOC concentrations in ambient and workplace atmospheres are put into place, more data on the behaviour of solid adsorbents as well as improved modelling techniques will be required to meet their demands. Regarding EU directives it is hoped that the values of experimentally measured $V_b$ and calculated adsorption parameters reported in this thesis can be used as efficient tools for developing effective sampling strategies for monitoring ambient VOC concentrations using the reference methods chosen. As the data was measured for a wide range of environmental conditions they can be used to develop strategies in any part of the EU. The calculated adsorption parameters can also be applied to modelling purposes that are described in the Ambient Air Framework Directive that was mentioned earlier on.

This thesis comprises four chapters and is presented in theoretical, experimental and results-discussion sections. Chapter two begins with brief descriptions of the adsorption process and of the chosen adsorbents. The retention volume and frontal chromatographic methods of $V_b$ determination are then defined and described. The theoretical basis for the Langmuir, Freundlich and Dubinin-Polyani models of adsorption is introduced to explain how adsorption parameters can be calculated from the values of $V_b$ that are measured. This chapter comprises a brief review of the literature references so far available on these topics. Chapter three describes the experimental techniques used to generate and sample the atmospheres with known VOC concentrations. The analytical techniques employed to determine $V_b$ and VOC concentrations are also discussed. Chapter Four presents the experimental results for $V_b$ and also the isotherms and calculated adsorption parameters that are derived from the data. The effects of humidity, concentration and temperature on the experimental values of $V_b$ are quantified experimentally and discussed. The results that are reported will compare values of $V_b$ that have been measured at both $mgm^{-3}$ and $\mu gm^{-3}$ concentrations. The measured values of $V_b$ at $\mu gm^{-3}$ concentration will be compared to those that have been extrapolated from values calculated at $mgm^{-3}$ concentrations

using calculated adsorption parameters. This comparison will be used to test the validation of such usage of adsorption parameters as has been previously assumed. The experimentally measured breakthrough volumes are also used to calculate the values of the isosteric enthalpies of adsorption ($-\Delta H^{st}$) for some of the hydrocarbons and which can be used to predict the effect of temperature on $V_b$. Finally an example of how the calculated adsorption parameters have been applied to a diffusive sampler model is described.

# CHAPTER 2

## THEORETICAL DISCUSSION AND BACKGROUND

## 2.1 Adsorption and Adsorption Isotherms

Adsorption and adsorption processes have been studied for several centuries. Vast volumes of data and information on adsorption have been published over the years so that an exhaustive treatment of adsorption theory and adsorption isotherms is beyond the scope of this thesis. While an understanding of the adsorption process and several isotherms was necessary to manipulate the experimental results obtained during this project, the aim of the project was to use those adsorption isotherms as simple tools to calculate adsorption parameters from experimental values of $V_b$. These adsorption parameters were intended to help devise methods for VOC sampling applications and to be used as data for pumped and diffusive sampling modelling applications. A brief discussion of adsorption processes and of the three isotherms used is given. The experimental $V_b$ were not intended to be used to either prove or disprove existing theories of adsorption

Extensive reports explaining adsorption processes from thermodynamic (Katsanos *et al* 1998), statistical (Vidal-Madjar *et al* 1975), kinetic (Young and Cromwell 1962), and adsorption potential theory (Kouznetzov *et al* 1969) approaches are widely available in the literature. Further detailed information on adsorption and the various adsorption isotherms that have been developed can be found in a review published by Brivio and Grimley, (1993). Also the list of references provided with this chapter is a useful source of information for the adsorption process and the relevant adsorption isotherms. The aim of this section is to briefly define adsorption and introduce adsorption isotherms in general. Three different adsorption models were used to calculate adsorption parameters from experimental $V_b$. These models will be discussed individually. The following references provided most of the information used to develop the following discussion of adsorption and adsorption isotherms: Brunauer (1945), Young and Cromwell (1962), Brunauer et al (1967), Cromwell (1967), Kovach (1978), Gregg and Sing (1982) and Atkins (1987).

### 2.1.1 Adsorption

When a gas is allowed to come to equilibrium with a solid or liquid surface, the concentration of gas molecules is always found to be greater in the immediate vicinity

of the surface than in the free gas phase, regardless of the nature of the gas or surface. The process by which this surface excess is formed is termed *adsorption*. *Absorption* on the other hand involves bulk penetration of the gas into the structure of the solid or liquid by some process of diffusion. The term adsorption appears to have been introduced by Kayser (1881). McBain, (1909), proposed the term *sorption* to embrace adsorption on the surface, absorption into the bulk of the adsorbing species and capillary condensation within any pores present in the system. The term *sorption* generally refers to a situation where both adsorption and absorption are taking place. A general adsorption system is shown in Fig 2.1 and normally has three components:

- An adsorbent
- An adsorbate
- An adsorptive

The adsorbent is the surface onto which the gaseous molecules are adsorbed. The adsorptive refers to the gas molecules in the free gaseous phase. When adsorptive molecules collide with the adsorbent surface, a number of outcomes are possible. The adsorptive molecules may be reflected elastically or in-elastically. There may be a chemical reaction between the adsorptive and the adsorbent molecules or an adsorbent-adsorptive product may be formed due to forces of attraction between them.

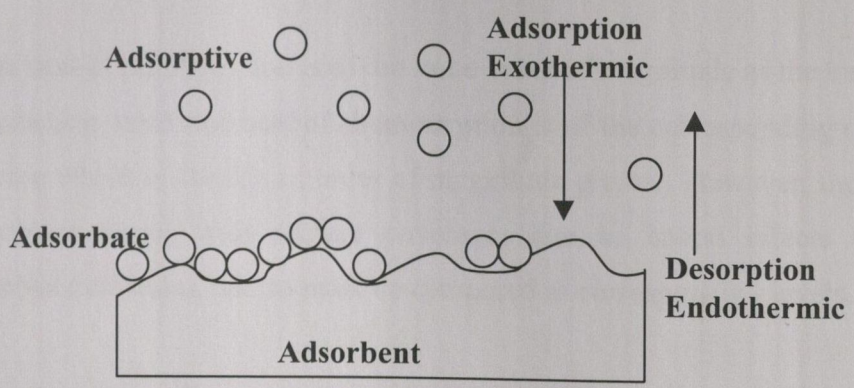


**Fig.2.1 General adsorption system**

The term adsorbate refers to the adsorbed molecules resulting from the interactions between the adsorptive and adsorbent molecules.

Adsorption of a gas on a solid is a spontaneous process. It is accompanied by a decrease in the free energy of the adsorption system. Since the process involves the loss of degrees of freedom of the gas molecules, in passing from the adsorptive to adsorbate, there is also a decrease in entropy. It follows from Eq. (2.1) that the adsorption process must always be exothermic regardless of the nature of the forces involved.

$$\Delta G = \Delta H - T\Delta S \qquad \text{Eq. (2.1)}$$

where $\Delta G$ is the change in Gibbs free energy, $\Delta H$ is the enthalpy change, T is temperature and $\Delta S$ is the entropy change. The forces that bring about adsorption are of two main kinds, physical and chemical. Molecular interaction forces cause physical adsorption, more commonly referred to as physisorption. The formation of a physically adsorbed layer is analogous to the condensation of a vapour. Chemical adsorption, or chemisorption, involves transfer of electrons between the solid and gas molecules. The process essentially involves the formation of a chemical bond between the adsorbate and outermost layer of adsorbent atoms. The theoretical differences between physical and chemical adsorption may be clear, however in practice the distinction is not as simple as it may seem. The following parameters can be used to determine the type of adsorption:

- The heat of physisorption is of the same order of magnitude as the heat of liquefaction, while the heat of chemisorption is of the corresponding chemical reaction which is usually an order of magnitude greater. However, the heat of adsorption varies with surface coverage, due to lateral effects between adsorbed molecules, and so must be compared at corresponding levels.

- Physisorption will occur under suitable temperature and pressure conditions in any gas-solid system, while chemisorption will only take place if the gas is capable of forming a chemical bond with the adsorbent surface.

- A physically adsorbed molecule can be desorbed unchanged under

isothermal conditions by simple reducing the pressure of the system. The removal of a chemisorbed layer is far more difficult.

- Physical adsorption allows for the multi-layer adsorption whereas chemisorption only allows the formation of a monolayer of adsorbate.

- Physisorption is instantaneous, while chemisorption may be instantaneous but normally requires the availability of an activation energy for the chemical reaction.

Physisorption is the preferred process for VOC sampling and TD-GC analysis applications as it is a reversible process that allows complete recovery of the sampled compound. When chemisorption or chemical reactions occur between the analyte and the adsorbent or between adsorbed compounds they are seen as an adverse effect leading to a deterioration of the quality of the sample. (Walling *et al* 1986, Bates *et al* 2000). Physisorption involves a combination of both dispersive forces, which are attractive in nature, and short range repulsive forces for non-polar molecules. If the adsorptive and-or adsorbent molecules are polar in nature, then there will in addition be electrostatic forces. Dispersive forces derive their name from the close connection between their origin and the cause of optical dispersion. They were first characterised by London (Young and Cromwell (1962) and arise from the rapid fluctuation in electron density within each atom, which induces an electrical moment in a near neighbour and thus leads to attraction between the two atoms. Repulsive forces occur when the atoms are close enough to allow inter-penetration of the respective electron clouds. The overall potential energy, $\varepsilon(r)$, between the two atoms ca be designated by the Lennard –Jones potential as:

$$\varepsilon(r) = -Cr^{-6} + Br^{-12} \qquad \text{Eq. (2.2)}$$

The term describing the dispersive forces, $-Cr^{-6}$, was arrived at by London using quantum mechanics and was later developed by others. C represents the dispersion constants associated with dipole and quadropole interactions while r is the distance between the centres of the two atoms. The repulsive term, $Br^{-12}$, is a simple empirical

form of attempts to calculate the difference between the total energy of the bimolecular structure and the energy of the separated molecules; B is an empirical constant.

Dispersion interactions are relatively long-range forces and the energy of interaction results from small perturbations in the charge distribution on the isolated molecules. The dispersive constant C can be expressed in terms of the physical properties of the individual molecules. Considering a system containing molecules of A and B, one of the best known formulae is that of Kirkwood and Müller:

$$C = \frac{6mc^2\alpha_A\alpha_B}{\left(\frac{\alpha_A}{\chi_A}\right)+\left(\frac{\alpha_B}{\chi_B}\right)} \qquad \text{Eq. (2.3)}$$

where c is the speed of light, $\alpha_A$ and $\alpha_B$ are the polarizabilities, and $\chi_A$ and $\chi_B$ are the magnetic susceptibilities of A and B. London derived the following:

$$C = \frac{3}{2}\frac{\alpha_A\alpha_B h\nu_A^{\circ} h\nu_B^{\circ}}{\nu_A^{\circ}+\nu_B^{\circ}} \qquad \text{Eq. (2.4)}$$

where $\nu^{\circ}_A$ and $\nu^{\circ}_B$ are characteristic frequencies related to optical dispersion, and h is the Planck quantum constant. Finally a third equation, due to Slater and Kirkwood is as follows:

$$C = \frac{\left(\frac{3eh}{4\pi m^{\frac{1}{2}}}\right)\alpha_A\alpha_B}{\left[\left(\alpha_A N_A\right)^{\frac{1}{2}}+\left(\alpha_B N_B\right)^{\frac{1}{2}}\right]} \qquad \text{Eq. (2.5)}$$

where e and m are the charge and mass of the electron and $N_A$ and $N_B$ are the numbers of electrons per molecule of A and B which are involved in the interaction. These formulae help to relate the process of physisorption to certain physical properties of both the adsorbent and adsorptive molecules. They may be used to try to explain the

different adsorptive properties of various compounds with different functional groups on the same adsorbent or even to establish patterns of the adsorption of homologous compounds on the same adsorbent. One of the adsorption models that will be described in a later section uses a similar approach to that used in these equations, and attempts to determine adsorptive affinity coefficients based on the physical properties of the gas molecules.

### 2.1.2 The Adsorption Isotherm

Adsorption isotherms are simple models that make it possible to conveniently plot and display the experimental amount adsorbed, $m_{ads}$, as a function of pressure under isothermal conditions. The general equation of an isotherm is:

$$m_{ads} = f(p)_{T,\,SOLID,GAS} \qquad \text{Eq. (2.6)}$$

Considering Eq.(2.1), isotherms are essentially plots of the Gibbs free energy change as a function of amount adsorbed. The shape of the isotherm can yield qualitative information about the adsorption process and can also indicate the fraction of the surface covered, when certain assumptions are made with respect to the surface area of the adsorbent. Due to this and the fact that they can more easily be measured directly, adsorption isotherms are the most commonly used method for reporting $m_{ads}$ in adsorption studies.

Giles *et al* (1974) classified sorption isotherms based on their initial slopes and curvatures. They distinguished between high affinity, Langmuir, constant partition and sigmoidal shaped isotherm classes. To account for points of inflexion, plateaux and maxima they further distinguished subgroups in each class. The classification was based on empirical observations and did not consider the adsorption process that lead to the different isotherm shapes. Hinz (2001) attempted to apply a mathematical interpretation to each of the classes and subgroups classified by Giles *et al* (1974). However this classification covered sorption isotherms in general especially when the retention processes are unknown. Brunauer *et al* (1938) introduced a classification for adsorption isotherms especially for gas-solid systems. They suggested five basic types and these are shown in Fig. 2.2 where $V_{ads}$ is the volume of adsorbate, $p_s$ is the

pressure of the saturated vapour of the adsorbate and p is the partial pressure of the adsorptive. Type I isotherms are associated with systems where adsorption does not proceed beyond the formation of a monomolecular layer of adsorbate. The rest all involve the formation of multilayers. Type II isotherms indicate an indefinite multilayer formation after the completion of a monolayer. Type III isotherms result when the amount of gas adsorbed increases without limit as

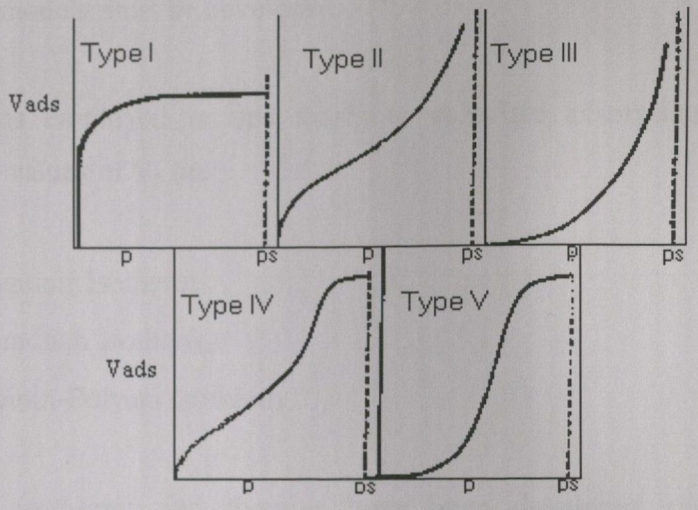


**Fig 2.2 Brunauer Classification of adsorption isotherms**

its relative saturation approaches unity. The convex structure is caused by heats of adsorption of the first layer being less that the heat of condensation due to molecular interaction in the monolayer. Types IV and V are characteristic of multilayer adsorption on highly porous adsorbents with the flattening of the isotherm at the highest pressures attributed to the complete filling of the capillaries present in the adsorbents porous structure. Type IV isotherms are variations of Type II while Type V are variations of Type III isotherms.

The simplest form of the adsorption isotherm, as expressed in Eq. (2.7), is analogous to the Henry's Law equation for absorption within liquids. The mass adsorbed, $m_{ads}$, is directly proportional to the adsorptive partial pressure.

$$\mathbf{m_{ads} = kp} \qquad \text{Eq. (2.7)}$$

where k is known as Henry's constant. This phenomenon is observed for adsorption systems where the adsorptive concentration is low, usually of the order of $ng/m^3$ or in the low $\mu g/m^3$ concentration ranges. However, under real conditions, as concentration increases the adsorption energy changes due to lateral interaction of adsorbed molecules and deviations from Eq. (2.7) takes place, which means that other equations or models must be developed.

The isotherms employed in this thesis to calculate adsorption parameters from experimental values of $V_b$ are:

- Langmuir Isotherm
- Freundlich Isotherm
- Dubinin-Polyani Isotherm

Many more isotherms and theories have been developed over the years and improvements to the above three isotherms have also been proposed. A discussion of these is again beyond the scope of this chapter and further information on other isotherms is available in the list of references quoted on page 12 of this document. The above three isotherms were chosen for their simplicity and the ease in which they could be applied to calculate adsorption parameters from experimental values of $V_b$. Each model will now be discussed in turn with one method of deriving each isotherm included in these discussions. Alternate methods that have been used to derive the isotherms will also be mentioned and references provided for each.

### 2.1.2.1 Langmuir Adsorption Isotherm

Langmuir (1916) was the first to propose an equation that described the relationship at constant temperature between the amount of gas adsorbed on a solid surface and the equilibrium pressure of the gas. Langmuir treated the adsorption equilibrium as a dynamic process: the gas molecules strike the surface where most of them are adsorbed and stay on the surface for a while before they acquire enough energy to

again leave the surface. Eventually, equilibrium is established where the amount adsorbed has a definite value and the rate of adsorption of gas molecules on to the adsorbent surface is equal to the rate of desorption of gas molecules from the surface of the adsorbent. Langmuir proposed that the surface forces were short range in nature and therefore, only those molecules striking the adsorbent surface were adsorbed while those striking already adsorbed molecules were elastically reflected back into the gas phase. The first basic assumption of the Langmuir isotherm was that adsorption was limited to the formation of a monomolecular layer of adsorbate. The Langmuir isotherm can be derived kinetically as follows. The number of molecules striking unit area of surface per unit time, $\mu'$, is given by the kinetic theory of gases as:

$$\mu' = \frac{p}{(2\pi mkT)^{\frac{1}{2}}} \qquad \text{Eq. (2.8)}$$

where p is the pressure, m is the mass of a molecule, k is the Bolztmann constant and T is the absolute temperature. The rate of adsorption of molecules per unit area of surface, $k_{ads}$, is given as:

$$k_{ads} = \alpha_o(1-\Theta_L)\mu' \qquad \text{Eq. (2.9)}$$

where $\Theta_L$ is the fraction of the surface covered with adsorbed molecules and $\alpha o$ is the "condensation coefficient" (the ratio of collisions resulting in adsorption to the total number of collisions of gas molecules with the adsorbent surface). The number of molecules desorbing from the surface, $\nu'$, depends on q, the heat of adsorption, as follows:

$$\nu' = k_o e^{-\frac{q}{RT}} \qquad \text{Eq. (2.10)}$$

where $k_o$ is a term that is dependent on temperature and R is the gas constant. The rate of desorption per unit area of surface, $k_{des}$, is given by:

$$k_{des} = \nu'\Theta_L \qquad \text{Eq. (2.11)}$$

At equilibrium $k_{ads}$ is equal to $k_{des}$ and solving Eq. (2.9) and Eq. (2.11) for $\Theta_L$ we get:

$$\Theta_L = \frac{\left(\frac{\alpha_o}{\nu'^{\mu'}}\right)}{1+\left(\frac{\alpha_o}{\nu'^{\mu'}}\right)} \qquad \text{Eq. (2.12)}$$

which can be written as:

$$\Theta_L = \frac{bp}{1+bp} \qquad \text{Eq. (2.13)}$$

where b, the adsorption coefficient is defined:

$$b = \frac{\alpha_o e^{\frac{q}{RT}}}{k_o (2\pi mkT)^{\frac{1}{2}}} \qquad \text{Eq. (2.14)}$$

Elastic collisions with the surface of the adsorbent were considered to be rare and so the value of $\alpha_o$ was considered to be close to unity. Langmuir also considered b to be constant which is equivalent to considering $k_o e^{-q/RT}$ constant. This consideration then leads onto the two other basic assumptions of the Langmuir isotherm; namely that adsorption takes place on an energetically uniform surface and that there were no lateral interactions between adsorbed molecules. Statistical and thermodynamical derivations of the Langmuir isotherm have been proposed (Brunauer, 1945). From these derivations $k_o$ has been shown to be dependent on the entropy of adsorption. The kinetic derivation may suggest that the adsorption is dependent only on the mechanism of condensation/evaporation of the gas molecules whereas, in fact, it depends on the entire sets of states, both adsorbed and gaseous.

The constancy of the variable $k_o e^{-q/RT}$ implies a constant free energy of adsorption and therefore b will only be constant if the free energy of adsorption does not vary with $\Theta$. However, the experimental energy of adsorption does change with variation in surface coverage and is also affected by lateral interactions. Therefore if Langmuir's assumptions were actually observed then very few experimental data should

accurately obey Langmuir's isotherm. This has been shown not to be true. It was suggested that variations in entropy and enthalpy due to changes in surface coverage compensate each other to such a degree as to make the free energy of adsorption approximately constant for an adsorption isotherm or at least for a considerable part of the isotherm. In short, although Langmuir's isotherm was the first to be developed and his assumptions have been shown to be simple in nature and are almost certainly an oversimplification of the real situation, the isotherm itself has been and continues to be used successfully in the interpretation of experimental data.

### 2.1.2.2 Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm is similar in nature to the Langmuir isotherm. It makes the assumption that only a single layer of adsorbent is formed. The general form of the Freundlich isotherm is an empirical expression of the relationship between $\Theta_F$, the fraction of surface coverage, and the adsorptive concentration as follows:

$$\Theta_F = k_F C^{\frac{1}{n}} \qquad \text{Eq. (2.15)}$$

where $k_F$ and n are empirical constants which depend on the nature of the adsorbent, adsorbate and also on the temperature. Zeldowitsch (1935) reviewed several attempts to give a theoretical interpretation of the Freundlich isotherm and proposed one of his own.

Freundlich's isotherm may be derived by assuming that the adsorbent surface comprises a range of adsorbent sites with each group having a different heat of adsorption associated with it. Each group of adsorption sites obeys the Langmuir isotherm so that we get a number of equations that are analogous to Eq.(2.13) as follows:

$$\Theta_i = \frac{b_i p}{1 + b_i p} \qquad \text{Eq. (2.16)}$$

where $\Theta_i$ represents the fractional surface coverage occupied by each group of adsorption sites and $b_i$ is the adsorption coefficient for each group. Therefore the overall surface coverage, $\Theta_F$, in the Freundlich model can be expressed as:

$$\Theta_F = \int_0^i n_i \Theta_i di \qquad \text{Eq. (2.17)}$$

where $n_i$ is the number of adsorbate molecules adsorbed on $\Theta_i$, the fraction of i sites covered. The assumption was made that the distribution of $n_i$ is governed by the Boltzmann distribution function. This function defines the distribution of energy among the independent particles present in a system at thermodynamic equilibrium. The sites with the higher energy of adsorption will be filled before those with lower energy of adsorption. This is expressed by the following equations:

$$n_i = n_o \exp^{-\frac{q_i}{q_o}} \qquad \text{Eq. (2.18)}$$

$$b_i = b_o \exp^{\frac{q_i}{RT}} \qquad \text{Eq. (2.19)}$$

where $n_o$ is the total number of adsorbate molecules, $q_i$ is the adsorption energy for $n_i$ molecules, $q_o$ is the adsorption energy for $n_o$ or the overall adsorption energy, and $b_o$ is the adsorption coefficient for $n_o$. T is temperature. Considering $q_i >> RT$, Eq. (2.17) can now be solved using Eq's. (2.16),(2.18) and (2.19) to give:

$$\Theta_F = (b_o p)^{\frac{RT}{q_o}} n_o q_o \qquad \text{Eq. (2.20)}$$

Once a complete monolayer of adsorbate has been formed, $\Theta_F = n_o q_o = 1$, and $q_i = 0$ as adsorption is no longer possible. Therefore the final form of the Freundlich isotherm with $n_o q_o = 1$ is:

$$\Theta_F = (b_o p)^{\frac{RT}{q_o}} \qquad \text{Eq. (2.21)}$$

The Freundlich isotherm resembles the Langmuir isotherm in shape at lower surface coverage but there is no linear portion at the origin and it remains convex to the concentration axis. It should be noted that the Freundlich isotherm is essentially an empirical equation but is found to experimental data very well. The amount adsorbed increases infinitely with increasing adsorptive concentration and so it does not show a saturation value. Nevertheless it provides a useful tool for analytical purposes.

### 2.1.2.3 Dubinin-Polyani Adsorption Isotherm

The potential theory of Polyani (1914,1916) offers no explicit isotherm equation. Instead Polyani's conception of an adsorption system considers a potential gradient of adsorption above the adsorbent surface. The force of attraction at any given point above the surface is measured by the adsorption potential, ε, which is defined as the work done by the adsorption forces in bringing a molecule from the gas phase to that point. The highest values of ε are found at the surface and the value of ε decreases with increasing distance away from the adsorbent. Polyani deduced that the amount adsorbed was a function of ε and made use of the following equation to determine ε:

$$\varepsilon = \mathbf{RT} \ln \frac{p_s}{p} \qquad \text{Eq. (2.22)}$$

where $p_s$ is the pressure of the saturated vapour of the adsorbate at a given temperature T and p is the partial pressure of the adsorptive. Polyani showed experimentally that ε was temperature invariant for a given adsorbent-adsorbate system. ε was also shown to be a function of both the adsorption and the molar volume of the adsorbate, $v_m$ as shown in Eq. (2.23). The curve obtained is called the characteristic curve because the adsorption potential does not change with temperature.

$$\varepsilon = f(\mathbf{a} v_m) \qquad \text{Eq. (2.23)}$$

where a is a parameter that defines the adsorption process. Dubinin and co-workers (Bering *et al* 1966) argued that the interpretation of the value of ε as the "adsorption potential" is physically invalid since the statement implies that in all adsorbent pores there is an equipotential surface on which the adsorbate pressure is equal to $p_s$. Instead they claim that ε should be interpreted as the differential change of Gibbs free energy, ΔG, measured during the reversible isothermal transfer of a mole of adsorbate from a bulk liquid to an infinitely large amount of adsorbate. Therefore ΔG is equal to the difference in the chemical potentials of the adsorbate in the state of bulk liquid and in the adsorbed state at the same temperature. As the term adsorption potential no longer applied to the value of ε, the modified theory of Dubinin and co-workers was called the theory of volume filling of micropores. The characteristic curve, borrowed from Polyani's theory and defined by Eq. (2.23) became:

$$\Delta G = \beta f(av_m) \qquad \text{Eq. (2.24)}$$

where β is defined as the affinity coefficient and is a parameter that relates the adsorption potentials of different compounds within an adsorption system. A reference compound, normally benzene, is given a value of β=1, to which the adsorptions of all other compounds are compared. Dubinin defined the capacity volume, $W_o$, as a constant representing the pore structure of the adsorbent that may be filled to volume W for any chemical at a given value of β. From an extensive set of experimental data and theoretical considerations (Bering *et al* 1966, Dubinin 1975), the general form of the Dubinin-Polyani isotherm was proposed as:

$$av_m = W = W_o \exp\left(-\frac{BT^n}{\beta^n}\log^n\frac{p_s}{p}\right) \qquad \text{Eq. (2.25)}$$

where B is a constant, independent of temperature and representing the pore structure of the adsorbent. Values of n vary but for this project the values chosen were n=1 (pore structures much larger than adsorbate molecules) and n=2 (pore structures similar in size to the adsorbate molecules) similar to the equations used by Reucroft et al (1971).

β has been calculated from a number of molecular physical parameters in much the same way as C, the dispersion coefficient in the Lennard-Jones equation as described in Eq, (2.2). The general format for calculating β has the adsorbate parameter divided by the reference compound parameter as given in Eq. (2.26):

$$\beta = \frac{\mathbf{par}_{\text{adsorbate}}}{\mathbf{par}_{\text{refernce}}} \qquad \text{Eq. (2.26)}$$

Dubinin and Timoyev (1946) calculated values of β from molecular polarizabilities and also from molar volumes. Molecular polarizabilities were calculated from the Lorenz-Lorenz equation:

$$\mathbf{P_c} = \frac{\left(\frac{\mathbf{M_w}}{\rho_L}\right)\left(\mathbf{n_D^2} - 1\right)}{\mathbf{n_D^2} + 2} \qquad \text{Eq. (2.27)}$$

where $P_c$ is the molecular polarizability, $M_w$ is the molecular weight, $n_D$ is the refractive index and $\rho_L$ is the liquid density. Molecular parachors calculated from molecular volumes and surface tensions have also been used to calculate β. A recent review describes the various methods used to calculate β and compares results obtained from various studies (Wood 2001).

Each of the three models can be used to draw linearised adsorption isotherms from experimental values of Vb. From these isotherms adsorption parameters, that describe the adsorption system, can be calculated. The relationships between $V_b$ and adsorption parameters will be discussed later in section 2.X.

## 2.2 Adsorbents

The term "sorbent" is a generic term that covers a wide range of materials including naturally occurring minerals, plant and animal material as well as synthetically produced liquids, gels and solid adsorbents. Each medium has its own properties and choice of applications and there are a number of factors that govern the choice of a specific medium. The technique to be used in this project was the sampling of air

through a tube containing a bed of solid adsorbent with the subsequent analysis being done by TD-GC. Some of the main advantages of this method are that adsorbent tubes are simple to produce and maintain and they are also relatively cheap compared to other methods, such as sampling with canisters. An ideal adsorbent has been described as one that is able to collect all compounds efficiently over the full concentration range of interest, and under all environmental conditions, and which will then efficiently give up all collected compounds to a simple analytical method (Harper 1994). This, unfortunately, is indeed an ideal and when choosing an adsorbent for a VOC sampling and TD-GC analysis application, it is only possible to choose an adsorbent that has as many as possible of the following properties (Melcher *et al* 1978, Crisp 1980, Moyer 1983, Dewulf and Van Langenhove 1997)

- A high capacity for the VOC of interest
- An affinity for as wide a range of VOC as possible
- Adequate mechanical strength
- Uniform particle size
- Same adsorption characteristics from batch to batch
- Good storage stability
- Chemically inert to ensure that the process is one of physisorption
- Low blank values for analysis
- Good reproducibility for repeated use
- Low affinity for water vapour, oxidising compounds and other species that may induce artifact formation and therefore loss of sample.

Most of these properties are self-evident while others may need some explanation. The adsorbent requires adequate mechanical strength to withstand the thermal shocks to which it may be subjected during analysis and conditioning of the tube as well as the mechanical shocks incurred during tube preparation and normal handling. Uniform particle size is important because this is one of the adsorbents properties that determine its surface area and hence its adsorption capacity. The adsorption capacity is a defining characteristic of an adsorbent for VOC sampling as previously discussed in Chapter 1. The low cost of using adsorbent tubes for sampling VOC is due to the

fact that the tubes can be used repeatedly after cleaning. Thus a knowledge of the reproducibility of the adsorbent tubes when used repeatedly is required.

The term sorbent applies to a wide range of media and even the term 'solid adsorbent' includes a large number of different materials. Although many exotic materials such as crab-shell (Park *et al* 1998) and dried cactus extracts (Elizalde-Gonzalez and Ruiz-Palma 1999) have been tested for their adsorptive properties, the majority of solid adsorbents that have been used for VOC sampling GC-TD analysis applications belong to one of the two groups:

- Carbon adsorbents, and
- Porous polymers

The two adsorbents chosen for this study, Carbotrap-B and Carbosieve SIII, belong to the first group and will be described in more detail after a brief discussion of porous polymers.

### 2.2.1 Porous Polymers

Porous polymers were first synthesised for use as resins in HPLC (Hollis 1973). They are copolymers the adsorption characteristics of which are determined by the proportion of monomers used in their manufacture (Crisp 1980). Commercial porous polymers comprise the Tenax, Poropak and Chromosorb series and the XAD resins. They have gained great popularity over the years. Some handling problems have been observed owing to static pick-up (Harper 1992), high backgrounds with storage (Peters 1994) and low capacities for highly volatile compounds have also been observed (Harper 1993). A review of the use of these adsorbents for air sampling has been published (Snyder *et al* 1976). More recent reviews that include discussions of these adsorbents for VOC sampling applications are also available (Dewulf and Van Langenhove 1999, Harper 2000).

### 2.2.2 Carbon Adsorbents

Carbon adsorbents have generally been developed in parallel with chromatographic adsorbents (Matisova *et al* 1995). Active carbons have long been of interest in the field of liquid chromatography while graphetized carbon blacks (GCB) were of interest in the field of non-polar gas-solid chromatography. The physical and adsorption characteristics of carbon adsorbents depend on:

- The type of starting material used in their manufacture, and
- The final stage in their synthesis.

Starting materials for carbon adsorbents range from plant material to synthetic polymers. The degree of order or structure of the starting material will ultimately determine whether or not a graphitic or amorphous carbon is synthesised by the above methods. There are four consecutive stages (Knox *et al* 1963) involved in the synthesis of carbon adsorbents:

- Homogenisation
- Carbonisation
- Volatilisation
- Graphitisation

***Homogenisation*** is the first stage of carbon synthesis. It covers all operations that lead to an improved ordering or homogenising of the structure of the starting material. It usually consists of heating the starting material at 723-973K in an inert atmosphere.

The second stage or ***carbonisation*** stage covers a number of processes. These involve coking, charring and reaction with oxidising gases such as oxygen, carbon dioxide and water vapour. The processes are carried out at temperatures ranging from 973-1473K. Carbonisation increases the carbon content of the adsorbent and also introduces some pores. The products so formed are termed active carbon and possess a high adsorptive capacity. Carbonisation also covers the processes whereby gaseous hydrocarbons are pyrolysed at temperatures between 1273-1973K to yield dense non-

porous layers of pyrolytic carbon. Carbons created by carbonisation may still have some inorganic impurities, such as sulphur or silica, present in their structure especially if they have been derived from plant or mineral matter. The impurities affect the physisorption characteristics of the adsorbent.

***Volatilisation*** involves heating the carbons to 1473-1973K in an inert atmosphere. This process removes the inorganic impurities remaining after the carbonisation stage, In doing so however, large numbers of defective sites are formed in the structure of the carbon resulting in a slight to moderate disordering of the layered effect brought about by the homogenising step.

***Graphitisation*** involves heat treatment in the region of 1973-3273K in an inert atmosphere. This results in the removal of the structural defects caused by volatilisation and increases the orderliness of the carbon structures. The extremes of final carbon structures range from amorphous, which have randomly oriented structures, to crystalline three-dimensional ordered graphitic structures. The degree of graphitization depends on the initial structure of the starting material. Most synthetic graphitized carbons assume a two-dimensional, or turbostratic, structure in which graphitic sheets are randomly orientated to one another (Warren 1941). The interlayer spacing in the two dimensional structure is slightly greater than that of perfect three dimensional graphite while the atomic spacing within the layers is slightly less. This is illustrated in Fig. 2.3.

Carbon adsorbents used for VOC sampling applications fall into one of the following four sub-groups:

- Activated carbons
- Porous carbons
- Graphitized carbon blacks (GCB)
- Carbon molecular sieves (CMS)

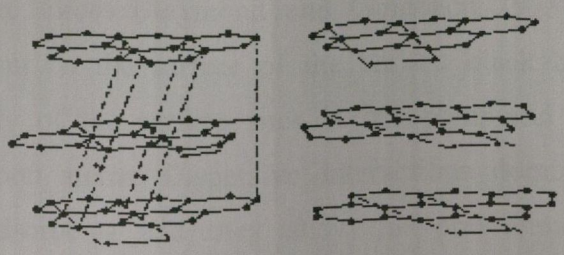

**Fig 2.3 Left - structure of perfect 3-dimensional graphite with layer registration Right - structure of 2-dimensional graphite with no layer registration**

***Activated Carbons***: are formed from natural precursors such as coconut shell (Matisova *et al* 1995), nutshell (Wartelle *et al* 2000) and palm shell (Daud *et al* 2000). They are produced by carbonisation followed by volatilisation. Their usefulness as adsorbents is due to their extensive surface areas, which are a result of their highly porous structures. Many organic functional groups are found to be still present in the amorphous carbon structure after the volatilisation stage. The presence of such groups leads to irreversible adsorption. As a result the application of these adsorbents to VOC sampling followed by TD-GC is limited.

***Porous Carbons***: the production of these carbons starts with the polymerisation of a resin mixture, such as phenol-formaldehyde, within the pore network of silica gel. The gel acts as a solid template for the polymer and the whole structure is carbonised at 1273K before the template is removed by treatment with alkali. A final heat treatment (2273-3073K) produces some graphitization and destroys micropores (Gilbert *et al* 1982). This final heat treatment influences the surface area and pore size range of the adsorbent. Porous carbon adsorbents are homogenous hydrophobic materials (Knox *et al* 1983). They are mechanically stable and can be used over a wide range of pH. The main applications of these adsorbents are as stationary phase adsorbents for HPLC.

***Graphitized Carbon Blacks (GCB)***: are prepared by heating ordinary carbon blacks to 3273K under an inert gas (Betz and Suppina 1989). This induces the growth of graphite crystallites, particles in which graphite crystals are arranged in the form of polyhedrons. These polyhedrons are between 2000-3000Å in diameter and are held

together by electrostatic forces (Raymond and Guiochon 1975). Any functional groups originally present on the surface of the carbon black before heating are destroyed. The majority of the surface sites is non-polar and corresponds to a graphitic array of carbon atoms. Dispersive interactions dominate the retention behaviour of these adsorbents and they show no preferential tendencies for compounds with functional groups (Betz and Suppina 1989). Some polar groups may be present but these can be reduced by selected preliminary treatment of the carbon blacks. Heating to 1273K in hydrogen reduces greatly if not eliminates any polar sites related to surface oxygen complexes. Washing with perchloric or phosphoric acid eliminates any carbonium-oxygen complexes or any sulphur present as sulphide (Di Corcia *et al* 1976 and 1981, Lopez-Garcon *et al* 1987, Crescentini *et al* 1987). These treatments produce an adsorbent with a homogenous or 'non-microporous' surface that is theoretically free of any surface functional groups. Adsorption occurs on the external surface of the adsorbent based on the molecular size and shape of the adsorbed molecule. The surface area of these adsorbents is determined by the extent of the graphitization. In general, the greater the graphitization, the smaller the surface area (Mastrogiacomo and Pierini 2000). GCB are thermally stable to 673K and this makes them suitable adsorbents for thermal desorption applications. (Supelco 1986, Bishop and Vallis 1990). Carbotrap-B, a GCB supplied by Supelco (Bellafonte, PA, USA), will be discussed later in more detail.

***Carbon Molecular Sieves (CMS)***: A CMS is the carbon skeletal framework remaining after the controlled pyrolysis of synthetic polymeric compounds such as polyvinylchloride, or petroleum pitch materials at temperatures usually above 673K (Betz *et al* 1989). They have a highly porous structure with almost uniform micropores (Matisova *et al* 1995) and are comprised of a disordered cavity-aperture structure made up of crosslinked crystallites. The choice and purity of the starting material and the carbonisation procedure determine the pore size and distribution as well as the particle size of the final product. Polymer impurities in the starting material substantially decrease the homogeneity of the porous structure. CMS are microporous and have a high surface area and a high retention capacity for organic compounds. However, they are easily contaminated by air impurities. CMS are also thermally stable to 673K and like GCB are suitable adsorbents for thermal desorption applications (Bishop and Vallis 1990). CMS are stronger adsorbents than GCB and

consequently are more suitable for sampling very volatile VOC (Betz *et al* 1989). Carbosieve SIII, a CMS supplied by Supelco (Bellafonte, PA, USA), will be discussed in more detail later on.

### 2.2.3 Classification of adsorbents and adsorbates

Up to this point adsorbents have been classed depending on whether they belong to the group of carbon adsorbents or porous polymer adsorbents. But it is possible that adsorbents within each of these groups will behave differently than other members of the same group towards a specific adsorbate. This difference in adsorption behaviour is due to the precursor or starting material from which the adsorbent was made and the various processes used in its manufacture. In the 1960's a lot of work was carried out on the characterisation of adsorbents and this led to a classification scheme for both adsorbents and adsorbates (Kislev and Yashin, 1969). The scheme classifies both adsorbents and adsorbates in terms of their adsorption behaviour as shown in Table 2.1. The principles exemplified in this classification of adsorbent/adsorbate interactions can form the basis for the choice of adsorbents for specific sampling applications. Adsorbents are categorised into three classes:

***Class I*** adsorbents are defined as adsorbents that possess no ionic charges, positive or negative, on the surface. Class I adsorbates interact non-specifically with the adsorbates. This means that adsorption occurs due to dispersive forces such as London or Van der Waal's forces. The non-specific surface characteristic of the adsorbent also exhibits hydrophobic properties. Examples of Class I adsorbents are the GCB sub-group of carbon adsorbents.

***Class II*** adsorbents possess localised positive charges that interact specifically with certain adsorbates. Specific interactions involve strong dipole-dipole interactions, resulting in weak electrostatic interactions between the adsorbent and adsorbate. Class II adsorbates exhibit hydrophilic characteristics and this has a disadvantage in that it may reduce the capacity of the adsorbent. An example of a Class II adsorbent is activated silica gel.

**Classification of Adsorbents**

| Class | Surface | Examples |
|---|---|---|
| I | no localised charges or ionic centres, surface is typical of graphitic carbon. | GCB |
| II | localised positive charges | Activated Silica gel |
| III | localised negative charges | Activated Charcoal. |

**Classification of Adsorbates**

| Group | Molecules | Examples |
|---|---|---|
| A | Spherical symmetrical shells $\sigma$-bonds | aliphatic hydrocarbons |
| B | Concentrated negative charge to $\pi$-bonds or lone electron pairs | aromatic hydrocarbons |
| C | Concentrated positive charge | organometallic compounds |
| D | Functional groups with both positive and negative charges | organic acids |

**Summary of interactions**

| Adsorbate Group | Adsorbent Class | | |
|---|---|---|---|
| | **Class I** | **Class II** | **Class III** |
| A | NS | NS | NS |
| B | NS | NS+S | NS+S |
| C | NS | NS+S | NS+S |
| D | NS | NS+S | NS+S |

NS: non-specific interactions

NS+S: non-specific and/or specific interactions

**Table 2.1: Kiselev and Yashin classification of adsorbents and adsorbates with a summary of the interactions between each.**

***Class III*** adsorbents possess localised negative charges that also interact specifically with certain adsorbates. An example of this type of adsorbent is activated charcoal.

Adsorbates are classified into four groups. This classification is based on the presence of certain functional groups in the adsorbate molecule. The functional groups and examples of each group are given in Table 2.1. This table also makes it evident that Class I are the only adsorbents that interact non-specifically with every group of adsorbate. For VOC sampling with TD-GC analyses applications these adsorbent are therefore the preferred choice.

***Porous and non-porous adsorbents***: Finally it is necessary to make one final distinction in this classification of adsorbents. This is the difference between porous and non-porous materials. Pore structures, pore volumes and surface areas are very influential on the adsorption characteristics of an adsorbent. Porosity in carbon adsorbents is produced during the carbonisation stage of their production, or it may simply result from the agglomeration of fine particles of adsorbent due to the attractive forces between their surfaces. The pore structure depends on particle size as well as the nature of the starting material and synthesis conditions. Pore sizes have been classified by Dubinin, (1960), according to their average width, W, as follows:

- Micropore W<20Å
- Mesopore 20Å > W<500Å
- Macropore W>500Å

Kislev and Yashin (1969) also devised a classification of adsorbents based on their pore size and surface area as follows:

***Type I - Non-porous adsorbents***: This group comprises adsorbents with amorphous or crystalline molecular structures typically having specific surface area varying between 0.01-100$m^2$/g. The cavities that exist between individual adsorbent particles are larger than typical macropore widths, as defined above, thus justifying their classification as non-porous or non-microporous adsorbents.

***Type II – Homogenous macroporous adsorbents***: These have larger specific surface areas, about 300-400$m^2/g$, and homogenous pores with diameters greater than 100Å.

***Type III – Homogenous microporous adsorbents***: have large specific surface areas, in excess of 1000$m^2/g$, and micropores only a few angstroms wide. Because such small pores will not admit large molecules, these adsorbents exhibit selective adsorption characteristics.

***Type IV – Heterogenous porous adsorbents***: These have large pore volumes. The pore structure is made up of pores the size of which cover the range of sizes defined above for micropores to macropores. Due to the varying pore sizes their adsorption characteristics are difficult to predict.

### 2.2.4 Carbotrap-B

Carbotrap-B is a high purity GCB supplied by Supelco (Bellefonte PA). It has an average particle size of 20/40 mesh and a reported specific surface area of 100$m^2/g$, was one of the adsorbents chosen for this project. Carbotrap-B can adsorb and release a wide range of airborne VOC. It is a Class I adsorbent and has no surface ions or active functional groups. The entire surface of the adsorbent is available for interactions that depend solely on dispersive London forces (Supelco 1986). It is an almost non-porous adsorbent with matted irregular nearly spheroidal particles clustered together. Average particle size is 1-1.5mm and the bulk density of the adsorbent has been determined to be 0.42g/mL (Hrouzkova 1997). The manufacturer, Supelco, states the specific density to be 0.38g/mL (Supelco 1986).

Carbotrap-B has been shown to have good desorption recoveries for aliphatic hydrocarbons, mono-aromatic hydrocarbons, chlorinated hydrocarbons and alcohols ranging from n-butanol to n-decane (Supelco 1986). However poor recoveries have been found for aldehydes and terpenes. Cao and Hewitt (1993) found decomposition of α and β-pinene when desorbing at temperatures as low as 473K. Rothweiler *et al* (1991) found low recoveries of hexanal and acrolein when desorbing at 533K but recovery was found to be better at these temperatures when compared to work at

573K used by De Bortoli et al (1987). These poor recoveries were suggested to be the result of the presence of active sites. Nunez et al (1984) suggested these sites were caused by impurities in the starting material and insufficient graphitization during synthesis of the adsorbent.

Carbotrap-B has a low affinity for the adsorption of water although it has been reported that small amounts can be adsorbed at high humidities (Helmig and Viering 1995). Matney *et al* (2000) have found 98% recovery of methanol on Carbotrap-B at relative humidities of 80%.

Schmidbauer and Oehme (1988) found contaminant traces in the $pg/m^3$ concentration range after cleaning Carbotrap tubes at 653K for four hours with helium. A number of studies have stored clean tubes for a period of time under various conditions before analysis. Helmig (1996) stored tubes that had been cleaned for five days at 243K and 298K respectively. He found slight traces of contaminants in both after analysis with higher levels (almost tenfold increase) found in the tubes that had been stored at 298K. His results confirmed those reported by Cao and Hewitt (1994) although the amount of benzene detected differed in each case. De Bortoli *et al* (1992) found traces of toluene and benzene in tubes that had been cleaned and stored for eight weeks. Tubes were stored at 263K and 298K and grater amounts of benzene and toluene were again detected in the tubes stored at 298K. The source of the benzene and toluene has been suggested to be emission from the tube caps or diffusion into the tubes from the ambient atmosphere due to faulty caps. (Schmidbauer and Oehme 1988).

Ciccioli *et al* (1986) found that adsorbed samples could be reliably recovered up to two months after sampling and also that no artifacts were produced from co-adsorbed nitrous oxides, water vapour or ozone. De Bortoli *et al* (1992) also found good recovery of adsorbed samples after fifty days of storage at room temperature and also at 263K. Cao and Hewitt (1994) found no artifact formation resulting from the exposure of adsorbed VOC to ozone, at concentrations of 180ppb, while passive sampling for one week.

De Bortoli *et al* (1992) sampled a VOC mixture with a tube that had already been used 800 times. They then analysed the adsorbed VOC and repeated the procedure

twenty-one times. They found no significant difference in the performance of the tube. Rothweiler *et al* (1991) found that the performance of Carbotrap-B was not affected by frequent use. They based their results on thirty analyses using the same tube that had been spiked with a discreet amount of a liquid VOC calibration standard each time.

Be Bortoli *et al* (1992) and Shirey *et al* (1991) found slight differences in results when investigating Carbotrap-B from different batches produced by Supelco.

Carbotrap-B has good desorption recoveries and low background values, is relatively hydrophobic and thermally stable to 673K. It has a range of use of $C_4$ to $C_{12}$ hydrocarbons and has been shown to be a good adsorbent for sampling and storage of these VOC. This makes it an ideal adsorbent for studying for VOC sampling with TD-GC analysis applications.

Carpopack-B is another GCB supplied by Supelco and both adsorbents are often confused with one another even to the point that they are thought to be the same adsorbent. Another confusion that arises for Carbotrap/Carbopack-B is the reporting of the mesh size and surface area of the adsorbent. Carbotrap-B and Carbopack-B are have been reported as follows:

| **Physical Property** | **Carbotrap-B** | **Reference** |
|---|---|---|
| Surface Area | $100m^2/g$ | Supelco 1986, Hrouzkova *et al* 1997 |
| Mesh Size | 20/40 | Supelco 1986, Hrouzkova *et al* 1997 |

| **Physical Property** | **Carbopack-B** | **Reference** |
|---|---|---|
| Surface Area | $100m^2/g$ | Betz and Suppina 1989, Supelco 1988, Tolnai *et al* 1999 |
| | $90m^2/g$ | Ciccioli *et al* 1976, Ciccioli *et al* 1986, Hrouzkova *et al* 1997 |
| | $200m^2/g$ | Lhuillier *et al* 2000 |

| Physical Property | Carbopack-B | Reference |
|---|---|---|
| Mesh Size | 60/80 | Betz and Suppina 1989, Supelco 1988, Hrouzkova *et al* 1997,Tolnai *et al* 1999 |
| | 20/40 | Ciccioli *et al* 1986 |
| | 80/100 | Ciccioli *et al* 1976 |

Mesh size relates to the size of the adsorbent particles, is analogous to surface area and has a great influence on the adsorption characteristics of the adsorbent. Mesh size 60/80 relates to the range 0.250-0.177mm while 20/40 relates to adsorbent particles in the size range 0.841-0.420mm. Hrouzkova *et al* (1997) measured the actual mesh size using scanning electron microscopy and the surface area by BET analysis. They also found that the NMR spectra of Carbopack-B showed a chemical shift that suggested the presence of metalohydride on the adsorbent surface. This indicates the presence of active sites. Analysis of Carbotrap-B on the other hand showed that it consisted mainly of graphite. Brown (HSE report 1995, Brown 1996) compared both in an inter-laboratory study of adsorbents. Desorption recoveries, breakthrough volumes and storage stabilities of the adsorbents for four VOC were measured. These were hexane, 1,2-dichloroethane, ethyl acetate and methyl ethyl ketone. Both adsorbents exhibited similar desorption recoveries for the four VOC. Breakthrough volumes for the four VOC on Carbotrap-B were an order of magnitude higher than those for Carbopack-B. Breakthrough volumes were measured using both the retention volume and frontal chromatography methods. Some problems were also observed with storage stability for Carbopack-B. These results suggested the presence of active sites on Carbopack-B and this seems to fit in with the results of Hrouzkova *et al*.

### 2.2.5 Carbosieve SIII

Carbosieve SIII is a CMS supplied by Supelco (Bellefonte PA). Carbosieve SIII was first produced by BASF (Ludwigshafen, Germany) before the patent was sold to Supelco. It is formed from the pyrolysis of polyvinylidene chloride (Lhuillier *et al* 2000). According to Supelco data (Supelco 1997, 1998a) Carbosieve SIII has a 60/80Mesh and a surface area of 820$m^2$/g. Another Supelco bulletin states that the surface area is 900 $m^2$/g (Supelco 1988b). It has weak Class III approaching Class I

adsorbent properties. It is stable at temperatures up to 673K and is ideal for sampling small airborne molecules such as the $C_2$ hydrocarbons and other very volatile organics. It is a microporous adsorbent with average pore sizes in the range 15-40Å. However, conflicting information is given about the adsorbent capacity for water. The manufacture data sheet (Supelco 1988a) claims the adsorbent to be hydrophobic where as the technical data suggests that it has a moderate affinity for water (Supelco 1988b).

Hrouzkova *et al* (1997) measured some of the physical properties of Carbosieve SIII. Using an electron-scanning microscope the adsorbent was shown to be a microporous adsorbent consisting of rigid, perfectly spherical particles with uniform surfaces. The specific surface area, measured by BET analysis, was determined to be $940m^2/g$. The bulk density of the adsorbent was calculated to be 0.71g/mL compared to a specific density of 0.61g/mL reported by Supelco. Pore sizes were found to be in the range of 8-16Å. NMR analysis of the adsorbent suggested the presence of organometallic compounds as well as aliphatic and aromatic functional groups on the adsorbent surface.

Helmig (1996) investigated the stability of the blank of the clean adsorbent. Cleaned adsorbent tubes were spiked with a deuterated benzene internal standard and one of the tubes was analysed straight away. Other tubes were stored at 243K for 78 days before analysis. Results showed good storage stability of the tubes with total contaminant/artifact amounts of less than 500pg observed. Clean tubes were stored for five days at 243K and 298K respectively. Contaminant levels were again found to be in the picogramme range after analysis. Good blank values were observed with the tubes stored at room temperature while the tubes stored at 243K had contaminant levels ten times less than the tubes kept at room level.

Dettmer *et al* (2000) observed poor recoveries of 1,3-butadiene and isoprene from Carbosieve SIII. The adsorbents were loaded with discreet volumes of a test gas mixture containing several VOC. Some tubes were analysed immediately while others were stored for up to one week. Analysis of the tubes showed poor recoveries for both compounds. Recovery of 1,3-butadiene ranged from 73% (immediate analysis) to 19% after seven days. The corresponding figures for isoprene were 54% and 26%,

respectively. The study suggested problems for the adsorption and recovery of VOC with double and triple bonds. However good recoveries (90+%) were observed for alkanes such as n-butane. Lhuillier *et al* (2000) found good recovery for toluene (91%) but poor recovery for hexane (63%). Although no explanation was given for the result for hexane, incomplete recovery or irreversible trapping of the hexane molecules in the adsorbent pore structure might be a feasible explanation. Carbosieve SIII is really only useful for thermal desorption applications involving $C_1$-$C_4$ and maybe some $C_5$ VOC. 1,3-butadiene and isoprene are very reactive compounds and reactions with surface functional groups or other adsorbing species may explain the poor recovery of both.

A number of studies have concentrated on the affinity of Carbosieve SIII for water. Helmig and Vierling (1995) conclude that Carbosieve SIII has a high affinity for water. This does not agree with the claims of the manufacturer. They report that Carbosieve SIII can adsorb in the region of 400mg/g of under experimental conditions with high relative humidities (RH). They also show saturation occurs slowly and that at a specific temperature the amount of water adsorbed is dependent on RH. They point out however, that to reach saturation requires sampling volumes that are far in excess of the volumes sampled when monitoring ambient air. Lhuillier *et al* (2000) report uptakes of between 4mg/g and 280mg/g of water when sampling humidified air at 294K. 4mg/g corresponds to a %RH of 50% while 280mg/g corresponds to a %RH of 100%. Matney *et al* (2000) report that Carbosieve SIII should not be used for sampling aldehydes from humidified air.

Carbosieve SIII, like Carbotrap-B is thermally stable to 673K and has good desorption recoveries and blank values. It is used for the adsorption of $C_1$ to $C_5$ hydrocarbons and has been chosen as the second adsorbent for this project. Both Carbosieve SIII and Carbotrap-B have been chosen for their suitability to VOC sampling TD-GC analysis applications and also because the range of hydrocarbons chosen for this project, $C_1$ to $C_{12}$, is covered by the two adsorbents.

## 2.3 Breakthrough Volume

Breakthrough volume, $V_b$, is defined as the volume of a gaseous sample that passes through an adsorbent bed before a fraction of the analyte is eluted from the adsorbent (Lovkvist and Jonsson, 1987). $V_b$ is a function of the adsorbent capacity. The value of breakthrough volume, $V_b$, depends on the definition of breakthrough. Breakthrough is taken to occur when the concentration of the analyte in the effluent of the adsorbent bed reaches a predefined fraction of the inlet concentration. Various studies have defined this fraction as 50% (Russell 1975, Pellizarri *et al* 1976), 10% (Nelson and Harder 1976, Comes *et al* 1993), 5% (Foerst *et al* 1979) and 1% (Jonas and Svirbely 1972, Sansone *et al* 1979). Breakthrough has also been defined as when the effluent concentration attains the limit of detection of the analytical instrument being used to monitor concentration (Namiesnik *et al* 1981, Lochmuller *et al* 1980). Harper (1993) measured the loss of sample in the effluent to be typically 0.25% at $V_b5\%$ and 5% at $V_b33\%$.

Both NIOSH (1977) and OSHA (1985) have defined $V_b$ as $V_b5\%$ i.e. breakthrough fraction of 5%. The most useful measure of an adsorbent tube for VOC sampling applications is the Safe Sampling Volume, (SSV), which is the volume of air that can be sampled without appreciable loss of analyte in the effluent. According to both the NIOSH and OSHA standards, the SSV has been set at two-thirds the value of the $V_b5\%$.

The Specific Breakthrough Volume can be defined as the breakthrough volume per unit mass of adsorbent. All values of $V_b$ referred to in this thesis, whether they are actual experimental results or results quoted from the literature, are in fact breakthrough volumes expressed in litres of gas sampled per gramme of adsorbent (L/g). The experimental breakthrough values that are reported later in the thesis, and which were used to calculate adsorption parameters, are $V_b10\%$ values due to practical limitations and experimental error in measuring $V_b$ using the experimental set-up described in chapter 3. $V_b10\%$ values were the lowest that could be measured repeatedly with confidence.

Several studies of $V_b$ measurement have been described in the literature. They can be classed as either an indirect or a direct method for measuring $V_b$.

### 2.3.1 Indirect or Retention Volume Methods

Indirect methods involve pre-loading an adsorbent tube with a known volume of adsorbate. The adsorbent tube can then be treated in a number of ways.

In the first instance the tube replaces the analytical column in a chromatographic analysis and $V_b$ is calculated as a function of the retention volume ($V_r$) of the analyte on the tube at the respective temperature (Supelco 1986). $V_r$ can be defined as the volume of gas that has passed through the column before 50% of the analyte is eluted from the adsorbent. The relationship between $V_b$ and $V_r$ is then expressed as:

$$V_b = V_r - \left(\frac{\omega}{2}\right) \qquad \text{Eq. (2.28)}$$

where $\omega$ is the base width of the resulting chromatographic peak as shown in Fig. 2.4.

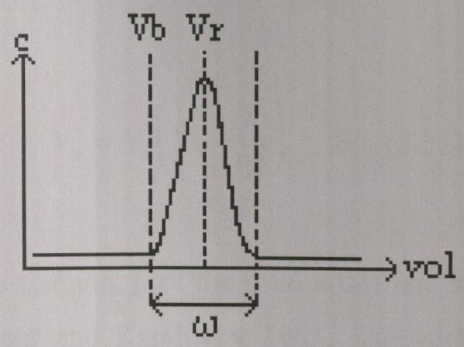


**Fig 2.4 Relationship of $V_b$ to $V_r$ using an indirect method.**

where c is the adsorptive concentration and vol is the volume of gas that has passed through the column. $V_r$ is measured at various temperatures and a plot of the ln $V_r$ against 1/T is drawn according to a van't Hoff type equation (Brown and Purnell,

1979). Extrapolation of the linear curve yields $V_r$ at ambient temperatures. The van't Hoff type equation is of the form:

$$\ln V_r = -\frac{\Delta H_{ads}}{RT} + k_r \qquad \text{Eq. (2.29)}$$

where R is the gas constant, $\Delta H_{ads}$ is the enthalpy of adsorption and $k_r$ is a constant. A disadvantage of this method is the temperature dependence of $\Delta H_{ads}$. This limits the linearity of the van't Hoff equation to a temperature range of about 50K (Van der Straeten *et al* 1985), and can lead to errors in extrapolation to determine $V_r$ at room temperature. Another disadvantage of this method is that $V_r$ cannot be used to measure the effects of adsorptive concentration on $V_b$.

$V_b$ has also been related to N the number of theoretical plates of the adsorbent and so can be used to determine chromatographic qualities of the adsorbent (Guiochon and Raymond 1975, Laurens and Rohwer 1997). N was given as:

$$N = 16\left(\frac{V_r}{\omega}\right)^2 \qquad \text{Eq. (2.30)}$$

and $V_b$ was defined as:

$$V_b = V_r\left(1 - \frac{2}{\sqrt{N}}\right) \qquad \text{Eq. (2.31)}$$

Another approach defined $V_b$ as a fraction, *f*, of the total adsorbate sampled which is lost at the sampler outlet (Cropper and Kaminsky 1963, Saelwechter *et al* 1977, Senum 1981). *f* was derived as a function of $V_r$ and N. This approach assumed a standard Gaussian chromatographic response to a narrow pulse injection of a trace concentration of adsorbate. However, as concentration increased, the response became skewed Gaussian or some other function and the theory failed.

A more recent indirect approach involved bringing the tube to a certain temperature and before passing known volumes of an elution gas through it (Bertoni and Tappa 1997). The amount of adsorbate remaining on the tube was then analysed by TD-GC. The percentage eluted was measured and a breakthrough profile was obtained for each specific temperature. Again a linear plot of ln ($V_r$) against 1/T yielded the $V_r$ at ambient temperature.

### 2.3.2 Direct or Frontal Chromatography Methods

Direct methods involve passing a continuous flow of air containing analyte of known concentration through the adsorbent tube. The tube is kept at a constant temperature. The effluent flow at the outlet of the tube is checked for the presence of any analyte that may have eluted. The effluent flow can be monitored in a number of ways:

- By placing two adsorbent tubes in series with the second tube being replaced and analysed at regular intervals. $V_b$ is determined once the analyte is detected in the analysis of the second tube. This method has the disadvantage of not allowing real time monitoring of the effluent (Harper 1993, Simon *et al* 1985).

- The effluent flow can be monitored continuously by an analytical detector (Comes *et al* 1993).

- An analytical detector can be used for periodical analysis of discrete volumes of the effluent flow. This can improve the sensitivity of the method by employing a pre-concentration step in the sampling of the effluent (Bertoni and Tappa 1997).

Direct methods involve dynamic adsorption. This is best explained using Fig 2.5, which shows the adsorptive phase concentration profile of a gas X being drawn through an adsorbent bed. Gas X has an adsorptive concentration of $C_{inlet}$. When the adsorptive molecules are drawn into the tube they first come into contact with the adsorbent molecules at the front of the adsorbent bed. Certain adsorptive molecules

are adsorbed while others are reflected and some adsorbate molecules are desorbed. The adsorption depends on temperature, concentration and the affinity of the adsorbent for gas X. Eventually, a state of dynamic equilibrium is established at the front of the adsorbent bed, where the rate of adsorption equals the rate of desorption. There are always molecules present in the adsorptive phase. As the sample is drawn further into the adsorbent bed this process of adsorption-desorption is repeated until

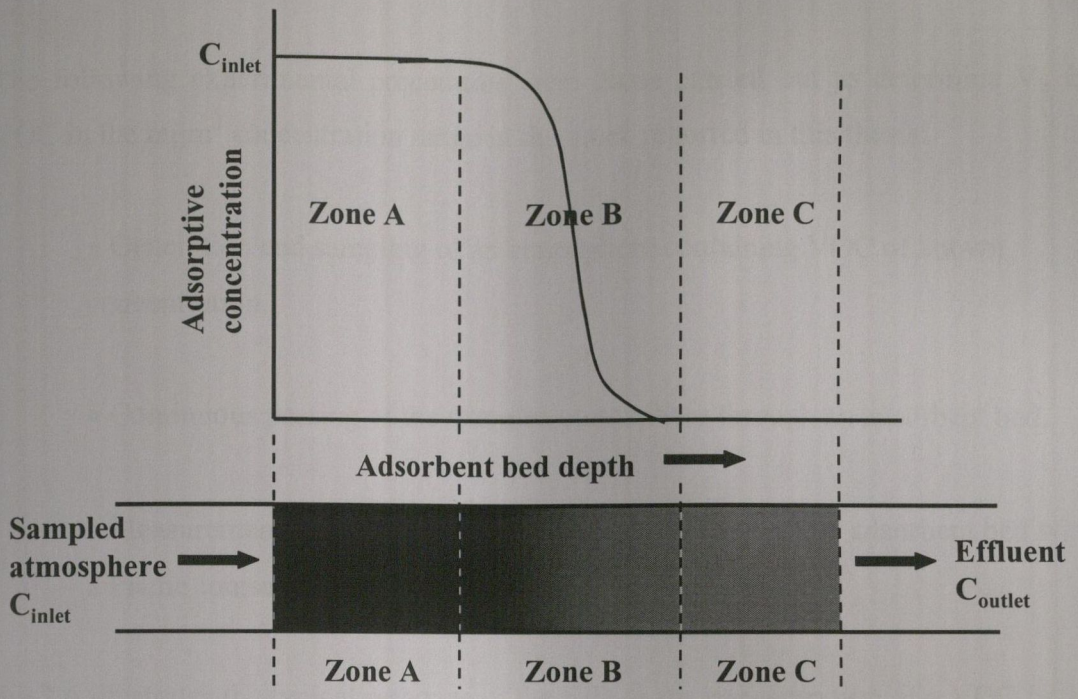


**Fig 2.5. Adsorptive phase concentration profile of gas X being drawn across an adsorbent bed.**

dynamic equilibrium is reached throughout the adsorbent bed. Three zones are identified in the adsorbent bed throughout the process. These are:

- Zone A, a saturated zone where dynamic equilibrium has been reached.

- Zone B, a zone of continuous adsorption where dynamic equilibrium is being attained. There is a concentration gradient from $C_{inlet}$ to zero of the adsorptive phase concentration of X. As the measurement proceeds this zone moves through the adsorbent bed leaving an extended saturated zone behind it.

- Zone C, a zone of non-adsorption where gas X has not yet reached. This

zone becomes smaller as the measurement proceeds and eventually disappears as breakthrough occurs.

Once breakthrough occurs the concentration of VOC in the effluent of the adsorbent bed, $C_{outlet}$ increases until at $V_b100\%$, $C_{outlet}$ is equal to $C_{inlet}$ and no adsorption is occuring.

The following experimental procedures were those carried out to determine $V_b$ for VOC in the $mgm^3$ concentration range in the work reported in this thesis:

- Generation and sampling of an atmosphere containing VOC of known concentration.

- Continuous passing of the sampled atmosphere through an adsorbent bed.

- Measurement of VOC concentration in the effluent of the adsorbent bed with a Flame Ionisation Detector (FID).

Fig 2.6 illustrates the typical response of the FID to the concentration of a VOC in the effluent flow of the adsorbent bed, during a $V_b$ measurement. Fig 2.6 can be explained as follows: A sample of the generated atmosphere passes into the adsorbent tube housing at a flow rate of 100mL/min. The adsorbent tube housing will be described in detail in Chapter 3. Before $V_b$ measurement, the sampled atmosphere bypasses the adsorbent tube by means of a three-way valve situated at the entrance to the adsorbent tube housing. The FID is never bypassed. $C_{inlet}$ in Fig 2.6 represents the response of the FID to the VOC concentration in the sampled atmosphere. This response is measured for about an hour before the measurement of $V_b$ begins in order to verify that a stable response is obtained. This is done to ensure that there are no leaks in the system and that the VOC concentration in the generated atmosphere is constant. When $V_b$ measurement begins, the flow of sampled atmosphere across the adsorbent tube housing is directed through the adsorbent tube. As the VOC is adsorbed the FID response drops. The response of the FID before breakthrough is equivalent to the response that the FID would produce if a flow of 100mL/min of zero air passed

through the system. Once breakthrough occurs, the FID response increases in response to the increasing VOC concentration in the effluent at the adsorbent tube outlet until complete breakthrough is obtained ($V_b$100%). At this point the FID response is the same as the response obtained when the sampled atmosphere bypassed the adsorbent tube.

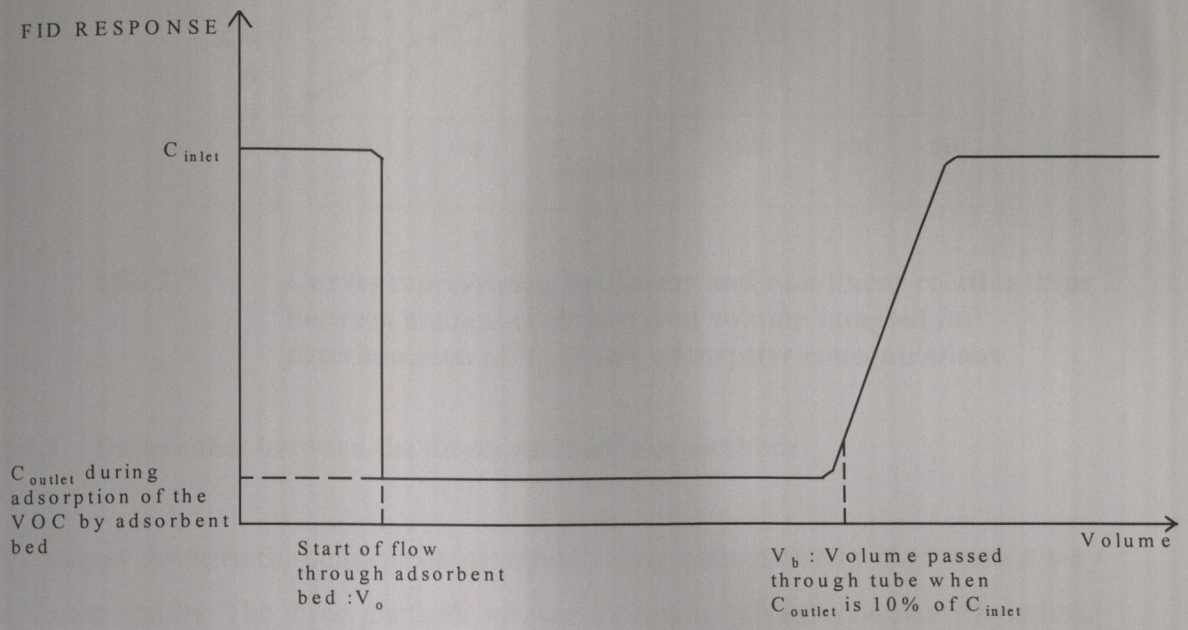


**Fig 2.6 Typical FID response during a $V_b$ determination.**

The direct method approach for $V_b$ measurement at low adsorptive concentrations, VOC in the $\mu g/m^3$ concentration range, involved passing different volumes of a generated atmosphere of known VOC concentration through an adsorbent bed. The amount of adsorbate for each volume was then determined by TD-GC. It is similar to the approaches used by Przyjazny *et al* (1982), Simon *et al* (1995) and Bertoni *et al* (1997). A linear relationship between the amount of adsorbate and volume sampled exists until breakthrough occurs. The linear relationship can be expressed mathematically as, $y = ax$, where the parameter a is calculated using the least squares method. The non-linear relationship that occurs after breakthrough can be expressed by the power function $y = cx^d$, where c and d can also be calculated by the least squares method. An example of the typical curves represented by both equations is shown in Fig. 2.7. $V_b$ is determined by calculating the points of intersection of the two curves.

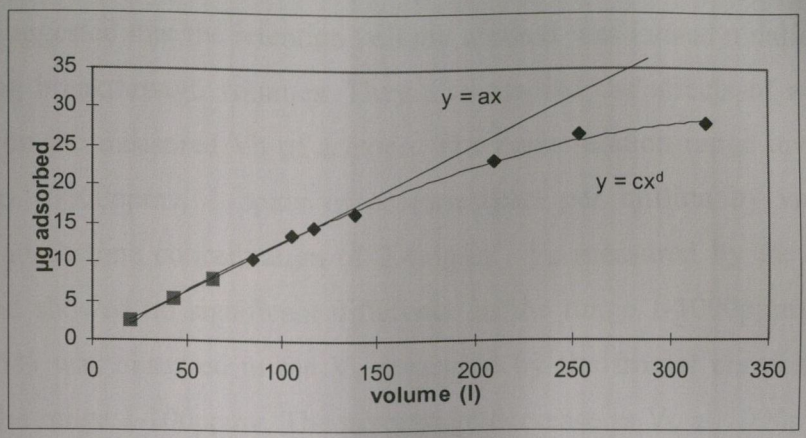


**FIG 2.7** **Curves representing the linear and non-linear relationships between amount adsorbed and volume sampled for determination of $V_b$ at low adsorptive concentrations.**

### 2.3.3 Differences between the direct and indirect methods

$V_b$ values for specific compounds measured using both methods have shown very different results. The direct methods has the following advantages over the indirect methods:

- The direct methods reproduce field sampling conditions better than the indirect methods, especially as $V_b$ is generally determined at ambient temperatures by the direct methods.

- Other environmental factors such as relative humidity, concentration fluctuations and the competitive effects of mixtures of VOC cannot be studied using the indirect methods.

- The chromatographic instrumentation employed in the indirect methods does not allow for measurements at high flow-rates.

A number of studies have compared $V_b$ measured by indirect and direct methods. Brown and Purnell (**1979**) measured $V_b1\%$ for acetone, dichloromethane, n-propanol and acrylonitrile on Tenax-GC using the frontal chromatography method. Their

results were compared to $V_b$ determined by the retention volume method. The authors claimed that there was only a difference of between 2% and 8% between the two methods and suggested that the retention volume method was indeed a valid method for determining breakthrough volumes. They also studied the effects of adsorptive concentration on the measured Vb of acetone. The concentration range investigated was 1ppmv to 10000ppmv. 1 ppmv of acetone (part per million by volume) is equivalent to an acetone concentration of $2.4mg/m^3$. $V_b$ measured by the retention volume method showed no significant difference in the range 1-1000ppmv while a decrease of 35% was observed in the $V_b$ measured by the frontal chromatography method over the range 1-100ppmv. The percentage decrease in $V_b$ at 1000ppmv was 75%. All the breakthrough volumes were less than 1L/g. According to Woolfenden (1997) adsorbents exhibiting $V_b$ of less than 1L/g for specific VOC should not be considered for sampling application for those VOC.

Other studies have showed that when $V_b$ is greater than 1L/g there is a significant difference between the values of $V_b$ determined by the retention volume method and those determined by the frontal chromatography method. A report on the study of sorbing agents for sampling VOC from air was published by the HSE (1995). $V_b$ were measured for four target compounds, hexane, 1,2-dichloroethane, ethyl acetate and 2-butanone on a number of different adsorbents including Carbotrap-B. $V_b$ were measured using both an indirect and a direct method and the results were compared. The measured $V_b$ were all greater than 1L/g and there was a significant difference between the values given by the two methods with the indirect method $V_b$ always greater than those measured by the direct method. This was due to the fact that reported values of $V_b$ measured using the indirect method are a function of chromatographic $V_r$ values and are obtained by extrapolation from log $V_r$ vs 1/T graphs of values obtained at higher temperatures and experimental error is exaggerated by this extrapolation. Also the values reported do not take concentration as well as other environmental effects into account. These environmental effects result in a decrease of $V_b$ and are measured using the direct method.

Mastrogiacomo *et al* (1995) have reported $V_b$ for the adsorption of benzene, hexane, methyl ethyl ketone (MEK), 1,1,1-trichloroethane, decane and a number of other VOC on Carbotrap-B. $V_b$ were measured by both an indirect and a direct method.

Again the values of the indirectly measured $V_b$ are greater than those measured by the direct method. Bertoni and Tappa (1997) measured the $V_b$ of benzene, toluene and ethylbenzene, with adsorptive concentrations in the $\mu g/m^3$ concentration range, on Carbotrap-B using both an indirect and a direct method. They found the values measured indirectly and directly to be similar for the adsorption of benzene but not for the other compounds. They concluded that the values of indirectly measured $V_b$ approach the real sampling capacity of a trap only for very dilute atmospheres and then only when the sampling volume is less than 400L/g.

The indirect method can therefore only really be considered to be useful for qualitatively comparing the adsorption capacity of different adsorbents. Considering that some indirect $V_b$ values reported in the literature are as high as billions of litres per gram, (n-$C_{11}$ on Carbotrap-B is given as $V_r > 10^{10}$L/g – Supelco 1986), they cannot be considered to be realistic. They would require that a couple of hundred milligrams of adsorbent are able to retain several grams of adsorbate. For these reasons it has been decided to use a direct method for determining $V_b$ for the work to be reported here.

### 2.3.4 Reported effects of several parameters on the values of $V_b$ measured by a direct method

The majority of breakthrough volume studies have been carried out in the field of research concerned with occupational hygiene, especially in investigating the use of respiratory cartridges. The adsorbent used was normally activated charcoal. A number of parameters that affect the value of $V_b$, as determined by the direct method, apart from the nature of the interactions between the adsorbent and adsorptive molecules, have been identified (Saalwechter *et al* 1977, Melcher *et al* 1978, Laurens and Rohwer 1997, Roh et al 2000). The main parameters are:

- Flow rate through the adsorbent bed
- Adsorptive concentration
- Temperature
- Humidity

- Mass of adsorbent and the adsorbent tube dimensions
- Competitive effects of other adsorbing species

Vahdat *et al* (1995) measured $V_b$ for the adsorption of hexane and toluene on Carbotrap-B and MEK and for methylene chloride on Carbosieve SIII at different sampling flow rates. They found that the values of $V_b$ were not affected by changing flow rates in the range 20-100mL/min. Harper (1993) measured $V_b$ for hexane and toluene on Chromosorb 106 and Tenax TA. 300-400mg of adsorbent was used for each experiment and the breakthrough volumes were measured for flow rates ranging from 100mL/min to 1L/min. No significant difference between measured values of $V_b$ was observed.

The adsorptive phase concentration of the adsorbing species also plays an important role in determining the value of $V_b$. At constant temperature there is a fixed number of adsorption sites present on the adsorbent surface. As adsorptive concentration increases these sites are filled or occupied more quickly and so the value of $V_b$ decreases. As mentioned above, Brown and Purnell (1979) observed a 75% decrease in the value of $V_b$ of acetone on Tenax GC as the concentration of acetone in the adsorptive phase was increased from 1 to 1000ppmv. Harper (1993) measured the $V_b5\%$ of toluene, hexane, ethyl acetate, 2-butanone and 2-propanol on both Chromosorb-106 and Tenax TA adsorbents for the adsorptive concentration range of 1 to 300mg/m$^3$. He also observed a decrease in $V_b5\%$ values for each compound over the concentration range. The effect was seen for the adsorption of each compound on both adsorbents. However, the percentage decrease in $V_b5\%$ for each adsorption system was different and these results highlight the need to establish relationships or produce parameters that can be used as tools to predict the effect of concentration on certain adsorption systems when developing a method for VOC sampling applications. Roh *et al* (2000) also observed a decrease in $V_b$ due to an increase in adsorptive concentration when comparing NIOSH and OSHA standard methods for the sampling of vinyl chloride monomer on activated carbon.

Temperature has also been shown to have an effect on the values of $V_b$. The adsorption coefficients b from the Langmuir isotherm as defined in Eq. (2.14), and $b_o$

of the Freundlich isotherm as defined by Eq. (2.19) are both temperature dependent. The activation energy required for a molecule to move from the adsorbate phase to the adsorptive phase is given by a similar expression in both equations and which contains the term $e^{-RT}$. As temperature increases, the activation energy required decreases and the adsorption capacity of the adsorbent also decreases, as the adsorbed molecules are more likely to desorb. Brown and Purnell (1979) in their study suggested that $V_b$ doubled for each 10°C decrease in temperature. However, this statement was based on $V_b$ that had been determined by the retention volume method in which the values of $V_b$ at ambient temperature was obtained by extrapolation of $V_b$ values measured at higher temperatures using Eq. (2.29). Harper (1995) measured the values of $V_b$ of a number of VOC on activated charcoal and Anasorb CMS using a direct method. He observed a 50% decrease in measured $V_b$ as temperature increased from 298K to 313K.

As mentioned above Helmig and Vierling, (1995) measured the affinity of both Carbotrap-B and Carbosieve SIII for water. Carbotrap was determined to be relatively hydrophobic while Carbosieve SIII adsorbed up to 400mg/g of water vapour. They also calculated the water content of air as a function of temperature and relative humidity at a pressure of 1 bar. At 293K the water content of air is 6.9mg/L at RH40% while it is 13.8mg/L at RH80%. This doubling of water content may pose a problem in the use of Carbosieve SIII. At high humidities water molecules can outnumber VOC molecules by factors of $10^3$ to $10^6$, and therefore humidity is bound to have an effect on the values of $V_b$ for some adsorbents. Lodewyckx and Vansant (1999) investigated the influence of humidity on breakthrough times of organic vapours on activated carbon. The VOC chosen included alcohols, hydrocarbons and chloro-hydrocarbons. Their results suggest that water vapour present in the airstream, i.e. adsorptive phase, only affects the adsorption capacity at high humidities. The main effect on adsorption capacity was due to the presence of pre-adsorbed water on the adsorbent surface. Harper (1995) studied the effect of humidity on the adsorption of acetone, methyl chloride and methanol on activated carbons and Anasorb CMS. The results show a decrease in $V_b$ at RH values above 50%. A decrease of 70% in the measured $V_b$ is observed at the higher %RH. Methanol was an exception to this rule. The $V_b$ of methanol increased at higher %RH due to hydrogen bonding between

methanol molecules in the adsorptive phase and the water molecules present in a pre-adsorbed film of water.

Tube dimensions and the adsorbent bed weight have also been shown to have an effect on the values of $V_b$. Harper (1993) showed that adsorbent bed weight, flow rate and tube diameter had an effect on the pressure difference across the adsorbent bed. This pressure difference must be measured as it can affect the performance of the pump during active sampling of VOC. Harper showed that the back pressure produced by 6, 8 and 9mm i.d. tubes was similar and that back pressure increased as the i.d. of the tube was decreased to 5mm and again to 4mm. The tubes used for this project are Supelco glass tubes with an i.d. of 4mm. This size is becoming the standard size used as most automatic analytical instrumentation is designed to handle these tubes. Harper used the 4mm-i.d. tubes to measure the backpressure produced when sampling at different flow rates using different adsorbent bed weights. Flow rates up to 1000mL/min were used and it was found that up to 900mg of adsorbent could be used before the NIOSH (1977) recommended maximum backpressure for an adsorbent tube was exceeded. This maximum has been set at 25mm Hg at a flow rate of 1000mL/g. However, due to size restriction of adsorbent tubes imposed by the design of analytical instruments, and also the size and density of adsorbent particles, adsorbent bed weights used for sampling applications are normally between 50mg and 300mg. Supelco data for Carbotrap-B and Carbosieve SIII show that the back pressure produced by both adsorbents when used for active sampling applications performance is well below the limits defined by NIOSH. When sampling VOC actively onto an adsorbent bed there is a linear relationship between the amount adsorbed and volume sampled. This relationship can be used to determine the adsorption capacity of that particular adsorbent bed weight. Therefore the Specific breakthrough volume can be easily calculated from a $V_b$ measured on an adsorbent bed weight of less than one gramme by simple extrapolation. Harper (1992 and 1993) and Harper *et al* (1993) show that this relationship only holds true for adsorbent beds above a certain weight, This weight has been defined as the critical bed weight and is specific to each adsorption system. Therefore care has to be taken when reporting specific breakthrough volumes that have been extrapolated from $V_b$ measured at lower bed weights.

Competitive effects of other adsorbing species will also affect the $V_b$ of a specific compound as these other molecules are competing for the same limited number of adsorption sites. Other adsorbed species may pose a steric hindrance to the adsorption of other molecules or even displace already adsorbed molecules of a different species as reported by Robbins and Breysse (1996).

## 2.4 $V_b$ and adsorption parameters

The experimental values of $V_b$ were used to draw experimental Langmuir, Freundlich and Dubinin-Polyani isotherms. Such experimental isotherms were drawn for each adsorption system studied and from the experimental isotherms it was possible to calculate adsorption parameters for each adsorption system. The experimentally measured values of $V_b$ were also used to calculate the values of the isosteric, near zero fractional surface coverage, enthalpies of adsorption ($-\Delta H^{st}$) and temperature related adsorption parameters for some of the hydrocarbons using a van't Hoff type equation analogous to Eq. (2.29). These parameters can be used to predict the effect of temperature on $V_b$ for the adsorption systems studied and also to provide a semi-qualitative measure of the effect of temperature on the adsorption of VOC in general on both adsorbents. The isotherms and adsorption parameters presented in this thesis are useful data for pumped tube sampling applications and adsorption modelling applications for diffusive samplers because they provide calculated values of $V_b$ that are very close to experimental results that allow the effects of concentration and temperature to be taken into account. The method of calculating adsorption parameters for each of the theoretical models will be considered individually. Then the calculation of the temperature dependent adsorption parameters from the van't Hoff equation will be discussed. Finally, this section will finish up with a discussion of other studies where adsorption parameters have been reported in the literature. Before considering each of the isotherms, it must be stated that there is one equation that is relevant to all calculations. It expresses $V_b$ in terms of mass of adsorbate ($m_{ads}$) as follows:

$$V_b = \frac{m_{ads}}{c} \qquad \text{Eq. (2.32)}$$

where c is the adsorptive phase concentration of the adsorbing species.

### 2.4.1 Langmuir adsorption parameters

The Langmuir isotherm is expressed in terms of b, the adsorption coefficient Eq. (2.13). This is the first of two Langmuir adsorption parameters that can be calculated from experimental values of $V_b$. $\Theta_L$, the fraction of surface coverage in the Langmuir isotherm, can also be expressed in terms of the second parameter as follows:

$$\Theta_L = \frac{m_{ads}}{m_{max}} \qquad \text{Eq. (2.33)}$$

where $m_{max}$ is defined as the maximum adsorbent capacity under the experimental conditions. In Eq (2.13) $\Theta_L$ was defined in terms of b, the adsorption coefficient, and p. An analogous expression using c, the adsorptive concentration, instead of p has also been conventionally used for expressing $\Theta_L$ (Comes *et al* 1993). Using this analogous form of Eq (2.13), as well as Eq (2.32) and Eq (2.33), the Langmuir model can be used to relate $V_b$ to the adsorption parameters b and $m_{max}$ as follows:

$$V_b = \frac{bm_{max}}{1+bc} \qquad \text{Eq. (2.34)}$$

This can then be transformed into the linear expression:

$$\frac{1}{V_b} = \frac{1}{bm_{max}} + \frac{c}{m_{max}} \qquad \text{Eq. (2.35)}$$

A plot of $1/V_b$ against c is used to calculate the parameters b and $m_{max}$. The breakthrough volume of any one compound, j, in a mixture of i compounds can be calculated from the competitive Langmuir adsorption equation which is expressed as:

$$V_b^{\,j} = \frac{m_{max}{}^{j} b^{j}}{1+\Sigma\left(b^{i}c^{i}\right)} \qquad \text{Eq. (2.36)}$$

This equation has been used to show that the adsorbent capacity of an adsorbent for a compound is significantly affected by the presence of other adsorbing species (Comes *et al* 1993).

### 2.4.2 Freundlich adsorption parameters

The Freundlich isotherm is expressed in terms of two empirical adsorption parameters, $k_F$ and n in Eq. (2.15). $\Theta_F$, the fraction of surface coverage according to the Freundlich isotherm is normally quoted in terms of $m_{ads}$ per gram of adsorbent as the isotherm does not define an adsorbent capacity. The value of $m_{ads}$ can be calculated from experimental values of $V_b$ using Eq. (2.32). Expressing $\Theta_F$ in terms of $m_{ads}$ a linear expression of the Freundlich isotherm is obtained by taking the log of both sides of Eq. (2.15) and this linear expression is:

$$\log(m_{ads}) = \frac{1}{n}\log C + k_F \qquad \text{Eq. (2.37)}$$

The Freundlich parameters can be calculated from a plot of log ($m_{ads}$) versus log C.
C represents $c/c_{ref}$ where c is the adsorptive concentration and $c_{ref}$ is an arbitrarily chosen value. In this work $c_{ref}$ was chosen to be 1500ppmv, as previously used by van den Hoed and Halmans (1987). The reason for choosing this arbitrary value was to allow comparison of our experimental data with data that had already been published and was been used for modelling purposes elsewhere.

### 2.4.3 Dubinin-Polyani adsorption parameters

The general form of the Dubinin-Polyani isotherm is given in Eq. (2.25). A linear form of this equation is obtained by again taking the log of both sides of the equation. The linear form of the equation that was used for the results presented here is the form reported by Reucroft *et al* (1971) and is expressed as:

$$\log(W) = \log(W_o) - \frac{B}{2.303}\left[\frac{T}{\beta}\log\frac{p_s}{p}\right]^n \qquad \text{Eq. (2.38)}$$

All parameters have been defined in section 2.1.2.3. W, the volume of condensed adsorbate, is expressed in $cm^3$ of adsorbate per gram of adsorbent. W for any VOC is calculated from $m_{ads}$ and the density of the bulk liquid state of the VOC. The value of $m_{ads}$ is again calculated from experimental values of $V_b$ using Eq. (2.32). The value of n can be either 1 or 2 as explained in section 2.1.2.3. Both values were used for this work. The resulting forms of Eq. (2.38) can be written in terms of two parameters from which linearised log-log isotherms can be drawn. For n equal to 2, Eq. (2.38) becomes:

$$\log(W) = \log\left(W_{o(DP1)}\right) - k_{DP1}\varepsilon^2 \qquad \text{Eq. (2.39)}$$

and for n equal to 1, Eq. (2.38) becomes:

$$\log(W) = \log\left(W_{o(DP2)}\right) - k_{DP2}\varepsilon \qquad \text{Eq. (2.40)}$$

where ε is the adsorption potential expressed in calories per mole and which has been defined in Eq. (2.22). The Dubinin-Polyani adsorption parameters, $k_{DP}$, for the two equations are related to B and β as follows:

$$k_{DP1} = \frac{B}{\beta^2(2.303)^3 R^2} \qquad \text{Eq. (2.41)}$$

$$k_{DP2} = \frac{B}{\beta(2.303)^2 R} \qquad \text{Eq. (2.42)}$$

ε can be calculated from the adsorptive concentration at which $V_b$ was measured. Eq. (2.39) from here on will be referred to as the DP-1 equation with adsorption parameters log ($W_{o(DP1)}$) and $k_{DP1}$ and Eq. (2.40) will be referred to as the DP-2 equation with adsorption parameters log ($W_{o(DP2)}$) and $k_{DP2}$. Taking one of the VOC as the reference compound, experimental affinity coefficients can then be calculated by:

$$\beta_{DP1} = \sqrt{\frac{k_{DP1}ads}{k_{DP1}ref}} \qquad \text{Eq. (2.43)}$$

$$\beta_{DP2} = \frac{k_{DP2}ads}{k_{DP2}ref} \qquad \text{Eq. (2.44)}$$

where the appendages ads and ref refer to the adsorbed molecules of a VOC and the reference compound, respectively.

### 2.4.4 Temperature related adsorption parameters

Adsorption of a gaseous molecule onto a solid adsorbent results in the release of heat. The change in enthalpy during the adsorption process can be related to experimentally measured breakthrough volumes by means of a van't Hoff type equation. Assuming the adsorptive phase VOC behaves like an ideal gas then the adsorptive concentration c, can be expressed as p/RT, where p is the partial pressure of the adsorptive phase VOC (Katsanos *et al* 1978). $V_b$ can be expressed as:

$$V_b = m_{ads}\frac{RT}{p} \qquad \text{Eq. (2.45)}$$

At dynamic equilibrium the chemical potential of the VOC in the adsorbed state, $\mu_S$, is thermodynamically equal to the chemical potential of the VOC in the adsorptive state, $\mu_g$ so that:

$$\mu_S = \mu_G = \mu^{\theta}(T) + RT\ln\frac{p}{1} \qquad \text{Eq. (2.46)}$$

where $\mu^{\theta}$ is the chemical potential of the adsorbate in its standard state of the pure adsorptive phase at 1 atm. The change in Gibbs free energy, $\Delta G$, which would occur if one mole of adsorptive phase vapour were transferred from its standard state of 1 atm, at temperature T, to the adsorbed state is expressed in terms of p as follows:

$$\Delta G = \mu_S - \mu^{\theta}(T) = RT\ln p \qquad \text{Eq. (2.47)}$$

Taking Eq. (2.1), Eq. (2.45) and Eq. (2.47), $V_b$ can now be expressed in terms of enthalpy of adsorption, $\Delta H$, as follows:

$$V_b = RTm_{ads} \exp\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right) \qquad \text{Eq. (2.48)}$$

Taking the log of both sides the general form of the van't Hoff equation becomes:

$$\ln(V_b) = -\frac{\Delta H}{RT} + k_{temp} \qquad \text{Eq. (2.49)}$$

where $k_{temp}$ is a parameter relating to $\ln (RTm_{ads})+\Delta S/R$. Eq. (2.49) is a linear expression and by measuring $V_b$ over a small range of temperatures, the energy of adsorption relating to $-\Delta H$, and which from here on will be referred to as $\Delta H_{ads}$, is obtained from the slope of the plot of $\ln (V_b)$ vs $1/T$. The calculated $\Delta H_{ads}$ is concentration dependent. Using the Langmuir adsorption parameter $m_{max}$, the fraction of surface coverage, $\Theta_L$, for a given adsorptive concentration can be calculated using experimental $m_{ads}$. The point of intercept of the plot of $\Delta H_{ads}$ vs $\Theta_L$ yields the value of the isosteric heat of adsorption $\Delta H^{st}$ for the adsorption system under investigation. The VOC rarely behave as ideal gases but the calculated $\Delta H_{ads}$ and $k_{temp}$ are useful parameters for calculating the effect of temperature on values of $V_b$.

### 2.4.5 Application of $V_b$ and adsorption parameters

A number of studies, reported in the literature, have applied adsorption models and isotherms to $V_b$ measured by a direct method in order to calculate adsorption parameters. Comes *et al* (1993) measured $V_b$ for the adsorption of hydrocarbons on Tenax GC. The Langmuir isotherm was applied and values of b and $m_{max}$ were calculated for each adsorption system. The authors also investigated the effect of competitive adsorption on the values of $V_b$. $V_b$ calculated using the competitive Langmuir equation, Eq. (2.36), compared well to analogous experimental values for multi-component atmospheres. The authors also reported Langmuir adsorption

parameters for the adsorption of oxygenated hydrocarbons (1998a) and chlorinated hydrocarbons (1998b) on Tenax GC and for organic amine and sulphide compounds on Carboxen 569 and HayeSep Q (1996). All experiments were carried out with adsorptive concentrations in the $mg/m^3$ range. The assumption was made that the calculated adsorption parameters, determined in the $mg/m^3$ range, could be used to calculate values of $V_b$ in the $\mu g/m^3$ range. One of the aims of the work in this thesis was to investigate the validity of this assumption.

Azou *et al* (1992) studied the adsorption of four chlorinated hydrocarbons on active carbon. Although values of $V_b$ were not reported directly, experimental isotherms for both the Langmuir and Freundlich models were drawn from the experimental $V_b$. The adsorptive concentration range was the low ppmv (36-67 $mg/m^3$) range. The Freundlich isotherm was found to be the more successful of the two isotherms in describing the adsorption process. Adsorption energies were calculated using the Van't Hoff type equation. The results were used to develop a kinetic desorption model based on the concept of mass transfer.

Cal *et al* (1994) examined the adsorption of acetone and benzene, in the ppmv adsorptive concentration range, on activated carbon fibres. Freundlich and Dubinin-Radushkevic adsorption parameters were calculated from the experimental results. The Freundlich isotherm was the more successful of the two models in describing the adsorption process over the concentration range studied. Calculated affinity coefficients were used to compare the performance of each of the adsorbents.

Simon *et al* (1995) measured $V_b$ of monoterpenes on Tenax TA. Freundlich adsorption parameters were calculated to measure the effect of concentration on the values of $V_b$ while the Van't Hoff type equation was used to quantify their variation with temperature. Both equations gave values in good agreement with the experimental data and the calculated adsorption parameters were used to determine safe sampling volumes for field experiments.

Van den Hoed and Halmans (1987) calculated Freundlich adsorption parameters for the adsorption of four hydrocarbons on Tenax TA and Chromosorb 106. The

calculated parameters were then used in a non-steady state diffusive sampling model. From the results obtained the authors were able to develop a straightforward procedure for determining the optimal adsorbent for diffusive sampling of specific compounds.

Vahdat *et al* (1995) measured breakthrough times, $t_b$, for the adsorption of toluene, hexane, MEK and methyl chloride on Carbotrap-B, Tenax GR, Carboxen and Carbosieve SIII. The modified Wheeler (Wheeler and Robell 1969) equation was applied to the experimental results. The Wheeler equation is used to calculate two adsorption parameters, $W_c$ the adsorbent capacity and $k_w$ the rate constant. These parameters are analogous to the Langmuir adsorption parameters, $m_{max}$ and b. The Wheeler equation is:

$$t_b = \frac{W_c}{C_o Q}\left[W - \frac{\rho_{BQ}}{k_w}\ln\left(\frac{C_o - C}{C}\right)\right] \qquad \text{Eq. (2.50)}$$

where $C_o$ and C are the adsorptive phase and adsorbent bed effluent VOC concentrations, respectively. Q is the volumetric flow rate across the adsorbent bed, W is the weight of adsorbent and $\rho_B$ is the bulk density of the adsorbent bed. The calculated Wheeler parameters were then used to calculate Langmuir adsorption parameters for the adsorption systems.

Finally, Yoon and Nelson (1992) developed a model, similar to the Wheeler equation, that relates breakthrough time to fractional breakthrough of the adsorbing species. Although not applied to any results in this work, the model has been widely used in adsorption studies, especially in occupational hygiene. The model introduced the concept of a undimensionalised breakthrough time that is defined as the breakthrough time divided by the 50% fraction breakthrough time. For each breakthrough fraction the result is a concentration invariant parameter that can be used to calculate $t_b$ for the adsorption of the VOC at any concentration.

# CHAPTER 3

## EXPERIMENTAL

## 3.1 Introduction

Breakthrough volumes, $V_b$, have been measured for the adsorption of 63 VOC on one of two adsorbents, Carbotrap B or Carbosieve SIII, using the frontal chromatographic method. The effects of temperature, humidity and concentration on the values of $V_b$ were studied and different techniques were used depending on the parameter being investigated. However, four basic steps were followed for each experiment and these were:

- The generation of an atmosphere that contained VOC of known concentration
- Sampling of the generated atmosphere
- Determination of $V_b$ and
- Determination of the VOC concentration in the generated atmospheres.

This chapter will begin with descriptions of the different techniques used to generate atmospheres and the sampling procedures employed. These are followed by details of the different methods and experimental set-ups used to measure $V_b$. Finally a description of the analytical techniques used to verify VOC concentrations and determine values of $V_b$ will be given.

## 3.2 Generation of Atmospheres.

Three different methods were used for the generation of atmospheres. The method chosen for each experiment depended on two simple factors:

- The concentration of VOC required in the generated atmosphere and
- Whether or not the VOC was a gas or a liquid at S.T.P.

Atmospheres containing VOC in the $mgm^{-3}$ and $\mu gm^{-3}$ ranges were generated. A description of each of the methods follows.

### 3.2.1 Generation of atmospheres with VOC in the $mgm^{-3}$ concentration range using liquid VOC.

All VOC were purchased from Sigma-Aldrich France and where possible at a purity of 99+%. A $mgm^{-3}$ Dynamic Atmosphere Generator, developed at INERIS, was used to generate the atmospheres containing VOC in the $mgm^{-3}$ concentration range from liquid VOC. This generator has been described in previous publications (Comes *et al* 1991, Comes *et al* 1993) but a brief description also follows here. A schematic diagram of this generator is shown in Fig 3.1.

The generator consisted of a 5m high stainless steel pipe that had a diameter of 290mm. An electric turbine heater was used to heat a flow of air that entered the base of the pipe. An extraction fan at the top of the pipe drew a flow of about $200m^3h^{-1}$ through the generator. The flow rate through the generator was adjusted by opening or closing a number of air inlet valves that were situated at various points of the generator and also at the inlet of the extraction fan.

The temperature of the air entering the base of the pipe was about 473K, but could be adjusted by changing the flow rate through the generator. The temperature was controlled to ensure that the temperatures throughout the generator, especially at the sampling point, marked as point B in the diagram, were above the boiling points of the VOC being introduced into the generator. As a rule of thumb the temperature at the base of the generator was set at 100K above the boiling point of the VOC of interest. This insured that the temperature at point B was high enough to prevent condensation of the VOC on the walls of the generator.

The VOC was introduced in the form of an aerosol spray. It was pumped from the VOC reservoir by means of a Shimadzu HPLC pump, model LC-10AT, into a small pipe and through a small nozzle situated at the end of the pipe. The uptake of VOC was measured by weighing the reservoir at regular intervals. A Mettler PJ3000 analytical balance was used for this purpose. While passing through the nozzle the VOC was mixed with compressed air resulting in the aerosol spray. This pipe was inserted into the bottom of the larger pipe and this was held in place in such a way that

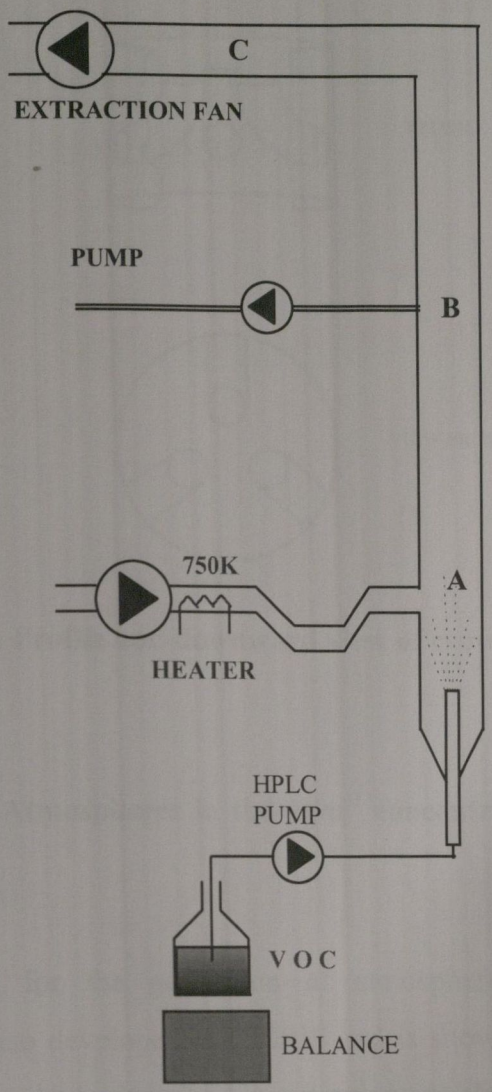


**Fig 3.1 Schematic of $mgm^{-3}$ Dynamic Atmosphere Generator.**

the aerosol spray was aspirated into the heated air stream, produced by the electric turbine, and was vaporised. This is marked as point A in the diagram. At this point the aerosol-hot air mixture passed through a section of the generator known as the crown and which is best described using Fig 3.2. The crown was situated just above point A and both the profile view and the view from point B are shown in the diagram. It consists of three small air inlets that are used to control the temperature of the generated atmosphere. The main function of this device, however, was to cause turbulence in the air flow through the generator and to ensure a homogenised mixture by the time the generated atmosphere had reached point B where sampling was carried out.

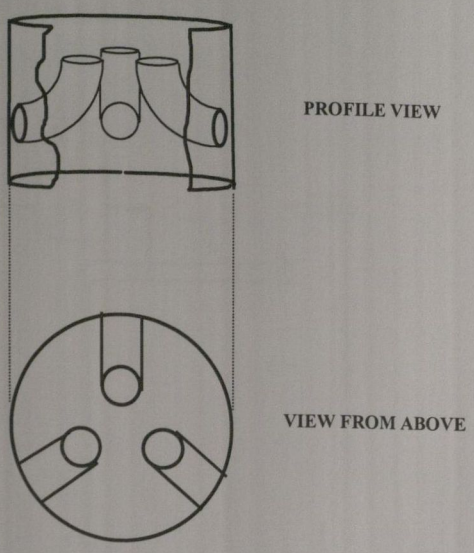


**Fig 3.2 Profile and downward view of crown device.**

### 3.2.2 Generation of Atmospheres in the $\mu gm^{-3}$ concentration range using liquid VOC

The generator used for the generation of atmospheres with VOC at $\mu gm^{-3}$ concentrations was also developed at INERIS and is shown schematically in Figure 3.3. This generator has been described in a previous publication (Jaouen *et al* 1995) but a brief description also follows here. This generator was constructed alongside the Dynamic Atmosphere Generator described in Section 3.1.1. It consists of a zero air generating device, a transfer pipe, a mixing pipe and an exposure chamber. The principle of the $\mu gm^{-3}$ generator is simple. A small volume of an atmosphere generated in the $mgm^{-3}$ generator was continuously transferred, by Venturi effect, into the mixing pipe where it was diluted to the required $\mu gm^{-3}$ concentration by mixing with zero air. Zero air was generated by blowing ambient air through an activated charcoal/glass fibre filter using a fan at a steady nominal rate of $28m^3/h$. This filter removed VOC and dust from the incoming ambient air. Firstly, the air passed through a stainless steel mesh containing 20L of activated charcoal, 6/12 MESH. The activated charcoal front area was $1m^2$. The air then passed through three fibreglass filters to remove any dust or adsorbent particles that may have came from the

activated charcoal filters. The contact surface of these filters was $0.5m^2$. The residence time of the air in the filter was 2.5s.

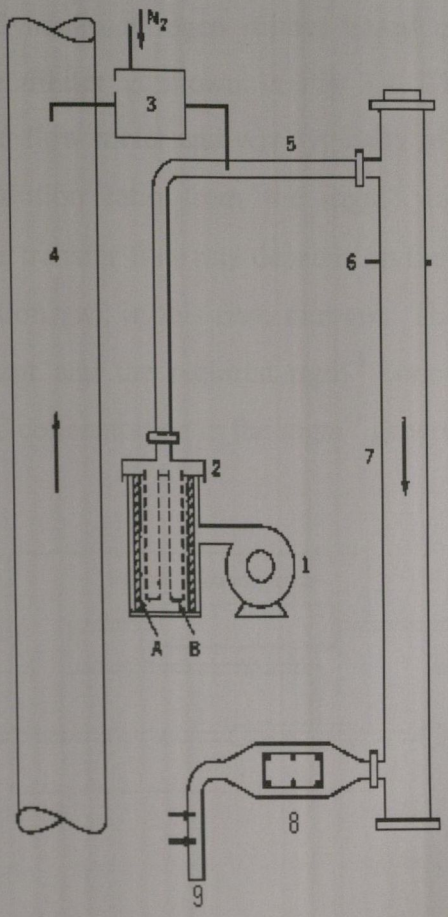


**Fig 3.3 Schematic of the $\mu gm^{-3}$ Dynamic Atmosphere Generator**

(1.fan, 2.activated charcoal filter A, fibre glass filter B, 3.dynamic dilution device, 4. $mgm^{-3}$ generator, 5.mixing pipe, 6.support, 7.homogenising pipe, 8.exposure chamber, 9.exhaust)

The $mgm^{-3}$/zero air mixture passed through a stainless steel mixing pipe, 6m in length and with an internal diameter of 0.06m, giving a homogenous atmosphere. An exposure chamber at the end of this pipe was situated in a room whose temperature was kept at a constant 298K. This exposure chamber permitted both passive and active sampling of the generated $\mu gm^{-3}$ atmosphere.

### 3.2.2.1 Transfer from $mgm^{-3}$ to $\mu gm^{-3}$ generators

A volume of the generated $mgm^{-3}$ atmosphere was continuously transferred to the $\mu gm^{-3}$ generator by a dynamic nitrogen diluter based on the Venturi effect and operating at 395K. The diluter is shown in Fig 3.4. The transfer flow rate was measured by a calibrated flow meter and was typically of the order of $20m^3/h$. This flow rate ensured a dilution ratio from the $mgm^{-3}$ to the $\mu gm^{-3}$ generator of approximately 1000. The transfer flow rate depends on the $\Delta p$ at the Venturi and also the pressure of the dilution gas, in this case nitrogen. The flow rate of the purified airflow remained constant and the required $\mu gm^{-3}$ concentration was obtained by adjusting either the VOC concentration in the $mgm^{-3}$ generator or transfer flow rate.

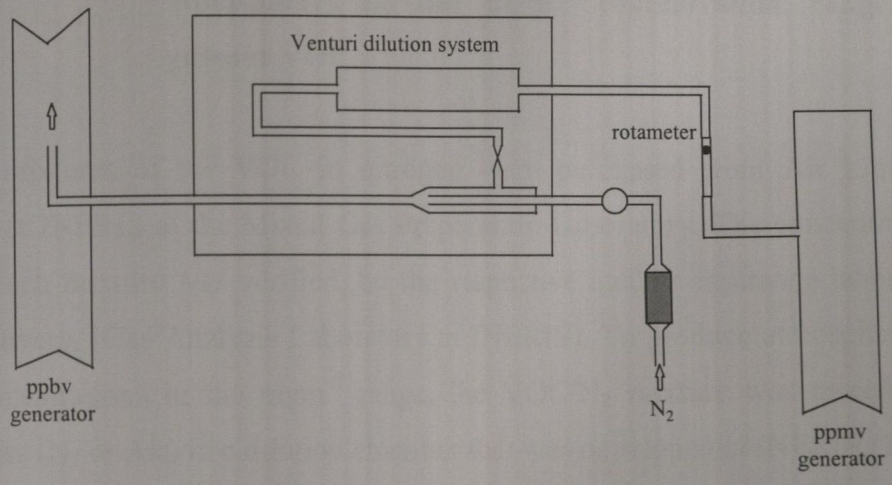


**Fig 3.4 Schematic of transfer from $mgm^{-3}$ to $\mu gm^{-3}$ generators**

### 3.2.3 Generation of atmospheres in the $mgm^{-3}$ concentration range from gaseous VOC.

$V_b$ studies were also carried out on compounds that occur as gases under ambient conditions and this necessitated a different approach to generate atmospheres of known VOC concentration. Fig 3.5 shows the experimental set-up that was designed and purchased by me and employed for the generation of atmospheres using gaseous VOC.

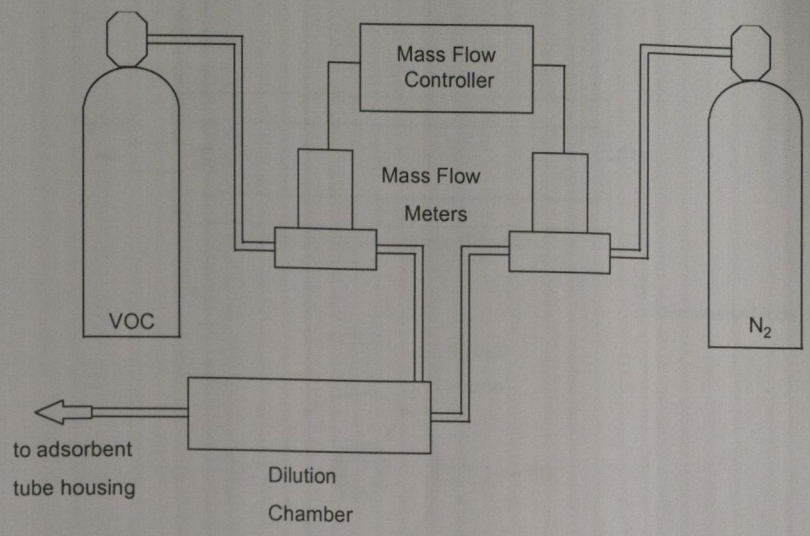


**Fig 3.5** **Schematic of experimental set-up for generation of atmospheres in the $mgm^{-3}$ concentration range from gaseous VOC.**

1-% v/v mixtures of the VOC in nitrogen were purchased from Air Liquide or produced at INERIS at the Mixed Gas Preparation Laboratory. The concentration of VOC in each mixture was verified, by the respective quality assurance laboratories, before delivery, (Gas Analysis Laboratory at INERIS). To produce atmospheres with VOC concentrations in the $mgm^{-3}$ range, the VOC/$N_2$ mixture was mixed with a dilution gas ($N_2$ or Air) in a dilution chamber that was developed at INERIS. The flow rates of the various gases into the dilution chamber were controlled by Tylan FC2900 4S mass flow meters, (500SCCM for the dilution gas and 10SCCM for the VOC/$N_2$ mixture). The dilution chamber is shown in greater detail in Fig 3.6.

The dilution gas entered the dilution chamber through a nozzle in the base of the chamber. The design of the nozzle created a jet of dilution gas and high turbulence in the dilution chamber. The VOC/$N_2$ mixture entered perpendicularly to the dilution flow into a low-pressure area. The jet of dilution gas dragged the VOC/$N_2$ mixture into the zone of high turbulence and dilution took place. There were four inlets, perpendicular to the dilution gas flow path, incorporated into the chamber design to facilitate the study of breakthrough volumes of complex atmospheres. Only one inlet was used for the experiments reported in this thesis.

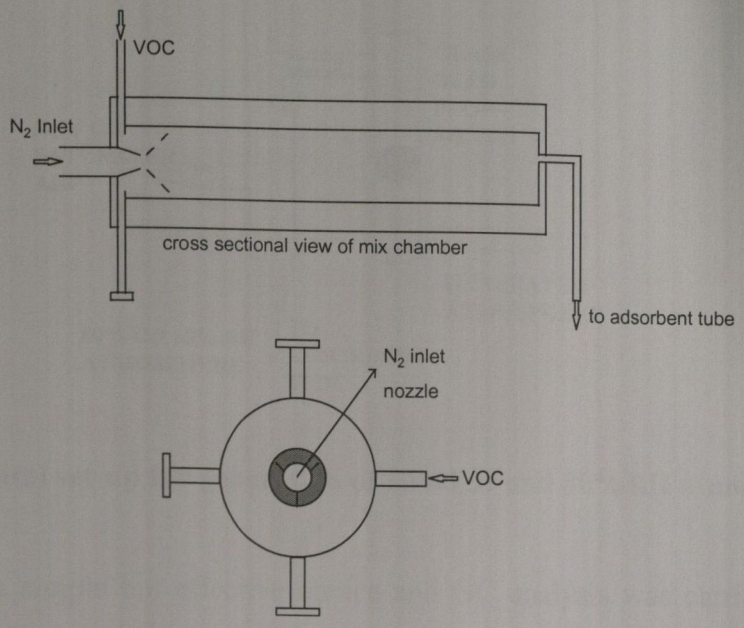


**Fig 3.6 Dilution Chamber used in experimental set-up for generation of atmospheres in the $mgm^{-3}$ concentration range from gaseous VOC. Top part shows the design of the chamber while the bottom part shows the inlet nozzle for diluant gas.**

### 3.2.4 Generation of Atmospheres with VOC in the $mgm^{-3}$ concentration range and Relative Humidity of 20% or 80% RH.

In order to measure the effects of RH on the values of $V_b$, atmospheres containing the same VOC concentrations but different %RH was generated. RH values of 20% and 80% were chosen for the study as these represent the extreme values that could be expected to be encountered when sampling in the field. The atmospheres generated using the Dynamic Atmosphere Generator described in Section 3.1.1 were generated using ambient air. The RH of these atmospheres corresponded to the atmospheric RH. Values of RH for these generated atmospheres were normally in the range of 40% to 60%RH. Atmospheric RH was measured with a hand held RH meter. In order to generate atmospheres with a final RH of 20% a known calculated volume of the generated atmosphere was mixed with a known volume of dry air in a small mixing chamber. The concentration of VOC in the generated atmosphere was adjusted to account for the dilution by the dry air. The mixing chamber used is shown in Fig 3.7: the T junction was a Swagelok ¼ inch i.d T-joint.

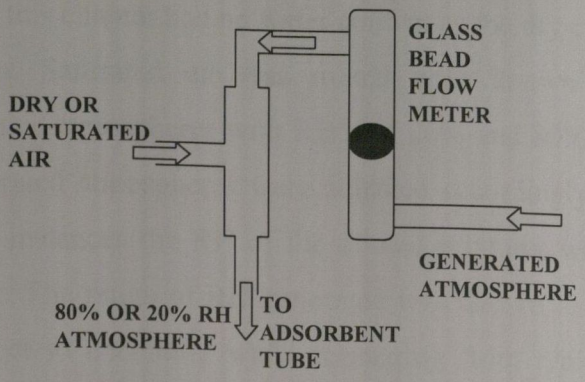


**Fig 3.7 Experimental set-up for generation of 20%RH and 80%RH atmospheres**

This T-joint was a simple but effective choice and GC analysis was carried out to verify the concentration of VOC in the diluted mixture. To generate atmospheres with an RH of 80% the dry air was substituted with air that was saturated with water. This air was produced by passing dry air through a bottle containing water that had been heated up to 350K and then through a bottle containing water heated to 300K in a water bath as shown in Fig 3.8

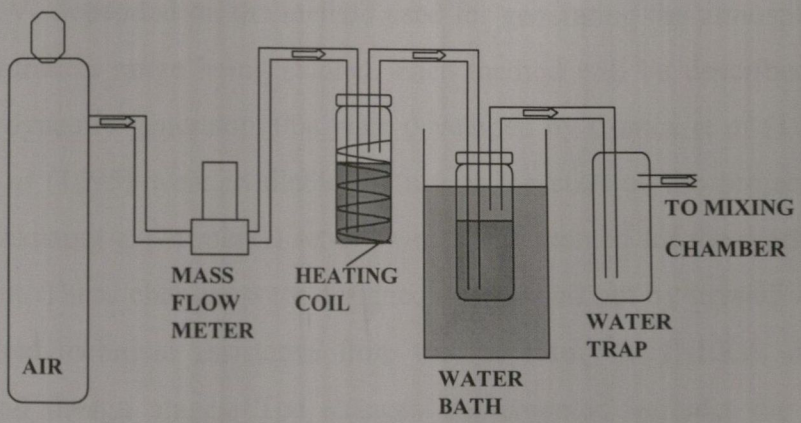


**Fig 3.8 Experimental set-up for producing air saturated with water vapour.**

The flow of air was controlled by a Tylan FC2900 4S mass flow meter. The function of the water trap was to prevent flooding of the mixing chamber in the case of an accident.

The atmospheres generated from gaseous VOC using the experimental set-up described in 3.2.3 of this chapter had no water content as the dry cylinder air was used for their generation. Saturated air was mixed with known volumes of these atmospheres to produce atmospheres with RH's of 20% and 80%. The concentration of VOC in the generated atmospheres were adjusted accordingly to take account of each dilution. In all instances the RH of the diluted mixtures were verified using a hand held RH meter. The range of RH generated was chosen to cover the extremes that one might expect to encounter while measuring from typical occupational or ambient atmospheres. It also covers the range of RH specified in recent legislation for measurement and definition of $V_b$ (EU Directive 1998).

## 3.3 Sampling from the $mgm^{-3}$ Dynamic Atmosphere Generator and measurement of $V_b$.

$V_b$ measurements were made by drawing samples of 100ml/min of the generated atmospheres through an adsorbent tube containing a bed of adsorbent and then measuring either the amount of VOC adsorbed onto the tube or monitoring the VOC concentrations in the effluent of the adsorbent tube. The methods used for sampling and measuring $V_b$ depended on the method used for generating the atmospheres and also the concentration range being studied. Each method will be described in turn. While the two dynamic generators that were developed by Comes *et al* (1991,1993) and Jaouen *et al* (1995) were available for use at the start of the project, several changes to the existing experimental set-ups were implemented for the work reported in this document. These changes were designed and carried out by myself with some much appreciated technical assistance from the laboratory at INERIS during the manufacture and design stages. The changes implemented include: the complete insulation of the $mg/m^3$ dynamic atmosphere generator, development of new systems for measurement of experimental values of $V_b$, purchase of a new HPLC pump and setting up of the data acquisition system for real time monitoring of the working parameters of the generators during measurement of experimental $V_b$ values. All experimental set-ups described in sections 3.2.3 to 3.8 were developed during the course of the project.

### 3.3.1 Early Experiments.

The flow rate through the $mgm^{-3}$ atmosphere generator was typically of the order of $200m^3h^{-1}$. During the early experiments the injection pump used to introduce the VOC into the generator was a Chromatem 380 HPLC pump. One disadvantage of this pump was the fact that the lowest flow rate possible for VOC injection was 1mL/min. This meant that the VOC concentrations of the generated atmospheres were ten times greater than the concentrations required for $V_b$ determination. Therefore a dilution system was needed. Several dilution systems were investigated but the most promising was a Venturi type dilution system that was used to sample the generated atmosphere. The dilution system was developed at INERIS and is shown in Fig 3.9. Although the dilution system was used previously for different applications it needed to be fully evaluated during these early experiments. Dilution gas flows into a dilution tube that has a restriction at one end and which is connected to the generator via a capillary and Venturi tube. The dilution gas has a high flow rate and is pressurised.

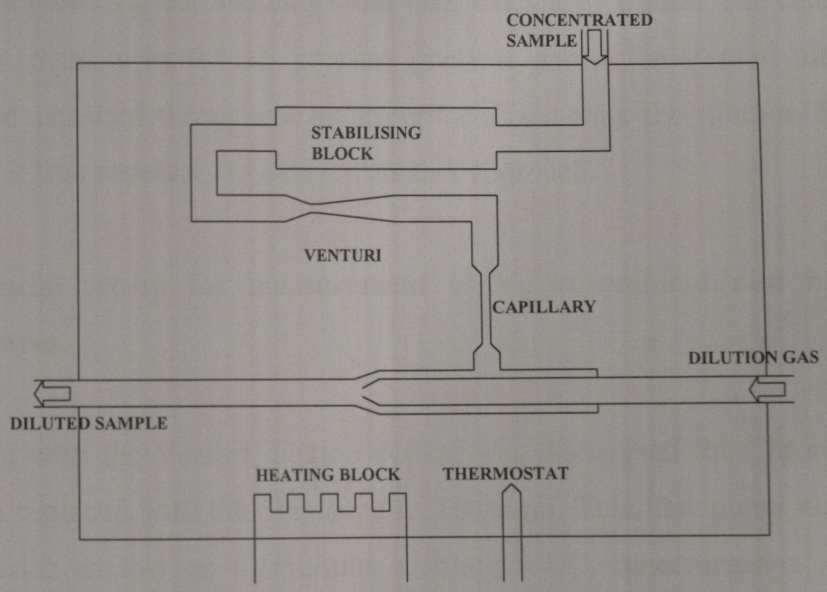


**Fig 3.9 Schematic of the Venturi type dilution system used for sampling the generated $mg/m^3$ atmospheres.**

The concentrated VOC sample is drawn in by Venturi effect and mixes with the diluted gas at the restriction. The rate of dilution depends on the pressure differential ($\Delta p$) across the Venturi tube and also the pressure of the dilution gas. The dilution

system was heated to 393K and the pressure of the dilution gas was set above 300mBar to ensure a constant dilution factor of 6. The dilution system sampled from point B of the generator (see Fig 3.1). The flow rate through the dilution system and hence the sampling rate from the atmosphere generator was $20m^3h^{-1}$. A membrane pump was used to sample $6Lhr^{-1}$ of this diluted sample.

The concentrations of VOC in both the generated atmosphere and in the diluted sample could be calculated from measuring the VOC uptake into the generator, the flow rate through the generator and then by applying the dilution factor of 6. In order to verify that the system was functioning properly Gas Chromatographic analyses of the generated atmospheres and diluted samples were carried out. The methods used are described later in section 3.5. Upon completing several analyses it became apparent that the VOC concentrations in the generated atmospheres agreed well with those that had been calculated (INERIS Report 1998). However, the concentrations in the diluted sample did not agree at all with the calculated concentrations. The measured concentrations varied randomly from their calculated values. The cause of this problem was found to be the $\Delta p$, pressure gradient, across the Venturi tube. It could not be held constant throughout an experiment and thus the dilution factor varied. Therefore it was necessary to develop another approach.

### 3.3.2 Experimental set-up for measurement of $V_b$ at ambient and higher temperatures.

After the problem with the Venturi dilution system was discovered the Chromatem HPLC pump was replaced with the Shimadzu LC10 pump. This new pump allowed VOC injection rates as low as 0.1mL/min enabling VOC concentrations in the required range to be generated directly and thus removing the necessity of a dilution step between the sampling point B and the experimental set-up for measuring values of $V_b$. The generated atmosphere was sampled directly by means of a membrane pump at a rate of $6Lhr^{-1}$. The general experimental set up for the measurement of $V_b$ is shown in Fig 3.10

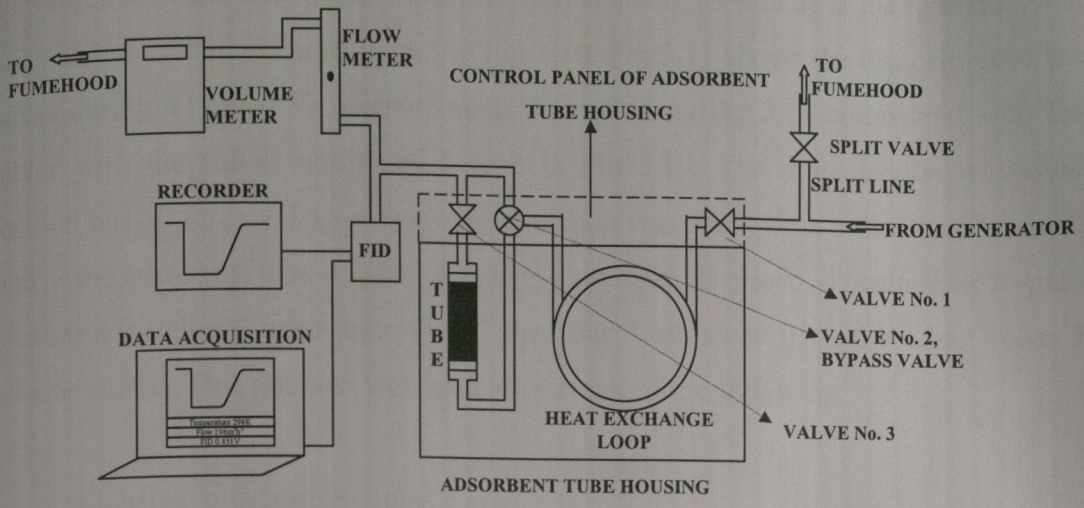


**Fig 3.10 Experimental set-up for the measurement of $V_b$ at $mgm^{-3}$ concentrations.**

The set-up shown in Fig 3.10 is the experimental set-up that was used for the measurement of $V_b$ at 298K and above. The experimental set-up consisted of:

- A series of splits and valves called the Flow Regulation System,
- The adsorbent tube housing,
- A Flame Ionisation Detector (FID),
- Flow rate measuring apparatus,
- A data acquisition system.

### 3.3.2.1 Flow Regulation System

The generated atmosphere was sampled by means of a membrane pump at a rate of $6Lh^{-1}$. The flow rate through the adsorbent tube during a $V_b$ measurement was $100mLmin^{-1}$. Most of the atmosphere that was sampled was directed through a split line before reaching the adsorbent tube housing. The flow rate through the split line was adjusted using the split valve. Adjustment of this valve controlled the volume of sampled atmosphere that passed through the adsorbent tube housing. A series of three way valves, known as the Flow Regulation System, controlled the flow rate of the sampled atmosphere that passed through the adsorbent tube housing. This system was incorporated into the front panel of a Girdel 30C Gas Chromatograph. The valves

were situated at the inlet of the adsorbent tube housing as well as at the tube inlet and outlet and are labelled valves 1 to 3 in Fig 3.10. Fig 3.11 shows the disposition of the valves during a typical $V_b$ measurement. The valves in Fig 3.11 correspond with the valves with the valves numbered 1 to 3 in Fig 3.10. The first position or closed position has all three valves closed. This position was used when either the adsorbent tube or the adsorbent tube housing was being changed. The second position or Bypass position has valve 1 open and valve 2 directing flow away from the tube. Valve 3 remains closed. This position was used after either of the following:

- Change of adsorbent tube
- Generation of a new atmosphere
- When the flow rate through the adsorbent tube housing was being adjusted using the split valve.

The flow of gas passed right through the adsorbent tube housing while the adsorbent tube was been heated or cooled to the required temperature. The advantage of this was the FID could be used to verify that the VOC concentrations in the generated atmosphere were stable, and also the flow through the adsorbent tube housing could be measured to ensure a flow rate of $100mLmin^{-1}$. The valves were in position three, or experimental position during a $V_b$ measurement, all the valves were open and valve 2 directed the flow through the adsorbent tube.

### 3.3.2.2 Adsorbent Tube Housings

***$V_b$ measured at 298K and above*:** The adsorbent tube housing used for $V_b$ measurements at ambient temperature and above (298K to 323K) was the oven of the Girdel 30 GC of which the front panel contained the Flow Regulation System. A heat exchange loop was inserted to ensure isothermal conditions. It was made from 1/8inch i.d. stainless steel tubing. The tube was connected using Swagelok fittings containing Teflon ferrules. The temperature of the adsorbent tube housing was controlled using the oven of the GC.

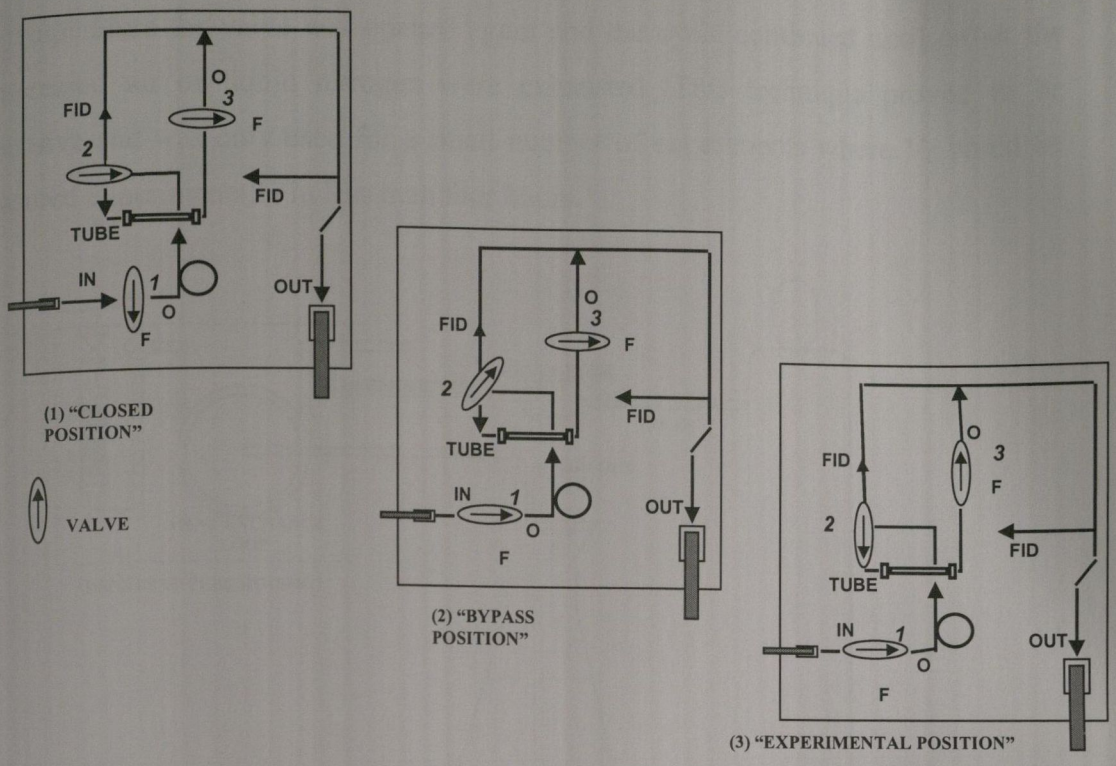


**Fig 3.11** **Schematic of the actual control panel used for the adsorbent tube housing flow regulation system showing the disposition of the valves during a typical experiment to measure $V_b$. Position one was used during the replacement of the tubes, position 2 during generation of the atmosphere and position 3 for measurement of $V_b$.**

*$V_b$ measured between 285K and 290K:* The adsorbent tube housing used was again the oven of the Girdel 30 GC. The temperature of the oven during a $V_b$ measurement was controlled by the introduction of liquid nitrogen into the oven. The set-up is shown in Fig 3.12. The liquid nitrogen was contained in a 50L Dewar flask. Compressed air from a cylinder was pumped into the Dewar flask through an EVP 118 B1 Electrovalve (CPOAC France). The valve was opened or closed by a 220V All or Nothing Relay switch (RKC France). The temperature of the oven was monitored using a platinum PT 100 probe that fed back into the relay switch. The required oven temperature was programmed into the relay. When the actual temperature of the oven, as measured by the probe, was higher than the required temperature the valve was opened to allow the compressed air into the Dewar flask which in turn displaced the cold $N_2$ gas into the oven. Once the required temperature was reached the feedback from the probe caused the relay to close the valve and so the flow of liquid nitrogen stopped. Once the measured temperature rose 1K above the

set temperature the valve was opened again and the cycle continued until either the compressed air or liquid nitrogen were exhausted. This technique proved to be expensive and was only used for a small number of experiments where $V_b$ could be measured experimentally in less than four hours.

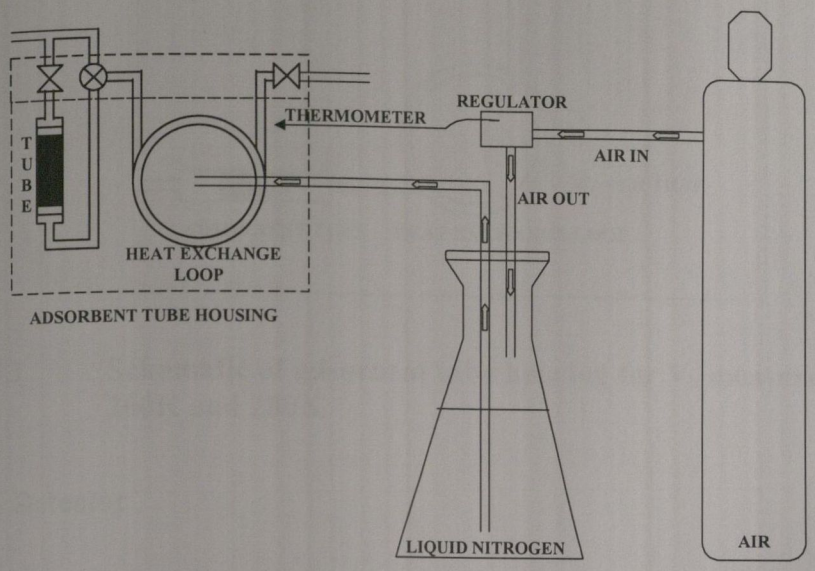


**Fig 3.12 Experimental set-up for $V_b$ measured between 285K and 290K**

***$V_b$ measured between 260K and 280K:*** An Engel 10 portable fridge was used as the adsorbent tube housing for these experiments. Fig 3.13 shows the set-up within the fridge. The inlet was connected to the bypass valve (Fig 3.10) while the outlet was connected to valve 3 of the Flow Regulation System (Fig 3.10).

The tube was held in place by Swagelok fittings containing Teflon ferrules. The heat exchange loop was made from 1/8 inch i.d. stainless steel and measured over 1m in length. A simple water trap was in place to condense any excess water present in the generated atmosphere. This was used to prevent the heat exchange loop from becoming blocked with ice during experiments carried out at temperatures lower than 273K.

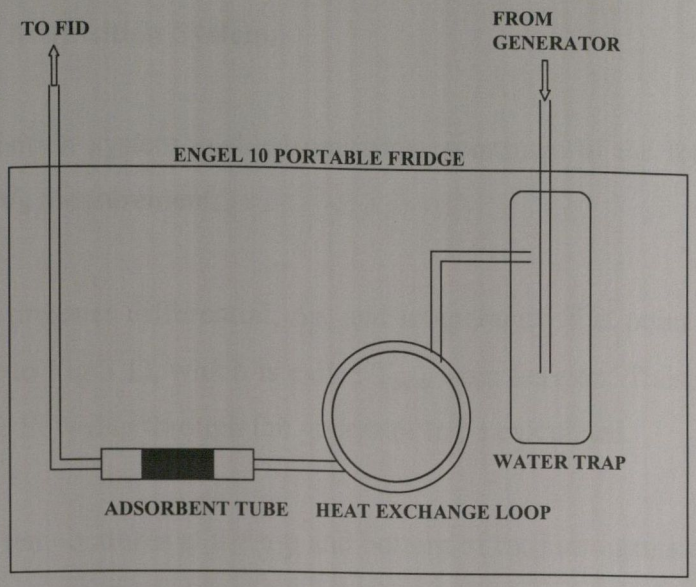


**Fig 3.13** **Schematic of adsorbent tube housing for $V_b$ measured between 260K and 280K**

### 3.3.2.3 Detector

The detector used was a Flame Ionisation Detector (FID) which was situated in the Girdel 30 GC. Of the 100mL/min that passed through the adsorbent tube housing, 2ml/min passed through the FID. The remaining 98mL/min passed through the volume meters. The values of $V_b$ quoted have been calculated on a basis that has taken this into account.

### 3.3.2.4 Flow Rate Measurement Apparatus.

Two flow meters were used. The first was a glass bead flow meter that had been previously calibrated using the Gillian Gillibrator-2 flow meter. This flow meter gave an acceptable reading for different flow rates in the 50-250mLmin$^{-1}$ range. This flow meter was of particular use when adjusting the flow using the split valve. A Schlumberger precision volume meter was used to measure accurately the volume of gas that passed through the system during an experiment.

### 3.3.2.5 Data Acquisition System.

A data acquisition system enabled real time recordings of the following parameters during the a $V_b$ measurement:

- the pressure differential, $\Delta p$, and temperature T at point C of the generator (refer to Fig 3.1), which is called $T_{ppm}$ from here on. These parameters enable Q, the flow rate through the generator to be calculated.

- the temperatures at the top and bottom of the homogenisation pipe, $T_{haut}$ and $T_{evap}$, respectively, to ensure that these temperatures are sufficient for complete volatilisation of the VOC and hence homogenisation of the atmosphere.

- the FID response and

- the temperature of the Girdel 30GC oven, in which the adsorbent tube was placed. This temperature was monitored to ensure isothermal conditions throughout a $V_b$ determination.

The data acquisition system consisted of an Analog Devices Series 5B signal conditioning subsystem, an RTI-800 interface device and a Goupil G5 286 computer. A programme based on Labtech Notebook was written to manipulate the acquired data.

The Analog Devices Series 5B signal conditioning subsystem accepted the signals from various thermocouples, platinum probes and a manometer. These measuring devices were placed at various points on the generator to measure the parameters relevant to the calculation of flow through the generator. The subsystem conditioned and amplified the signals by means of the interface devices listed below:

*5B 32 Current Input Module* - this measured a 4 - 20 mA or 0 - 20 mA current signal by reading the voltage across a precision 20Ω resistor. It provided a 0 to +5V output

signal. This module accepted and transformed the signal from the Siemens manometer.

*5B 34 RTD Input Module* - accepted a wide variety of RTD types as inputs and provided a linearised output of 0 to +5V. This module processed the signals from the platinum probes.

*5B37 Thermocouple Input Module* accepted input signals from types J,K,T,E,R,S and B thermocouples and provided a 0 to +5V output.

The output from each of these modules was recorded by the Goupil G5 286 PC, via the RTI-800 interface device.

The written programme is based on Labtech Notebook. It is basically a series of channels, each one carrying out a particular function or calculation. A flow chart of the various channels in the programme and how they relate to each other along with a brief description of the calculations is provided in Appendix 1.

#### 3.3.2.5.1 Measurement of Parameters

The temperatures at points A and B were measured by K type (Nickel Chromium-Nickel alloy) thermocouples. A J type (Iron-Constantan) thermocouple measured the temperature at point C. The reference temperature for these thermocouples is 273K so that corrections must be made for ambient temperature. The Analog Devices Series 5B signal conditioning subsystem has an in-built sensor which compensated for this difference in reference temperature during the processing of the signals from the thermocouples. The temperature of the GC oven was measured with a platinum probe and is defined as $T_{oven}$. Finally $\Delta p$ was measured at position C by a Siemens manometer (Transmitter Teleperm K for pressure differential and flow rate measurements).

### 3.3.2.5.2 Calibration of Measurement Devices

Before the programme could be used it was essential to calibrate the signal from each measuring device to ensure a linear response for all parameters. The calibrations were carried out as follows.

*Calibration of Thermocouple Signals:* Using standard reference tables of potential difference a function of temperature for each type of thermocouple, the millivolt signal for different temperatures, in the working ranges of the respective section of the generator, were produced using an AOIP Model PJN 5208 voltage and current generator. The corresponding displayed voltages were recorded and a plot of voltage observed as a function of millivolt signal was drawn. A linear response was observed and this relationship was incorporated into the programme to calculate the temperatures from the recorded voltages.

*Calibration of platinum probe signals:* A resistance generator was used to generate resistances corresponding to temperatures in the range 273 – 473K. The resistance generator was connected to the 5B32 Current Input Module. The output of the module for each resistance generated was measured in terms of voltage. A plot of measured voltage against resistance generated was used to calibrate the platinum probe signals.
*Calibration of the Siemens manometer:* A U-tube water manometer was employed to measure the pressure differential, $\Delta p$, at position C (Fig 3.1) alongside the Siemens manometer. The signal produced by the Siemens manometer was recorded by the data acquisition system. A linear relationship between $\Delta p$ observed using the U-tube manometer and the displayed on screen voltage of the Siemens manometer was noted and the calibration plot constructed. $\Delta p$ was changed by adjusting the flow rate of the generator. The flow rate was measured with a Pitot tube. The use of the Pitot tube for measuring flow rates is discussed in Section 3.8 of this chapter. The calibration curves obtained are shown Appendix 1.

*FID Response:* The FID response was also plotted in real time using a Zipp et Konen 100 chart recorder.

## 3.4 Sampling from the $\mu gm^{-3}$ Dynamic Atmosphere Generator and measurement of $V_b$.

Fig 3.14 shows the experimental set-up for the determination of $V_b$ at $\mu gm^{-3}$ concentrations. The generated atmospheres are sampled onto adsorbent tubes. The tubes are inserted into the exposure chamber of the $\mu gm^{-3}$ atmosphere generator and are held in place by Swagelok fittings. The generated atmospheres were drawn through the tubes by a Gilian dual mode low flow sampler at a rate of 100mL/min. A Gilian Gilibrator-2 flowmeter was place between the tube and sampler to measure accurately the sampling flow rate. Different discreet volumes of the generated atmospheres were sampled and the adsorbent tubes were analysed using Thermal-Desorption Gas Chromatography (TD-GC) to determine the adsorbate loading for each volume sampled. A graph of adsorbate loading against volume sampled is drawn and a typical graph for the determination of $V_b$ is shown in Fig 3.15.

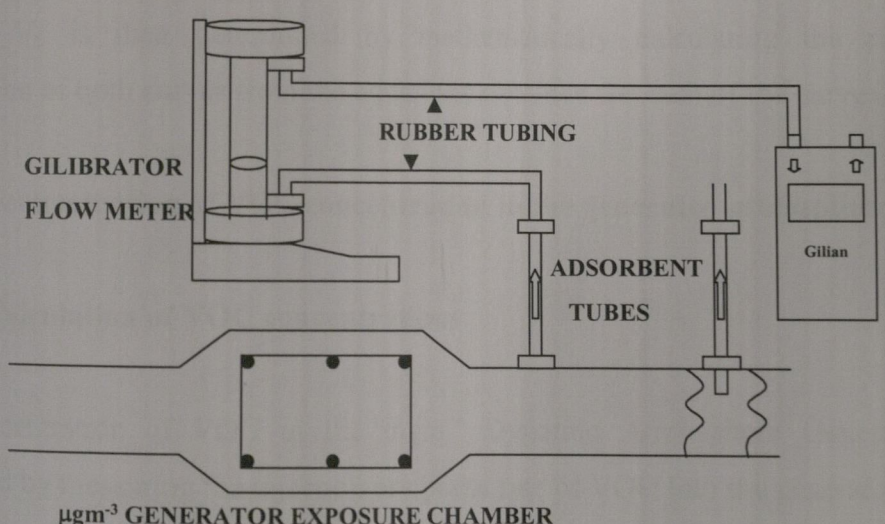


Fig 3.14 **Experimental set-up for the sampling of $\mu gm^{-3}$ atmospheres**

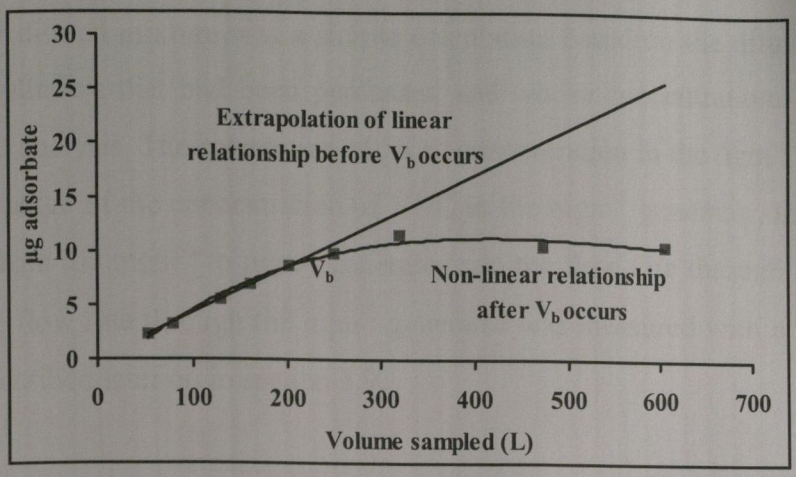


**Fig 3.15** **Typical graph of adsorbate loading vs. volume sampled used for determining $V_b$**

A linear relationship between amount adsorbed and volume sampled exists before breakthrough occurs and this is seen in Fig 3.15. The equation of the curve representing this linear relationship can be calculated using the least mean square method. After breakthrough has occurred a non-linear relationship is established between adsorbate loading and volume sampled and the equation of the curve representing this relationship can also be calculated using the least mean squares method. $V_b$ is then determined by mathematically calculating the points of intersection of both curves from the equations obtained for each of the curves.

## 3.5 Determination of VOC concentration in the generated atmospheres.

### 3.5.1. Calculation of VOC concentrations

The concentration of VOC in the $mgm^{-3}$ Dynamic Atmosphere Generator was calculated by measuring the injection or uptake rate of VOC into the generator and the flow rate through the generator. The uptake rate was measured by weighing the VOC reservoir at various intervals during the measurement of $V_b$. The flow rate through the generator was calculated in real time using the data acquisition system that has been described earlier. These calculated flow rates were verified occasionally by measuring the actual flow rate with a Pitot tube. The flow rates through the mixing chamber

shown in Fig 3.5 were controlled using Tylan Mass Flow Meters. The concentration of VOC in the diluted mixture was a simple calculation based on the dilution of the VOC in the cylinders that had been purchased and whose concentrations had been verified by GC analysis. The calculation of VOC concentration in the $\mu gm^{-3}$ generator required knowledge of the concentration of VOC in the $mgm^{-3}$ generator, the transfer rate of VOC from the $mgm^{-3}$ to $\mu gm^{-3}$ generator and the flow rate through the $\mu gm^{-3}$ generator. The flow rate through the $\mu gm^{-3}$ generator was measured with a Pitot tube that will be described later on in section 3.9.

### 3.5.2 Measurement of VOC concentrations.

Although the VOC concentrations could be reliably calculated from the working parameters of the respective generating methods used, TD-GC analysis of the generated atmospheres was used quite often to verify the calculated concentrations. Two methods, depending on the concentrations of VOC generated, were used for sampling the generated atmospheres.

### 3.5.3 Sampling of $mgm^{-3}$ atmospheres.

A Hamilton 1001LTN gas tight syringe was used to sample 800μL samples of the generated atmospheres. The sampled atmosphere was then collected onto an adsorbent tube by using a Dynatherm Model 890 Thermal Desorption Unit (TDU). Fig 3.15 helps to explain this by showing the gas flow through the TDU. The TDU operates in two modes, a preparative mode and a desorption mode.

Preparative mode – The tube in the desorption chamber formed part of the gas flow that passed through Rotameter A. An empty glass tube is placed in the desorption chamber. An adsorbent tube containing a bed of either Carbotrap B or Carbosieve SIII, depending on the VOC to be analysed, was placed at the side port exit. The gaseous sample was injected into the empty tube in the tube desorption chamber which was heated to 573K for seven minutes. The injected VOC was collected on the adsorbent in the tube at the side port exit.

Desorption Mode - When the TDU was in desorption mode, the series of valves at the tube desorption chamber rotated so that the tube in the desorption chamber formed part of the gas flow that passed through Rotameter B. A tube containing the collected sample, was placed in the desorption chamber. It was heated to 573K for seven minutes and a fraction of the desorbed VOC was transferred to the analytical column. A split, incorporated into the transfer line determined the amount of desorbed VOC that was transferred. The transfer line to the GC was a heated fused silica line that was connected to the analytical column by a low dead volume connection.

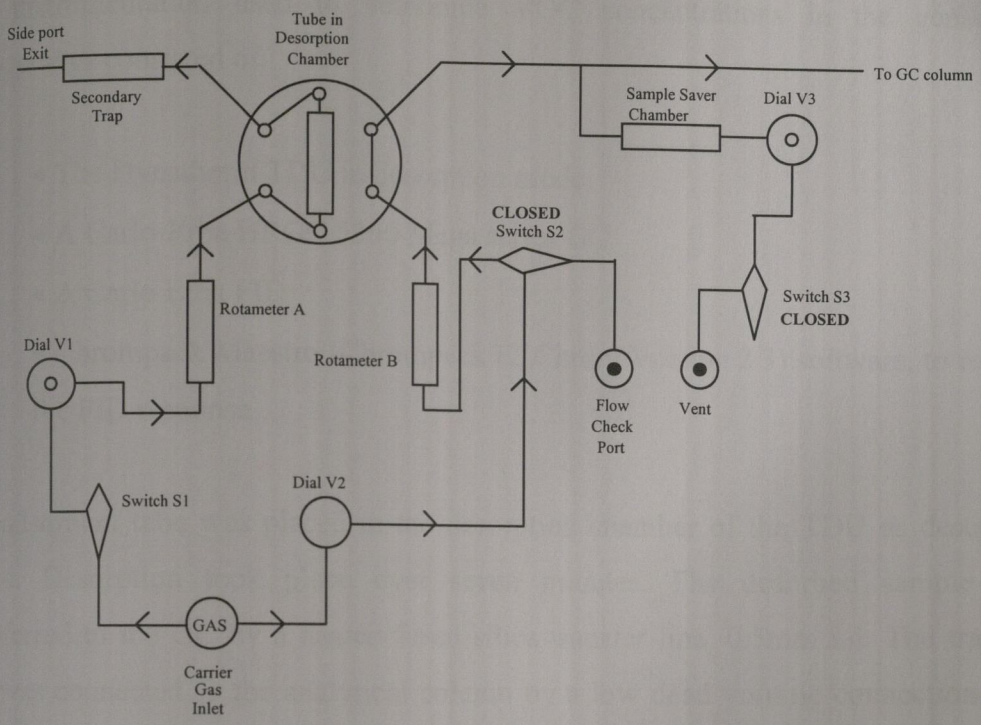


**Fig 3.15** **Schematic of carrier gas flow through the TDU**

The general settings of the TDU were as follows:

| | |
|---|---|
| Desorption/Preparation Temperature: | 573K |
| Desorption/Preparation Time: | 6min |
| Valve Temperature: | 493K |
| Transfer Line Temperature: | 493K |
| Carrier Flow Path A: | 8mL/min |
| Carrier flow Path B: | 15mL/min |
| Split Flow: | 11.7mL/min |

### 3.5.4 Sampling of $\mu gm^{-3}$ atmospheres.

Samples of these atmospheres were obtained by sampling directly onto adsorbent tubes using the Gilian samplers as shown in Fig 3.14.

### 3.5.5 Analysis of VOC.

The instrumentation used to determine VOC concentrations in the generated atmospheres consisted of:

- The Dynatherm TDU in desorption mode
- A Carlo-Erba HRGC 5300 Mega series GC
- A Carlo Erba FID
- Chrompack Maestro (Chrompack EZChrom Version 2.3) software, to record the FID response.

The adsorbent tube was placed in the desorption chamber of the TDU as described above. Desorption took place over seven minutes. The desorbed sample was transferred to the GC by a heated fused silica transfer line, 0.5mm i.d. The transfer line was connected to the analytical column by a low dead volume connection. The desorbed sample was pre-concentrated on a small section of column before analysis. This was done using a manual cryofocus stage. Fig 3.16 shows a schematic of the set-up. The low dead volume connection was attached to a sliding vertical support. Adjustment of this support lowered or raised a 3cm section of the column into or out of the cryogenic sludge. The sludge was made by mixing dry ice and acetone together and had a temperature of approximately 183K. When the adsorbent tube was desorbed the small section of the column was cooled in the cryogenic paste. Once desorption was complete the column was raised out of the paste and the GC programme was started.

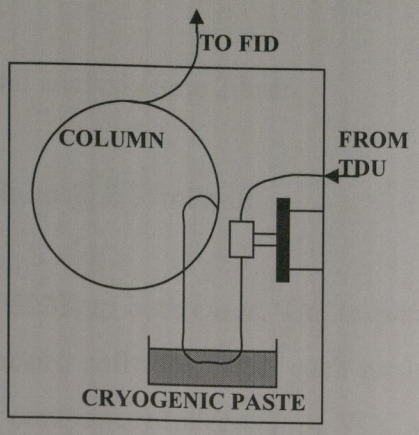


**Fig 3.16 Schematic of manual cryofocus used in analysis of VOC**

The analytical column and GC programme used for the analysis depended on whether Carbotrap or Carbosieve had been used to collect the sampled VOC. The details of the analyses are given below for each one

### 3.5.5.1 VOC collected on Carbotrap

Column: Chrompack CP-SIL 5 CB WCOT Fused Silica
25m x 0.25mm i.d.

Analysis: 308K – 343K @ 3.5K/min
343K – 348K @ 5K/min
348K – 548K @ 25K/min
Held at 308K for 1 min
Total analysis time 20min.

Carrier Gas Helium @ 1.5ml/min

### 3.5.5.2 VOC collected on Carbosieve SIII.

Column: Chrompack PLOT Fused Silica, coated with $Al_2O_3$/KCL
25m x 0.25mm i.d.

Analysis: 303K – 473K @ 10K/min
Held at 473K for 3 min

Total analysis time 20min.

Carrier Gas Helium @ 2.75ml/min

The FID was operated at 523K in both cases. The response of the FID was recorded using the Chrompack Maestro software. After each analysis, each tube was directly re-analysed to ensure that complete recovery of the VOC was obtained.

## 3.6 Determination of adsorbate loading for measurement of $V_b$ at $\mu gm^{-3}$ concentrations

As described above the $V_b$ for VOC at $\mu gm^{-3}$ concentrations were determined by sampling the generated atmospheres directly onto adsorbent tubes and then drawing a graph of adsorbate loading vs. volume sampled. The adsorbent tubes were not analysed on the Carlo Erba but instead on a Fisons Instruments GC. The Fisons had an integrated cryofocus built into the system and this was more practical to use than the manual cryofocus. The Fisons was not always available due to other commercial research that was ongoing in the laboratory and hence the reason for using the Carlo Erba on occassions. The Fisons instrumental set-up consisted of:

- A Envirochem Inc. Model 850 TDU
- A Fisons Instruments GC8000 GC
- A Fisons Intstruments MFA 815 interface unit
- The FID response was recorded using Chrompack Maestro (Chrompack EZChrom Version 2.3) software.

The TDU worked on exactly the same principles as did the Dynatherm TDU. The general settings were also the same. A fused silica transfer line connected the TDU to the GC and the GC was set-up as follows:

Column: Chrompack CP-SIL 5 CB WCOT Fused Silica
25m x 0.25mm i.d.

Analysis: 303K for 13mins
303K – 503K @ 4K/min
Total analysis time 63min.

Carrier Gas Helium @ 1.5ml/min

During the first 6min of this analysis a small section of the transfer line was cooled to 123K with liquid nitrogen to pre-concentrate the desorbed sample. The cryofocus set-up was similar to that shown in Fig 3.12. The same electrovalve and relay set-up was used. The system was focused on a small section of the transfer line. The Fisons MFA 815 interface unit controlled the whole analysis from the beginning of the desorption process.

## 3.7 Calibration of the GC

### 3.7.1 Calibration of GC with liquid VOC

Calibration standards were prepared for each VOC analysed. A mother solution was prepared by diluting 1mL of the VOC into a 250mL volumetric flask and making the solution up to volume with methanol. A small discrete volume of the mother solution was then diluted to 100mL in a second volumetric flask. Again methanol was used as the diluant. The volume of mother solution used was calculated on the basis of the concentration of VOC in the generated atmosphere. 1 to 10μL of the daughter solution were injected into the desorption chamber of the Dynatherm thermal desorber in the preparatory mode. The VOC present in the injected volumes was collected onto an adsorbent tube and then analysed as described above. The methanol used was purchased from Sigma-Aldrich and was of the pure grade used for analysing pesticides.

### 3.7.2 Calibration of GC with gaseous VOC

Scott II and Scott IV calibration gas mixtures purchased from Supelco (Bellefonte P.A) were used for calibration. Different volumes of the mixtures were sampled from the bottle by gas tight syringe and analysed in the same manner as described above.

## 3.8 Adsorbent Tubes

The adsorbent tubes used in all experiments were Supelco (Bellefonte PA) glass tubes that contained a known amount of adsorbent held in place by two plugs of silanised glass wool. The dimensions of the tubes were 115mm in length with an internal diameter of 4mm and an outer diameter of 6mm. Care was taken not to compress the adsorbent particles while sandwiching the adsorbent between the plugs of wool. The amount of adsorbent used in the adsorbent bed depended on both the type of adsorbent and the concentration of VOC in the generated atmosphere. For the experiments with Carbosieve SIII adsorbent loading was normally about 80mg. When Carbotrap-B was used the adsorbent loading was 80mg for the $V_b$ determined at low temperatures and $\mu gm^{-3}$ levels, and 150 to 190mg for $V_b$ determined at temperatures of 298K and above. The mass of adsorbent used was determined to be above the critical bed weight (see Section 4.3.1). The decision on which bed weight to use depended on the practical consideration of length of time for each experiment. Lower bed weights were used at lower concentrations and for experiments involving the higher boiling point VOC as they tended to have higher values of $V_b$. The mass of adsorbent used for each tube was weighed accurately using Mettler analytical balances and each weight was recorded. Each new Carbosieve SIII tube that was made was conditioned for 24 hours on a Dynatherm Model 60-tube conditioner at a temperature of 623K. Helium gas was used to flush the tubes at a flow rate 100mL/min. Ideally Carbotrap-B does not have any surface active sites. However, some studies have suggested that ineffective heating in the preparation of the adsorbent may result in some sites of this type being present (Matisova *et al* 1995). Therefore, before any $V_b$ measurements were carried out on Carbotrap B, all new adsorbent tubes were saturated with toluene in order to block off any active sites that might give rise to chemisorption. After this saturation the tubes where desorbed, under helium, at 623K for twenty-four hours at a flow rate of 100mL/min. All tubes were desorbed for a minimum of 6 hours after use. When not in use the tubes were kept sealed using Swagelok fittings containing Teflon ferrules that were hand tightened.

## 3.9 Measurement of flow rates in the generators using the Pitot Tube.

A Pitot Tube was used to measure the flow rate through both the $mgm^{-3}$ and $\mu gm^{-3}$ atmosphere generators. The flow rates through the $mgm^{-3}$ generator was measured at the point C shown in Fig 3.1 while that of the $\mu gm^{-3}$ was measured at the outlet of the exposure chamber shown in Fig 3.3. The theory behind the Pitot measurements is based on assuming imaginary zones of equal area in a cylindrical pipe. The velocity of gas that passes through each area is first calculated and the average gas velocity is then obtained. The flow rate through the cylindrical pipe is then calculated as a function of the arithmetic mean velocity of gas through the imaginary areas and the diameter of the pipe. Although Fig 3.17 does not depict zones of equal area, it will help explain the theory behind the calculations made from measurements made with a Pitot Tube.

The imaginary zones are labelled A to D. The velocity of gas through the pipe is equal to the arithmetic mean of the gas velocities in these zones. The Pitot tube, inserted parallel to the flow rate, is attached to a manometer and the pressure difference ($\Delta p_n$) is

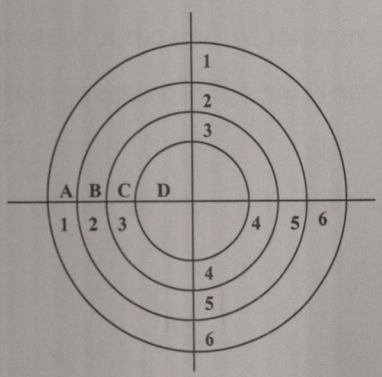


Fig – 3.17 **Imaginary zones of supposedly equal area in a cylindrical pipe showing the points at which measurements are made with the Pitot Tube.**

measured at each of the numbered points which are found in the imaginary zones. The numbered points represent the following distances from the walls of the pipe.

| Point | Distance |
|---|---|
| 1 | 0.0436d |
| 2 | 0.1465d |
| 3 | 0.2959d |
| 4 | 0.7041d |
| 5 | 0.8536d |
| 6 | 0.9564d |

where d is the internal diameter of the pipe. The $\Delta p_n$ is measured at each of the six points in both the X and Y planes. The static pressure in the pipe is then measured. The density of air ($\rho_T$) at the elevated temperatures at which the measurements were taken is calculated from the following equation:

$$\rho_T = \rho_a \frac{273(p_a - p_s)}{760(273 + T)} \qquad \text{Eq. (3.1)}$$

where $\rho_a$ is the density of air at 273K, i.e. 1.293kgm$^{-3}$

T is the temperature (K) of the pipe, when the measurements were taken

$P_a$ is atmospheric pressure at the time of measurement (mmHg)

$P_s$ is the measured static pressure in the pipe (mmHg).

The corresponding velocity of the air stream ($v_n$) for each of the measured $\Delta p_n$ is calculated by:

$$v_n = k\sqrt{\frac{\Delta p_n}{\rho_T}} \qquad \text{Eq. (3.2)}$$

where k is a constant related to the diameter of the pipe.

v, the mean gas velocity, is then calculated and from this the normalised flow rate Q is given by:

$$Q = v\frac{\pi d^2}{4}3600\frac{\rho_T}{1.293} \qquad \text{Eq. (3.3)}$$

When compared to the flow rates calculated by the acquisition programme the measured flow rates were found to show less than 5% differences.

# CHAPTER 4

## RESULTS AND DISCUSSION

## 4.1 VOC and physical parameters

The adsorption of sixty-three VOC in total was measured during the work reported in this thesis. The VOC consisted of aliphatic hydrocarbons, monocyclic aliphatic hydrocarbons, mono-aromatic hydrocarbons, halogenated aliphatic hydrocarbons, halogenated mono-aromatic hydrocarbons and simple alcohols. The VOC chosen belong to the list of 189 HAP listed in the US EPA Clean Air Amendment Act (USEPA 1994, WHO Document 1999). They were chosen on the basis of been the compounds that were mainly referred to in most of the research articles listed in this document. Many of the aliphatic and mono-aromatic hydrocarbons are of legislated for by current European legislation while others such as the halogenated compounds are under review with respect to future legislation. As stated in the introduction both of the adsorbents utilized are reported by their manufacturer to cover a certain range of VOC. Carbotrap-B is reported to cover the range of $C_5$ to $C_{12}$ VOC, and Carbosieve SIII to the range of $C_1$ to $C_5$ VOC, where the subscript on the C refers to the number of carbons present in the molecule. It will be shown later that functional groups and the nature of the substituent groups affect the value of $V_b$. Among other environmental parameters that have already been discussed, the value of $V_b$ for a VOC on an adsorbent is also a function of the temperature at which adsorption occurs. When selecting an adsorbent for VOC sampling TD-GC analysis applications the $V_b$ must be greater than 1 L/g and also some knowledge of the desorption efficiency of the adsorbent for the VOC is essential. Taking these facts into consideration it was found that Carbotrap-B could be used for sampling $C_2$ to $C_{12}$ VOC at ambient temperature depending on the functional group and the nature of the substituent groups. Due to concerns regarding desorption recovery Carbosieve SIII was used for the adsorption of $C_1$ to $C_4$ VOC. The following is a list of the VOC the adsorptions of which were measured on either Carbotrap-B or Carbosieve SIII. The list includes both gaseous and liquid VOC. The first group of compounds i.e., the group comprising the $C_1$-$C_4$ VOC were used in the experiments with Carbosieve SIII while the second group comprising $C_2$-$C_{12}$ VOC were used in the experiments with Carbotrap-B.

Carbosieve SIII

| *Aliphatic hydrocarbons* | *Halogenated Hydrocarbons* | *Alcohols* |
|---|---|---|
| ethane | dichloromethane | methanol |
| ethene | bromochloromethane | ethanol |
| ethyne | bromoethane | |
| propane | bromoform | |
| propene | chloroform | |
| butane | carbontetrachloride | |
| but-1-ene | | |
| iso-butene | | |
| cis-2-butene | | |
| trans-2-butene | | |
| 1,3-butadiene | | |

Carbotrap-B

| *Aliphatic hydrocarbons* | *Aromatic hydrocarbons* | *Halogenated Hydrocarbons* |
|---|---|---|
| pentane | benzene | 1,2-dibromoethane |
| hexane | toluene | 1,2-dichloroethane |
| heptane | ethylbenzene | 1,1,1-trichloroethane |
| octane | styrene | 1,1,2-trichloroethane |
| iso-octane | propylbenzene | 1,1,2,2-tetrachloroethane |
| nonane | iso-propylbenzene | trichloroethylene |
| decane | tert-butylbenzene | tetrachloroethylene |
| undecane | o-xylene | 1,2,3-trichloropropane |
| dodecane | m-xylene | 1,4-dichlorobutane |
| hexene | p-xylene | bromobenzene |
| cyclohexane | 1,2,3-trimethlybenzene | chlorobenzene |
| methylcyclohexane | 1,2,4-trimethylbenzene | 1,2-dichlorobenzene |
| | 1,3,5-trimethylbenzene | 1,3-dichlorobenzene |
| *Alcohols* | | 1,2,4-trichlorobenzene |

chloro-2-ethanol propan-1-ol butan-1-ol pentan-1-ol hexan-1-ol

The concentration of VOC in the atmospheres generated using various atmosphere generators was calculated by measuring flow rates through the atmosphere generators and the uptake rate of the VOC into the generators. Molecular weights, M, of all VOC and liquid densities, $\rho$, of the liquid VOC were required for these calculations. Table 4.1 lists the physical properties of each of the VOC the adsorption of which was measured. The Carbon number of the molecule as well as the melting points and boiling points of the VOC are shown. Also included in Table 4.1 are the values of $p_s$, the saturated vapour pressure of the adsorbates at a given temperature. These were calculated from data obtained in the CRC Handbook (1986). This molecular property was required for the calculation of the parameter $\varepsilon$ of the Dubinin-Polyani isotherm. Also shown in Table 4.1 are the surface tensions, $\gamma$, of the liquid VOC (those that were available) and the refractive index, $n_D$ of the VOC. Those parameters that were available were used to calculate theoretical $\beta$ values for the Dubinin-Polyani isotherm. However, theoretical $\beta$ values for the VOC with missing data were not calculated as no correlation between theoretical and experimentally calculated values was observed for those VOC whose data was available and this will be discussed in section 4.3.4. The values of all the physical properties quoted were obtained from the CRC Handbook of Physical Constants (1986).

| Compound | Carbon No. | M g/mole | ρ g/ml | mp K | bp K | $p_s$ mm Hg @ 298K | $n_D$ | γ dynes/cm |
|---|---|---|---|---|---|---|---|---|
| benzene | 6 | 78.1 | 0.88 | 278.5 | 353.1 | 95.6 | 1.50 | 28.2 |
| toluene | 7 | 92.2 | 0.87 | 178 | 383.6 | 27.9 | 1.50 | 27.9 |
| ethylbenzene | 8 | 106.2 | 0.87 | 178 | 409.2 | 9.3 | 1.50 | 28.8 |
| o-xylene | 8 | 106.2 | 0.88 | 247.8 | 417.4 | 6.5 | 1.51 | 29.8 |
| m-xylene | 8 | 106.2 | 0.86 | 225.1 | 412.1 | 7.7 | 1.50 | 28.5 |
| p-xylene | 8 | 106.2 | 0.86 | 286.3 | 411.3 | 8.2 | 1.50 | 28.0 |
| propylbenzene | 9 | 120.2 | 0.86 | 173.5 | 432.2 | 4.4 | 1.49 | |
| styrene | 8 | 104.2 | 0.91 | 242.4 | 418.2 | 6.4 | 1.55 | 32.1 |
| 1,2,3-trimethylbenzene | 9 | 120.2 | 0.89 | 247.6 | 449.1 | 3.0 | 1.51 | |
| 1,2,4-trimethylbenzene | 9 | 120.2 | 0.88 | 229.2 | 442.3 | 3.5 | 1.50 | 29.2 |
| 1,3,5-trimethylbenzene | 9 | 120.2 | 0.87 | 228.3 | 437.7 | 4.0 | 1.50 | 27.6 |
| pentane | 5 | 72.2 | 0.63 | 143 | 309.1 | 516.5 | 1.36 | 15.5 |
| hexane | 6 | 86.2 | 0.66 | 178 | 342 | 149.6 | 1.38 | 17.9 |
| heptane | 7 | 100.2 | 0.68 | 182.4 | 371.4 | 42.7 | 1.39 | 19.7 |
| octane | 8 | 114.2 | 0.70 | 216.2 | 398.7 | 13.9 | 1.40 | 21.1 |
| nonane | 9 | 128.6 | 0.72 | 222 | 423.8 | 5.3 | 1.41 | 22.4 |
| decane | 10 | 142.3 | 0.73 | 243.3 | 447.1 | 3.2 | 1.41 | 23.4 |
| undecane | 11 | 156.3 | 0.74 | 247.4 | 469 | 1.0 | 1.44 | 24.2 |
| dodecane | 12 | 170.3 | 0.75 | 263.4 | 489.3 | 1.0 | 1.42 | |
| iso-octane | 8 | 114.3 | 0.69 | 165.7 | 372.2 | 45.1 | 1.39 | |
| hexene | 6 | 84.2 | 0.67 | 133.2 | 336.3 | 169.9 | 1.38 | 17.9 |
| cyclohexane | 6 | 84.2 | 0.78 | 279.5 | 353.7 | 95.0 | 1.43 | 24.7 |
| methylcyclohexane | 7 | 98.2 | 0.77 | 146.4 | 373.9 | 44.4 | 1.42 | 23.3 |
| isopropylbenzene | 9 | 120.2 | 0.86 | 177 | 425.4 | 5.1 | 1.49 | 27.7 |
| tert-butylbenzene | 10 | 134.2 | 0.87 | 215.2 | 442 | 3.5 | 1.49 | |
| methanol | 1 | 32.0 | 0.79 | 179.1 | 338 | 123.3 | 1.33 | 22.1 |

| Compound | Carbon No. | M g/mole | ρ g/ml | mp K | bp K | $p_s$ mm Hg @ 298K | $n_D$ | γ dynes/cm |
|---|---|---|---|---|---|---|---|---|
| ethanol | 2 | 46.1 | 0.79 | 155.7 | 351.5 | 56.3 | 1.36 | 22.0 |
| chloro-2-ethanol | 2 | 80.5 | 1.20 | 205.5 | 401 | 8.5 | 1.44 | |
| propan-1-ol | 3 | 60.1 | 0.80 | 146.5 | 370.4 | 19.6 | 1.39 | 23.3 |
| butan-1-ol | 4 | 74.1 | 0.81 | 183.5 | 390.2 | 7.3 | 1.40 | 24.9 |
| pentan-1-ol | 5 | 88.2 | 0.81 | 194 | 410.3 | 3.7 | 1.41 | 25.4 |
| hexan-1-ol | 6 | 102.2 | 0.81 | 226.3 | 431 | 1.8 | 1.42 | 25.8 |
| dichloromethane | 1 | 84.9 | 1.33 | 177.9 | 313 | 415.2 | 1.42 | 27.2 |
| bromochloromethane | 1 | 129.4 | 1.93 | 186.5 | 341.1 | 165.3 | 1.48 | |
| chloroform | 1 | 119.4 | 1.48 | 209.5 | 334.7 | 197.7 | 1.45 | 26.7 |
| bromoform | 1 | 252.8 | 2.89 | 281.3 | 422.5 | 3.9 | 1.60 | 44.9 |
| carbontetrachloride | 1 | 153.8 | 1.59 | 250 | 349.5 | 109.4 | 1.46 | 26.4 |
| bromoethane | 2 | 109.0 | 1.46 | 154.4 | 311.4 | 467.2 | 1.42 | 23.6 |
| 1,2-dibromoethane | 2 | 187.9 | 2.18 | 282.8 | 404.3 | 15.1 | 1.54 | 39.6 |
| 1,2-dichloroethane | 2 | 99.0 | 1.18 | 176 | 330.3 | 218.3 | 1.42 | 31.9 |
| 1,1,1-trichloroethane | 2 | 133.4 | 1.34 | 242.6 | 347.1 | 125.6 | 1.44 | 25.2 |
| 1,1,2-trichloroethane | 2 | 133.4 | 1.44 | 236.5 | 386.8 | 25.3 | 1.47 | 34.0 |
| 1,1,2,2-tetrachloroethane | 2 | 167.9 | 1.60 | 237 | 419.2 | 6.6 | 1.49 | 35.6 |
| trichloroethylene | 2 | 131.3 | 1.46 | 200 | 360 | 74.7 | 1.48 | |
| tetrachloroethylene | 2 | 165.8 | 1.62 | 254 | 394 | 19.5 | 1.51 | |
| 1,2,3-trichloropropane | 3 | 147.4 | 1.39 | 258.3 | 429.8 | 3.9 | 1.49 | |
| 1,4-dichlorobutane | 4 | 127.0 | 1.14 | 235.7 | 426.9 | 22.0 | 1.45 | |
| bromobenzene | 6 | 157.0 | 1.50 | 242.2 | 429 | 5.1 | 1.56 | 35.2 |
| chlorobenzene | 6 | 112.6 | 1.11 | 227.4 | 405 | 17.7 | 1.52 | 33.0 |
| 1,2-dichlorobenzene | 6 | 147.0 | 1.30 | 256 | 453.5 | 2.5 | 1.55 | |
| 1,3-dichlorobenzene | 6 | 147.0 | 1.29 | 248.3 | 446 | 4.1 | 1.55 | 35.4 |
| 1,2,4-trichlorobenzene | 6 | 181.5 | 1.45 | 290 | 486.5 | <1 | 1.57 | |

**Table 4.1a Physical Parameters of the fifty-two liquid VOC whose adsorption was measured**

| Compound | Carbon No. | M g/mole | ρ g/ml | mp K | bp K | $p_s$ mm Hg @ 298K | $n_D$ |
|---|---|---|---|---|---|---|---|
| ethane | 2 | 30.1 | 0.57 | 89.7 | 184.4 | 12347.0 | 1.04 |
| ethene | 2 | 28.1 | - | 104 | 169.3 | 17093.8 | 1.36 |
| ethyne | 2 | 26.0 | 0.62 | 192.2 | 189 | 19609.4 | 1.00 |
| propane | 3 | 44.1 | 0.59 | 83.3 | 230.9 | 4592.4 | 1.29 |
| propene | 3 | 42.1 | 0.52 | 87.8 | 225.6 | 5203.3 | 1.36 |
| butane | 4 | 58.1 | 0.58 | 134.6 | 272.5 | 2171.0 | 1.33 |
| but-1-ene | 4 | 56.1 | 0.60 | 87.7 | 266.7 | 1915.3 | 1.40 |
| iso-butene | 4 | 56.1 | 0.59 | 132.7 | 266.1 | 1953.1 | 1.39 |
| cis-2-butene | 4 | 56.1 | 0.62 | 134.1 | 276.7 | 1468.3 | 1.39 |
| trans-2-butene | 4 | 56.1 | 0.60 | 167.5 | 273.9 | 1581.0 | 1.38 |
| 1, 3-butadiene | 4 | 54.1 | 0.62 | 164.1 | 268.6 | 1892.0 | 1.43 |



**Table 4.1b Physical Parameters of the eleven gaseous VOC whose adsorption was measured**

## 4.2 Comparison of VOC concentrations

The VOC concentrations used for the interpretation of the experimental data were generally calculated from the operating parameters of the generating systems. The concentrations of VOC were calculated from the flow rates through the respective generators and the uptakes of VOC into the generators. For atmospheres generated with liquid VOC the mass of liquid injected was measured during a $V_b$ measurement. When gaseous VOC were used to generate atmospheres, flow rates were controlled using mass-flow meters. The calculated concentrations were then compared to measured concentrations determined by TD-GC analysis. The FID used to monitor the VOC concentration in the effluent of the adsorbent bed was also useful for comparing calculated concentrations with those that were measured.

### 4.2.1 Determination of VOC concentration in generated atmospheres

Analyses were carried out for 22 of the 63 VOC listed above. For the analyses the generated atmospheres were sampled and the VOC concentrations in the sampled atmospheres were determined using GC-TD analysis. The methods used for sampling and analysis have been outlined in section 3.5 of this thesis. The measured concentrations were then compared to the calculated concentrations and the results are shown in Fig. 4.1, which shows the results for both the $mg/m^3$ and $\mu g/m^3$ concentration ranges. The results include 130 analyses for the $mg/m^3$ concentration range and 108 analyses for the $\mu g/m^3$ concentration range. Experimental $V_b$ were measured at concentrations ranging from $25\mu g/m^3$ to $500mg/m^3$. This range of concentrations covers both actual ambient and occupational exposure levels. VOC concentrations up to $600mg/m^3$ were generated for the comparison study. Experimental uncertainties for the $\mu g/m^3$ concentration range were calculated to be 6.4% while those for the $mg/m^3$ concentration range were 5.2%. Also shown in Fig 4.1 is the equation and regression coefficient of the least square line obtained from the 130 analyses carried out for the $mg/m^3$ concentration range data. The smaller graph inserted shows the least square line for the 108 analyses carried out for the $\mu g/m^3$ concentration range. The equation and regression coefficient for this line are $y = 0.99x + 1E\text{-}05$ and $R^2 = 0.998$, respectively. The concentration range of both axes shown in this graph are $0 - 0.35\ mg/m^3$.

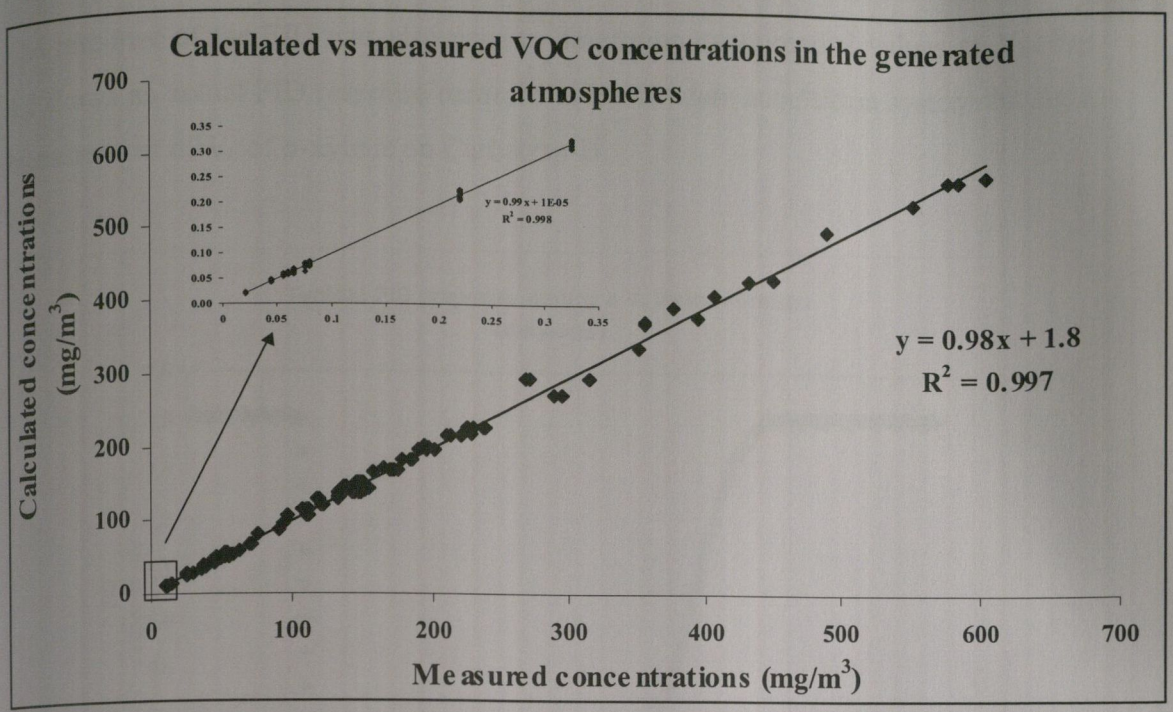


**Fig. 4.1** **Calculated vs. measured VOC concentrations in the generated atmospheres**

### 4.2.2 Response of the FID

The response of the FID to the VOC concentration in the sampled atmospheres was recorded using the data acquisition system as described in section 3.3. A Kipp and Zonen 100 chart recorder was also used to plot the response of the FID. The response of the FID was linear with respect to VOC concentration and also increased with increasing Carbon number within a homologous series. When the VOC concentrations in the sampled atmospheres were determined by TD-GC analysis the FID response was noted. A rough guide of FID responses to VOC concentrations within a homologous series was established from the results obtained by TD-GC analysis. When calculated concentrations were used for experimental data the FID response obtained was compared to a FID response corresponding to a VOC concentration measured by TD-GC analysis. This was used as a quick and simple method for checking that the calculated VOC concentrations were correct.

The response of the FID was also used to determine experimental values of $V_b$. Fig 4.2 shows an actual FID response recorded using the data acquisition system during a measurement of $V_b$ of o-xylene on Carbotrap-B.

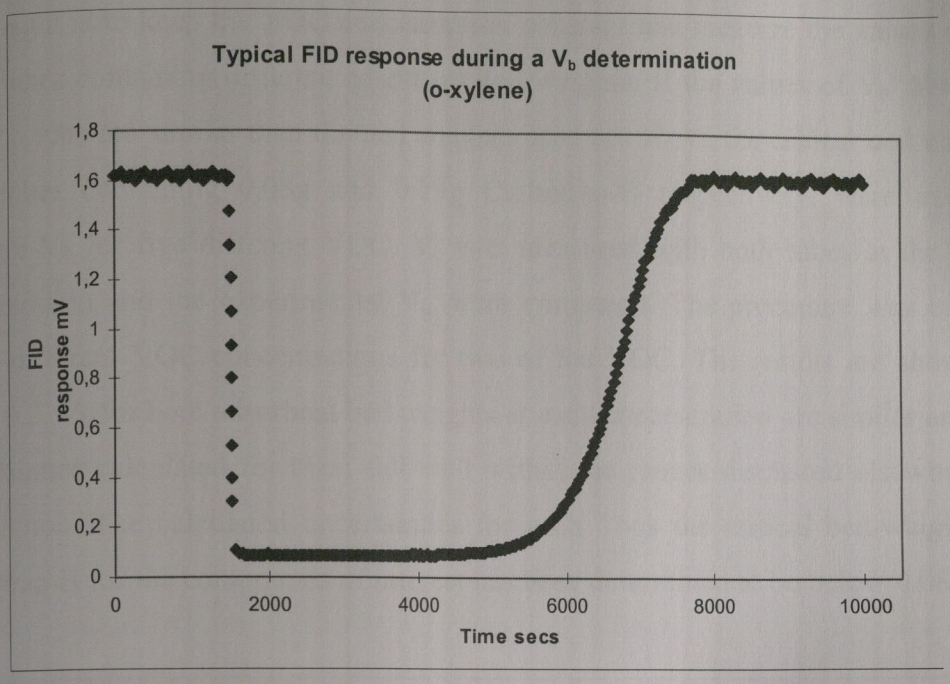


**Fig 4.2** **FID response recorded during an actual $V_b$ measurement of o-xylene on Carbotrap-B**

## 4.3 Breakthrough Volumes on Carbotrap-B

Experimental $V_b$ were measured for the adsorption of 44 VOC on Carbotrap-B. The influences of concentration, temperature and humidity on the measured $V_b$ were also investigated. Adsorption parameters were then calculated for each adsorption system studied. The experimental results and calculated parameters are now presented.

### 4.3.1 Uncertainty in measurement of $V_b$ and critical bed weight

Values of experimental $V_b$ reported in this thesis are specific breakthrough volumes, $V_b^t$ i.e., $V_b$ per gram of adsorbent. However due to the physical constraints of the adsorbent tubes that were used, adsorbent bed weights of between 0.08g and 0.19g were used for experimental measurements of $V_b$ on Carbotrap-B. The measured $V_b$ were then converted into $V_b^t$. A number of different tubes were also used for the

measurement of $V_b$. Before experimental $V_b$ can be reported, some information on whether the weights of adsorbent used were above the critical bed weight and also the uncertainty in the experimental determination of the value of $V_b$ needs to be known. A simple method for determining whether the weight of adsorbent is above the critical bed weight is to keep the VOC concentration constant and measure the values of $V_b$ using tubes containing different adsorbent bed weights. If the values of $V_b^t$ obtained for each tube are similar then the bed weights used are above the critical bed weight. Two tubes containing 0.08g and 0.19g Carbotrap-B respectively, were used to measure $V_b$ for five different VOC. $V_b$ was measured with both tubes at the same concentration and the experimental $V_b^t$ were compared. The procedure was carried out at different VOC concentrations for two of the VOC. The results are shown in Table 4.2. $V_b$ for both adsorbent bed weights at each concentration are similar and the uncertainties calculated for them fall well within the ranges discussed elsewhere in this section. The calculated uncertainties for each Thus the critical bed-weight for Carbotrap-B for the compounds of interest has been determined to be below 0.08g.

| VOC | Weight Adsorbent g | | Concentration mg/m$^3$ | | Measured $V_b$ L/g | | uncertainty |
|---|---|---|---|---|---|---|---|
| tetrachloroethylene | 0.08 | 0.19 | 120 | 118 | 56 | 55 | +/-2% |
| 1,1,2-trichloroethane | 0.08 | 0.19 | 157 | 155 | 12 | 13 | +/-3% |
| 1,1,2-trichloroethane | 0.08 | 0.19 | 529 | 529 | 7 | 7 | +/-1% |
| pentane | 0.08 | 0.19 | 34 | 35 | 6 | 7 | +/-2% |
| benzene | 0.08 | 0.19 | 258 | 259 | 6 | 6 | +/-3% |
| ethylbenzene | 0.08 | 0.19 | 55 | 55 | 125 | 125 | +/-1% |
| ethylbenzene | 0.08 | 0.19 | 136 | 136 | 92 | 90 | +/-2% |
| ethylbenzene | 0.08 | 0.19 | 191 | 192 | 78 | 77 | +/-1% |

**Table 4.2 Comparison of experimental $V_b$ at different adsorbent bed weights**

During the study of the adsorptions, experimental values of $V_b$ were measured for at least four different concentrations for each VOC. For each compound duplicate measurements were made at one of the concentrations studied. The same adsorbent tube was used to make the duplicate measurements. A comparison of the two values of $V_b$ gave a measure of the reproducibility of the measurements of $V_b$ at the same concentration. The overall experimental standard deviation from these comparisons was calculated to be 3.5%. A measure of the uncertainty in measuring $V_b$ with

different tubes was determined as follows: four tubes were used to measure $V_b$ for hexane. The concentration of hexane was kept constant at 201mg/m$^3$ for each determination. Different adsorbent bed weights were used. Five measurements of $V_b$ were made with each tube. The overall uncertainty (ISO GUM 1993), OU, was determined by the following expression:

$$\mathbf{OU} = \left( \frac{\left( \left| V_{bMean} - V_{bTrue} \right| + 2\sigma \right)}{V_{bMean}} \right) * 100 \qquad \text{Eq. (4.1)}$$

where $V_{bMean}$ is the average of all experimental $V_b$, $V_{bTrue}$ was taken to be the Langmuir isotherm value of $V_b$ at 201mg/m$^3$, and $\sigma$ is the experimental standard deviation. $\sigma$ was calculated for each tube. The values were combined to give the value of $\sigma$ used in Eq. (4.1). This was calculated to be 2.5%. The overall uncertainty due to measurement of $V_b$ using different tubes containing different adsorbent bed weights was determined from Eq. (4.1) to be 10.1%.

The overall uncertainty for any experimental $V_b$ measurement incorporates the uncertainty due to VOC concentration and the uncertainty due to the measurement of $V_b$ in accordance with ISO-GUM (1993). The uncertainty for an experimental $V_b$ is:

$$\sigma_{V_b} = \sqrt{\sigma^2_{conc} + \sigma^2_{measurement}} \qquad \text{Eq. (4.2)}$$

For $V_b$ measurements at mg/m$^3$ the overall uncertainty in $V_b$ incorporates the 5.2% uncertainty due to VOC concentration and the 10.1% uncertainty due to measurement. From Eq. (4.2) the overall uncertainty for $V_b$ at mg/m$^3$ concentrations is 11.4%. When measuring $V_b$ at µg/m$^3$ concentrations the generated atmospheres are sampled by means of a Gilian pump before the adsorbent tube is analysed by TD-GC. The uncertainty due to VOC concentration at µg/m$^3$ was determined to be 6.4% as stated above. The uncertainty due to the sampling pump was taken to be 5% in accordance with the specifications of the manufacturer. The overall uncertainty for $V_b$ measured at µg/m$^3$ concentrations was therefore determined to be 8.1% from Eq. (4.2).

### 4.3.2 Experimental $V_b$ at mg/m$^3$ concentrations on Carbotrap-B at 298K

Experimental $V_b$ were measured for the adsorption of the 44 VOC listed in section 4.1 on Carbotrap B at 298K in the mg/m$^3$ concentration range. VOC concentrations generated ranged from 50 mg/m$^3$ to 800mg/m$^3$. Of the 44 VOC in the list, 43 were found to have $V_b$ greater than 1L/g. Propan-1-ol was found to have instant breakthrough on Carbotrap-B under the experimental conditions. Table 4.3 summarises the experimental data collected. The table shows the range of concentrations of VOC in the generated atmospheres and also the range of measured $V_b$ that correspond to the concentrations generated. Values of $V_b$ were typically measured at four different adsorptive concentrations. Measurement of the value of $V_b$ was repeated for at least one of the adsorptive concentrations. The first conclusion that can be drawn from Table 4.3 is that the value of $V_b$ is concentration dependent. The concentrations of VOC in Table 4.3 correspond to occupational exposure levels. Carbotrap-B has $V_b$ ranging from a couple of litres per gram for the compounds least retained to several hundred litres per gram for the more strongly retained VOC. Ambient concentrations of VOC are not as high as the concentrations generated. $V_b$ is seen to increase as concentration decreases so another conclusion that can be drawn from the table is that Carbotrap-B is an ideal adsorbent for sampling applications of these VOC in urban atmospheres.

Carbotrap-B was described in section 2.2 of this thesis as a Class I adsorbent, i.e., an adsorbent that exhibits non-specific interactions between the adsorbent and the adsorbate molecules. Adsorption on a Class I adsorbent is therefore due to physisorption. A deeper analysis of the data in Table 4.3 reveals that a number of patterns emerge. There is an increase in the $V_b$ for alkanes with an increase in chain length within the homologous group. An increase in side-chain substitution of the benzene compounds corresponds also with an increase in the $V_b$ for these compounds. The measured $V_b$ for benzene and n-hexene are less than those measured for n-hexane which seems to suggest a specific interaction between the graphitic structure of Carbotrap-B and the $\pi$-electrons in both benzene and n-hexene. However, the $V_b$ for cyclohexane and methylcyclohexane are less than those for benzene and n-hexene and

| Compound | Conc range mg/m$^3$ | | Range of measured $V_b$ L/g of adsorbent | |
|---|---|---|---|---|
| benzene | 53 | 278 | 12.0 | 5.5 |
| toluene | 54 | 272 | 60.8 | 32.9 |
| o-xylene | 56 | 277 | 252.6 | 75.3 |
| p-xylene | 54 | 269 | 224.6 | 77.6 |
| m-xylene | 55 | 275 | 235.2 | 71.2 |
| styrene | 56 | 287 | 170.0 | 63.3 |
| ethylbenzene | 55 | 274 | 124.8 | 65.0 |
| propylbenzene | 54 | 273 | 356.0 | 94.8 |
| 1,2,3-trimethylbenzene | 67 | 335 | 320.5 | 73.9 |
| 1,3,5-trimethylbenzene | 64 | 371 | 314.7 | 63.3 |
| 1,2,4-trimethylbenzene | 54 | 293 | 397.5 | 83.2 |
| cyclohexane | 47 | 239 | 6.4 | 3.5 |
| methylcyclohexane | 45 | 238 | 20.1 | 14.1 |
| n-pentane | 34 | 188 | 6.6 | 4.0 |
| n-hexane | 34 | 208 | 22.6 | 11.5 |
| n-hexene | 39 | 227 | 17.6 | 8.9 |
| n-heptane | 43 | 218 | 137.5 | 52.5 |
| n-octane | 52 | 252 | 302.6 | 80.0 |
| iso-octane | 50 | 257 | 51.6 | 22.9 |
| n-nonane | 53 | 261 | 406.2 | 89.5 |
| n-decane | 54 | 269 | 449.7 | 96.8 |
| n-undecane | 45 | 311 | 594.5 | 94.0 |
| n-dodecane | 47 | 310 | 735.3 | 121.6 |
| chloro-2-ethanol | 104 | 428 | 6.4 | 4.1 |
| butan-1-ol | 68 | 329 | 16.0 | 10.2 |
| pentan-1-ol | 67 | 329 | 130.6 | 51.4 |
| hexan-1-ol | 61 | 299 | 299.1 | 108.5 |
| trichloroethylene | 107 | 535 | 10.0 | 6.1 |
| tetrachloroethylene | 120 | 599 | 55.1 | 34.6 |
| chlorobenzene | 81 | 410 | 74.8 | 38.0 |
| bromobenzene | 110 | 550 | 150.1 | 58.2 |
| 1,4-dichlorobutane | 83 | 416 | 49.2 | 40.5 |
| 1,2-dichloroethane | 93 | 461 | 3.9 | 2.0 |
| 1,2-dibromoethane | 144 | 790 | 14.4 | 8.7 |
| 1,1,2-trichloroethane | 157 | 529 | 12.5 | 7.0 |
| 1,1,1-trichloroethane | 83 | 409 | 7.5 | 2.6 |
| 1,1,2,2-tetrachloroethane | 118 | 574 | 38.4 | 25.5 |
| tertbutylbenzene | 94 | 282 | 270.7 | 111.5 |
| isopropylbenzene | 63 | 311 | 244.5 | 83.5 |
| 1,2,3-trichloropropane | 102 | 509 | 46.2 | 24.1 |
| 1,2-dichlorobenzene | 96 | 478 | 158.8 | 89.5 |
| 1,3-dichlorobenzene | 71 | 472 | 285.3 | 78.9 |
| 1,2,4-trichlorobenzene | 107 | 533 | 563.1 | 142.2 |

Table 4.3 **Range of mg/m$^3$ VOC concentrations generated and the range of measured values of $V_b$ for 43 VOC on Carbotrap-B at 298K**

this would suggest that the adsorptive interactions are indeed non-specific and that perhaps steric or other physical properties of the molecules play a role in the adsorption process. The possibility of steric effects is also suggested from the $V_b$ data for iso-octane and octane and also iso-propylbenzene and propylbenzene.

Physical adsorption is due to the sum of the attractive and repulsive forces that occur when a gaseous molecule comes sufficiently close to an adsorbent molecule for adsorption to take place. Physisorption involves a combination of both dispersive forces and repulsive forces. The sum of these interactions gives rise to an adsorption potential that can be designated by the Lennard-Jones potential as defined in Eq. (2.2). Kirkwood and Muller, Eq. (2.3), London, Eq. (2.4) and Slater and Kirkwood, Eq. (2.5), have expressed the dispersive forces in terms of physical properties of the individual molecules. Each of these equations expresses the dispersive forces in terms of the polarizability of the molecule. The three equations suggest that with an increase in the polarisability of compounds in a group, the 'attraction potential', with respect to adsorbent-adsorbate interactions, of the compounds in this group will also increase. As the polarisability of the n-alkanes increases with increasing chain length, then this effect is clearly seen in the adsorption of the n-alkane series of VOC. The larger compounds also interact with a larger surface area of the adsorbent thus increasing their ability to be adsorbed.

Alkyl groups are more polarisable than C-H bonds and usually function as weakly electro-repelling groups when bound to unsaturated systems such as vinyl or phenyl groups (Ingold, 1957). These vinyl or phenyl groups act as weak attractors of electrons when present in such systems. This results in a slight polarisation of the compounds due to an inductive effect. This polarisability should therefore increase with increased side chain substitution with respect to the compounds studied in these experiments. An ethyl group as a substituent is slightly more electron repelling than a methyl group. This explains the increased $V_b$ for ethylbenzene compared to those of toluene. The pattern of increasing $V_b$ from benzene, toluene, the xylenes and through to the trimethyl benzene's could therefore be a result of an increase in polarisability caused by increased side chain substitution.

A similar pattern is observed when an alkyl substituent group is replaced by a halogen. The greater the number of substitutions the greater the $V_b$. Bromine is more electronegative than chlorine and therefore the polarisation of the molecule will be greater when a bromine atom replaces a chlorine atom as the substituent. This effect is clearly seen in the $V_b$ for both chlorobenzene and bromobenzene. The $V_b$ for chlorobenzene are greater than those measured for toluene, but less than the $V_b$ measured for bromobenzene. The affinity of Carbotrap-B for $C_2$ VOC is greatly enhanced by the incorporation of a halogen into the molecular structure. This is most markedly observed in the case of chloro-2-ethanol. Both ethanol and propan-1-ol have instant breakthrough on Carbotrap-B. Yet chloro-2-ethanol has a $V_b$ of 4.1L/g at an adsorptive concentration of 428mg/m$^3$.

For the work reported in this thesis, molecular polarizabilities were calculated from the physical parameters given in Table 4.1 using the Lorenz-Lorenz equation, Eq, (2.27). The calculated molecular polarizabilities do increase with increasing chain length within a homologous series and also with increasing side-chain substitution of the benzene compounds. Betz and Suppina (1989) studied the adsorption of alkanes and alcohols on GCB using a retention volume method. They reported a linear relationship between the log of their measured values of $V_b$ and molecular polarizability. A plot of calculated molecular polarizabilities against the log of the measured values of $V_b$ for some of the VOC at the lower end of the ranges reported in Table 4.3, is shown in Fig. 4.3. $CH_3$-benzene refers to the group of substituted mono-aromatics where the substituent groups are methyl groups. $C_xH_y$-benzene refers to the rest of the alkyl mono-aromatic hydrocarbons and chloro-benzene refers to the chlorinated mono-aromatic hydrocarbons. It can be seen that $V_b$ does indeed increase with increased polarizability but that the increase in the value of the log of the measured values of $V_b$ is not always a linear function of polarizability. The difference between the non-linear relationship reported here and the linear relationship of Betz and Gisch may be due to the method chosen for the determination of $V_b$. Their reported values of $V_b$ are for low adsorptive concentrations using the retention volume method whereas the values reported here are for a higher adsorptive concentration range and the method has shown that $V_b$ is concentration dependent.

Although the use of molecular polarizability helps to explain the increase in the value of $V_b$ within certain groups of VOC, it does not provide a complete understanding of our results. Chloro-2-ethanol and propan-1-ol both have the same calculated values for their polarizabilities while that of bromobenzene is similar to chlorobenzene. Yet the adsorption behaviour of each on Carbotrap-B is quite different. There is evidence in Table 4.3 of some steric effects as previously mentioned. However, the results in Table 4.3 do lend evidence to the physical nature of the adsorption processes between Carbotrap-B and the VOC whose adsorption was studied, thus making Carbotrap-B quite a suitable adsorbent for VOC sampling applications.

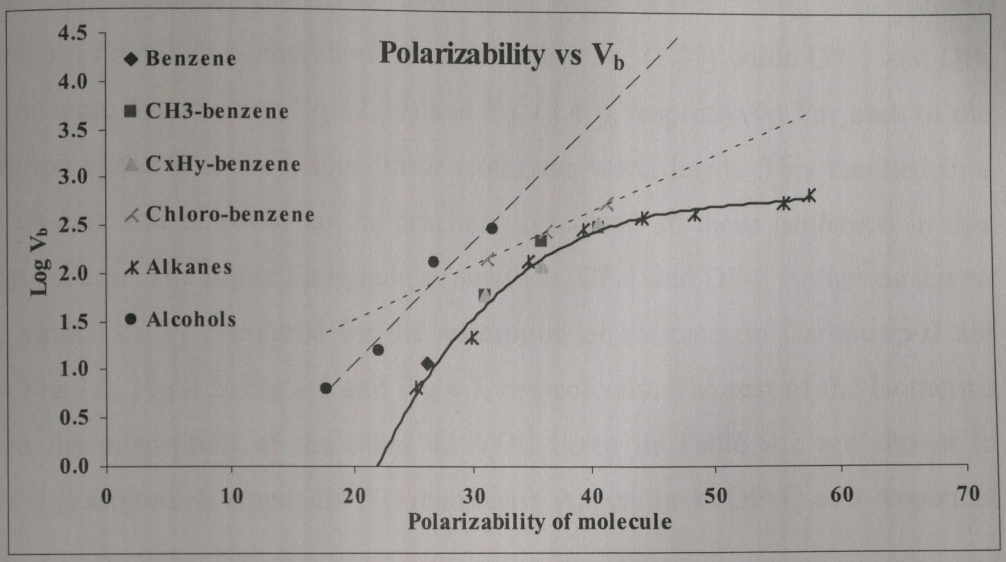


Fig 4.3 **Molecular polarizability, as calculated from the molecular properties reported in Table 4.1, against the values of the log of the values of $V_b$ that were measured for the adsorption of alkanes, alcohols, mono-aromatic hydrocarbons and chlorinated hydrocarbons on Carbotrap-B at mg/m$^3$ concentrations at 298K and which are reported in Table 4.3**

The values of $V_b$ measured for toluene and hexane for adsorptive concentrations between 150mg/m$^3$ and 300mg/m$^3$ are within ±5% of those calculated from the Wheeler equation parameters, Eq. (2.50), that were reported by Vahdat *et al* (1995). Mastrogiacomo *et al* (1995) reported $V_b$ values for the adsorption on Carbotrap-B of 2.4L/g for 1,2-dichloroethane, 6.4L/g for benzene and 23L/g for hexane. These $V_b$ values were determined by a direct method in each case although adsorptive concentrations corresponding to the $V_b$ are not reported. These values are in good

agreement with the measured values of $V_b$ for these compounds that are reported in Table 4.3.

### 4.3.3 Adsorption Isotherms for the adsorption of individual VOC at mg/m$^3$ adsorptive concentrations on Carbotrap-B at 298K

Experimental values of $V_b$ were measured for each VOC on Carbotrap-B for at least four different concentrations within the range reported in Table 4.3. Linear experimental isotherms were drawn using the linear expressions of each of the model isotherms. Experimental Langmuir isotherms were drawn using Eq. (2.35). Experimental Freundlich isotherms were drawn using Eq, (2.37) while DP-1 and DP-2 isotherms were drawn using Eq. (2.39) and Eq. (2.40), respectively. For each of the 43 adsorption systems studied, four linear isotherms were drawn. This resulted in a large set of data and it would not be practical to include all these isotherms in this discussion section. The linear Langmuir, Freundlich, DP-1 and DP-2 isotherms drawn from the values of $V_b$ measured for the adsorption of benzene on Carbotrap-B are shown in Fig 4.4, Fig 4.5, Fig 4.6 and Fig 4.7, respectively. The rest of the isotherms relating to the adsorption of the other 42 VOC listed in Table 4.2 are shown in Appendix 2 (Langmuir), Appendix 3 (Freundlich), Appendix 4 (DP-1) and Appendix 5 (DP-2).

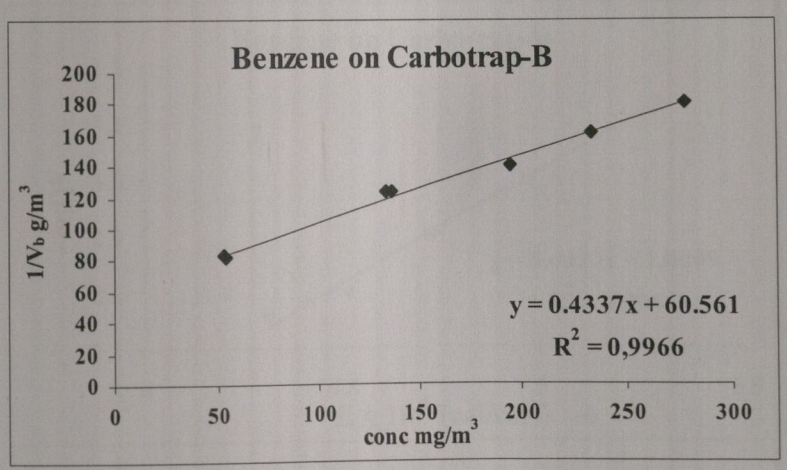


**Fig 4.4 Linearised Langmuir isotherm for the adsorption of benzene, in the mg/m$^3$ concentration range, on Carbotrap-B at 298K**

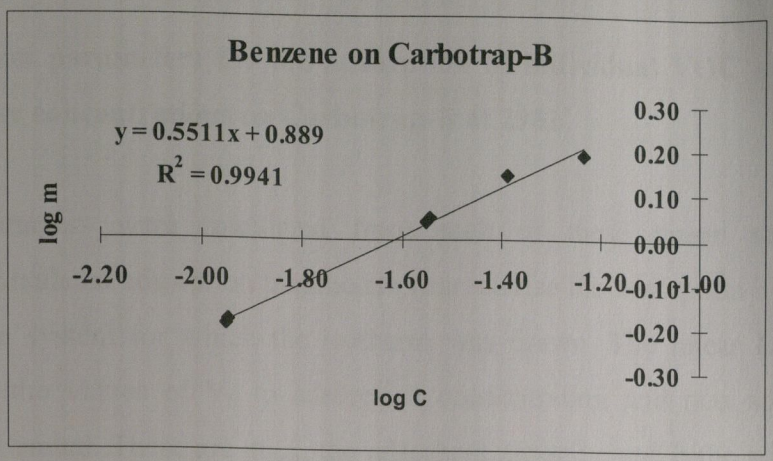


Fig 4.5 Linearised Freundlich isotherm for the adsorption of benzene, in the mg/m$^3$ concentration range, on Carbotrap-B at 298K

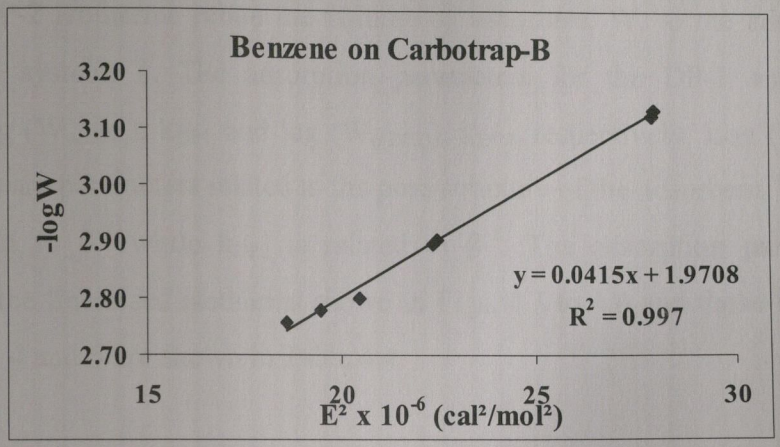


Fig 4.6 Linearised DP-1 isotherm for the adsorption of benzene, in the mg/m$^3$ concentration range, on Carbotrap-B at 298K

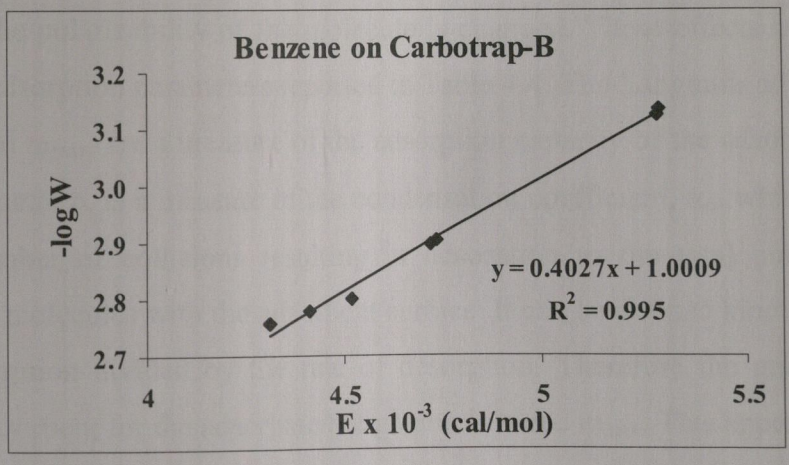


Fig 4.7 Linearised DP-2 isotherm for the adsorption of benzene, in the mg/m$^3$ concentration range, on Carbotrap-B at 298K

### 4.3.4 Adsorption parameters for the adsorption of individual VOC at mg/m$^3$ adsorptive concentrations on Carbotrap-B at 298K

Adsorption parameters were calculated from each of these linear adsorption isotherms. The calculated adsorption parameters characterise the adsorption behaviour of the adsorption system for which the isotherm was drawn. The linear Langmuir isotherm relates the values of $V_b$ to adsorptive concentration and two adsorption parameters are obtained. These are $m_{max}$, the adsorbent capacity, and b the adsorption coefficient. The Freundlich isotherm relates the mass of adsorbate, $m_{ads}$ to adsorptive concentration from which two empirical parameters, n and $k_F$ are calculated. Finally the DP-1 and DP-2 isotherms relate the volume of adsorbate, W, to the adsorption potential of the system, ε. The adsorption parameters for the DP-1 and DP-2 isotherms are log ($W_{o(DP1)}$), $k_{DP1}$ and log ($W_{o(DP2)}$), $k_{DP2}$, respectively. Log ($W_{o(DP1)}$) and log ($W_{o(DP2)}$) are parameters related to the pore structure of the adsorbent. $k_{DP1}$ is a parameter related to $\beta^{-2}$ while $k_{DP2}$ is related to $\beta^{-1}$. The adsorption parameters calculated from the linearised isotherms shown in Figs, 4.3 to 4.6 and those found in Appendices 2, 3, 4 and 5 are shown in Table 4.4.

From the data reported in Table 4.3 it was observed that the affinity of Carbotrap-B for VOC within a homologous group increases as the chain length of the VOC increases. Also side-chain substitution of the mono-aromatic hydrocarbons affects the value of $V_b$ as the polarizability of the molecule is changed. These effects are again reflected in the adsorption parameters reported in Table 4.4. The Langmuir adsorption parameters, b and $m_{max}$, are a measure of the adsorption capacity of the adsorbent for the VOC. Parameter b, is a measure of the condensation coefficient, $\alpha_o$, which is the ratio of the number of collisions resulting in adsorption to the total number of collisions of gas molecules with the adsorbent surface. It can be defined kinetically as the rate of adsorption divided by the rate of desorption. Therefore the greater the affinity of the adsorbent for the adsorbate the greater is b and $m_{max}$. This appears to be the case in Table 4.4 as b and $m_{max}$ increase with increasing side-chain substitution and increasing chain length within the alkane group.

| Compound | Langmuir Parameters | | | Freundlich Parameters | | | DP-1 parameters | | | DP-2 parameters | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | b (m3/mg) | $M_{max}$ (mg/g) | $R^2$ | n | $k_F$ | $R^2$ | $logW_{o(DP1)}$ | $k_{(DP1)}*10^8$ | $R^2$ | $logW_{o(DP2)}$ | $k_{(DP2)}*10^4$ | $R^2$ |
| benzene | 0.007 | 2.3 | 0.997 | 1.81 | 0.9 | 0.994 | -1.97 | 4.2 | 0.997 | -1.00 | 4.0 | 0.995 |
| toluene | 0.004 | 16.3 | 0.969 | 1.61 | 1.8 | 0.992 | -1.17 | 5.9 | 0.997 | -0.31 | 4.5 | 1.000 |
| o-xylene | 0.021 | 24.2 | 0.993 | 3.94 | 1.7 | 0.983 | -1.40 | 2.7 | 0.977 | -1.08 | 1.9 | 0.983 |
| p-xylene | 0.017 | 25.3 | 0.999 | 2.92 | 1.8 | 0.969 | -1.27 | 3.5 | 0.980 | -0.83 | 2.5 | 0.969 |
| m-xylene | 0.023 | 22.6 | 0.999 | 3.78 | 1.7 | 0.987 | -1.39 | 2.8 | 0.995 | -1.05 | 1.9 | 0.987 |
| styrene | 0.012 | 23.9 | 0.998 | 2.51 | 1.8 | 0.989 | -1.33 | 4.4 | 0.996 | -0.85 | 2.9 | 0.989 |
| ethylben | 0.006 | 29.2 | 0.996 | 1.65 | 2.1 | 0.995 | -1.09 | 6.1 | 0.999 | -0.28 | 4.4 | 0.995 |
| propylbenzene | 0.032 | 28.7 | 0.997 | 5.24 | 1.7 | 0.984 | -1.36 | 2.1 | 0.998 | -1.13 | 1.4 | 0.984 |
| 1,2,3-trimethylbenzene | 0.066 | 25.8 | 0.991 | 11.15 | 1.5 | 0.996 | -1.49 | 1.1 | 0.996 | -1.40 | 0.7 | 0.996 |
| 1,2,4-trimethylbenzene | 0.089 | 25.0 | 0.997 | 12.56 | 1.5 | 0.992 | -1.50 | 1.0 | 0.990 | -1.40 | 0.6 | 0.977 |
| 1,3,5-trimethylbenzene | 0.084 | 24.3 | 0.989 | 11.64 | 1.5 | 0.977 | -1.50 | 0.9 | 0.988 | -1.41 | 0.6 | 0.992 |
| cyclohexane | 0.005 | 1.5 | 0.992 | 1.57 | 0.9 | 0.996 | -2.04 | 4.7 | 0.998 | -0.89 | 4.7 | 0.997 |
| methylcyclohexane | 0.003 | 7.7 | 0.967 | 1.49 | 1.5 | 0.997 | -1.43 | 5.6 | 0.995 | -0.36 | 4.9 | 0.997 |
| n-pentane | 0.005 | 1.5 | 0.997 | 1.38 | 0.9 | 0.995 | -1.59 | 4.4 | 0.997 | 0.01 | 5.3 | 0.995 |
| n-hexane | 0.006 | 4.1 | 0.987 | 1.61 | 1.3 | 0.992 | -1.46 | 4.3 | 1.000 | -0.25 | 4.6 | 1.000 |
| n-hexene | 0.007 | 3.2 | 0.983 | 1.62 | 1.1 | 0.997 | -1.56 | 4.2 | 0.999 | -0.34 | 4.5 | 0.997 |
| n-heptane | 0.015 | 14.9 | 0.989 | 2.43 | 1.7 | 0.984 | -1.20 | 3.3 | 0.989 | -0.51 | 3.0 | 0.982 |
| n-octane | 0.043 | 21.9 | 0.999 | 6.07 | 1.5 | 0.998 | -1.36 | 1.5 | 0.998 | -1.12 | 1.2 | 0.998 |
| iso-octane | 0.009 | 8.6 | 0.998 | 1.92 | 1.5 | 0.982 | -1.34 | 4.1 | 0.990 | -0.47 | 3.8 | 0.982 |
| n-nonane | 0.148 | 23.7 | 0.999 | 18.69 | 1.5 | 0.994 | -1.45 | 0.5 | 0.971 | -1.39 | 0.3 | 0.983 |
| n-decane | 0.173 | 26.5 | 0.995 | 22.52 | 1.5 | 0.995 | -1.41 | 0.5 | 0.998 | -1.36 | 0.3 | 0.998 |
| n-undecane | 0.180 | 29.8 | 0.993 | 24.27 | 1.5 | 0.963 | -1.38 | 0.6 | 0.955 | -1.34 | 0.3 | 0.963 |
| n-dodecane | 0.200 | 38.5 | 0.986 | 20.24 | 1.7 | 0.953 | -1.27 | 0.7 | 0.973 | -1.22 | 0.4 | 0.953 |

| Compound | Langmuir Parameters | | | Freundlich Parameters | | | DP-1 parameters | | | DP-2 parameters | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | b (m3/mg) | $M_{max}$ (mg/g) | $R^2$ | n | $k_F$ | $R^2$ | $\log W_{o(DP1)}$ | $k_{(DP1)}*10^8$ | $R^2$ | $\log W_{o(DP2)}$ | $k_{(DP2)}*10^4$ | $R^2$ |
| chloro-2-ethanol | 0.002 | 3.9 | 0.996 | 1.42 | 1.0 | 0.996 | -2.24 | 5.4 | 0.999 | -1.46 | 5.2 | 0.996 |
| butan-1-ol | 0.002 | 7.5 | 0.997 | 1.38 | 1.4 | 0.998 | -1.78 | 8.5 | 1.000 | -0.95 | 5.3 | 0.998 |
| pentan-1-ol | 0.010 | 22.0 | 0.993 | 2.40 | 1.7 | 0.981 | -1.38 | 5.4 | 0.988 | -0.95 | 0.3 | 0.981 |
| hexan-1-ol | 0.014 | 40.8 | 0.997 | 2.63 | 2.0 | 0.965 | -1.14 | 5.4 | 0.981 | -0.79 | 2.8 | 0.965 |
| trichloroethylene | 0.002 | 7.0 | 0.981 | 1.41 | 1.4 | 0.994 | -1.70 | 5.7 | 0.998 | -0.52 | 5.2 | 0.997 |
| tetrachloroethylene | 0.001 | 43.3 | 0.988 | 1.40 | 2.2 | 0.994 | -1.13 | 6.8 | 1.000 | -0.13 | 5.3 | 0.999 |
| chlorobenzene | 0.004 | 25.1 | 0.962 | 1.70 | 1.9 | 0.989 | -1.23 | 5.7 | 0.995 | -0.42 | 4.3 | 0.989 |
| bromobenzene | 0.006 | 42.2 | 0.998 | 2.12 | 2.1 | 0.972 | -1.28 | 5.6 | 0.979 | -0.75 | 3.5 | 0.972 |
| 1,4-dichlorobutane | 0.001 | 76.9 | 0.999 | 1.13 | 2.4 | 0.999 | -0.84 | 8.1 | 1.000 | 0.44 | 6.5 | 0.999 |
| 1,2-dichloroethane | 0.003 | 1.5 | 0.992 | 1.69 | 0.6 | 0.997 | -2.19 | 4.2 | 0.999 | -1.08 | 4.3 | 0.997 |
| 1,2-dibromoethane | 0.001 | 14.1 | 0.994 | 1.41 | 1.7 | 0.992 | -1.77 | 7.4 | 0.998 | -0.74 | 5.5 | 0.996 |
| 1,1,2-trichloroethane | 0.003 | 5.8 | 0.992 | 1.69 | 0.6 | 0.997 | -2.01 | 4.9 | 0.999 | -1.29 | 3.8 | 1.000 |
| 1,1,1-trichloroethane | 0.010 | 1.3 | 0.998 | 2.90 | 0.5 | 0.996 | -2.57 | 2.5 | 0.999 | -1.94 | 2.5 | 0.996 |
| 1,1,2,2-tetrachloroethane | 0.001 | 33.6 | 0.991 | 1.34 | 2.1 | 0.993 | -1.40 | 8.4 | 0.998 | -0.52 | 5.5 | 0.993 |
| 1,2-dichlorobenzene | 0.018 | 47.4 | 0.999 | 4.81 | 1.9 | 0.994 | -1.35 | 2.8 | 0.999 | -1.14 | 1.53 | 0.99 |
| 1,3-dichlorobenzene | 0.011 | 43.7 | 0.998 | 3.05 | 2.0 | 0.992 | -1.29 | 3.9 | 0.998 | -0.93 | 2.40 | 0.99 |
| 1,2,4-dichlorobenzene | 0.025 | 80.6 | 1.000 | 6.89 | 2.1 | 0.992 | -1.21 | 2.4 | 0.999 | -1.10 | 1.07 | 0.99 |
| 1,2,3-trichloropropane | 0.003 | 20.3 | 0.999 | 1.66 | 1.9 | 0.993 | -1.61 | 7.5 | 0.998 | -0.97 | 4.41 | 0.99 |
| tertbutylbenzene | 0.026 | 35.6 | 1.000 | 5.22 | 1.8 | 0.993 | -1.27 | 2.4 | 0.997 | -1.06 | 1.4 | 0.993 |
| isopropylbenzene | 0.015 | 30.8 | 0.986 | 3.15 | 1.8 | 0.993 | -1.25 | 3.6 | 0.968 | -0.88 | 2.3 | 0.963 |

**Table 4.4** Adsorption parameters calculated from the linearised isotherms drawn from the $V_b$ measured for the adsorption of VOC in the $mg/m^3$ concentration range at 298K on Carbotrap-B

Although the Freundlich adsorption parameters are empirical in nature, an attempt to attribute some theoretical meaning to them was described in section 2.1.2. n is analogous to the enthalpy of adsorption as expressed in Eq. (2.21). The assumption used to explain this was that adsorption sites with the higher enthalpy of adsorption are filled before those with a lower enthalpy. The enthalpy of adsorption is a measure of the adsorption capacity of the adsorbent for the VOC, the higher the measured enthalpy the higher the surface coverage and hence the higher the capacity for adsorption. This appears to be the case for the values of n reported in Table 4.4. The DP-1 adsorption parameter $k_{DP1}$ and the DP-2 parameter $k_{DP2}$ are both inversely proportional to the affinity coefficient $\beta$. This implies that higher the affinity of the adsorbent for the VOC the smaller the value of the adsorbent parameter. This relationship holds true for the mono-aromatic hydrocarbons and the alkane group. However for the chlorinated hydrocarbons the assumption does not fit the data.

Experimental values of $\beta$ for each of the VOC were calculated from the calculated values of $k_{DP1}$ and $k_{DP2}$ using Eq. (2.43) and Eq. (2.44), respectively. Theoretical values were calculated from values of molecular polarizabilities and molecular parachor. Molecular polarizabilities were calculated using the Lorenz-Lorenz equation Eq. (2.27). Values of molecular parachor, $\Omega$, were calculated using the following expression (Reucroft *et al* 1971):

$$\Omega = \frac{\gamma^{\frac{1}{4}} M}{\rho} \qquad \text{Eq. (4.3)}$$

where $\gamma$ is the surface tension of the VOC, M is the molecular weight, and $\rho$ is the liquid density of the VOC. All the physical parameters are reported in Table 4.1. Benzene, pentane, 1,2-dichloroethane and chlorobenzene were first chosen as reference compounds. While the calculated experimental values of $\beta$ exhibited the same pattern as the measured $V_b$ i.e they increased when the measured $V_b$ increased with respect to the reference compound, they did not reflect the size of the increase in the values of the measured $V_b$. The values of the calculated experimental values of $\beta$ also differed greatly from those calculated from the physical properties of the VOC. Differences of between +/-20% to 150% were found. No correlation could be made

between the calculated experimental values of β and a physical property of the VOC. Similar findings have been reviewed recently by Wood (2000).

Also shown in Table 4.4 are the values of $R^2$, the regression coefficients for the linear isotherms. This parameter is a measure of the adherence of the data to the theoretical equation. Values of $R^2$ ranging from 0.96 to 0.99 are found indicating that each of the model isotherms describes equally well the adsorption behaviour of the VOC on Carbotrap-B under the experimental conditions. For pumped tube sampling applications the values of $V_b$ under various environmental conditions need to be known. The parameters in Table 4.4 have an advantage over parameters derived from $V_b$ determined by the retention volume method in that they can be used to calculate the effect of concentration on $V_b$ for the VOC studied at $mg/m^3$ concentrations. As such they provide a useful tool from which $V_b$ can be evaluated for different sampling procedures.

## 4.4. Application of the adsorption parameters to the $\mu g/m^3$ concentration range

The isotherms shown above from which the adsorption parameters have been calculated are all linearised forms of the Langmuir, Freundlich and Dubinin-Polyani isotherms. The calculated parameters can be used not only to reproduce the linearised forms of the isotherms but also to draw non-linearised experimental isotherms for each of the models. The non-linearised isotherms relate $m_{ads}$, the mass of adsorbate, to c the adsorptive concentration of the VOC. The calculated adsorption parameters are used to calculate values of $V_b$ for a range of concentrations similar to those reported in Table 4.3. Eq. (2.32) is then used to calculate values of $m_{ads}$. Fig 4.8 shows the non-linearised experimental isotherms for the adsorption of benzene on Carbotrap-B. The isotherms were drawn from values of $m_{ads}$ calculated from the adsorption parameters given in Table 4.4. Experimental values of $m_{ads}$ were calculated from the $V_b$ measured under experimental conditions, using Eq. (2.32) and these are also shown in Fig 4.8. As can be seen from the graph each of the model isotherms fits well with the experimental data and any one set of adsorption parameters can be used to calculate values of $V_b$ and $m_{ads}$ for the adsorption of the VOC under the experimental

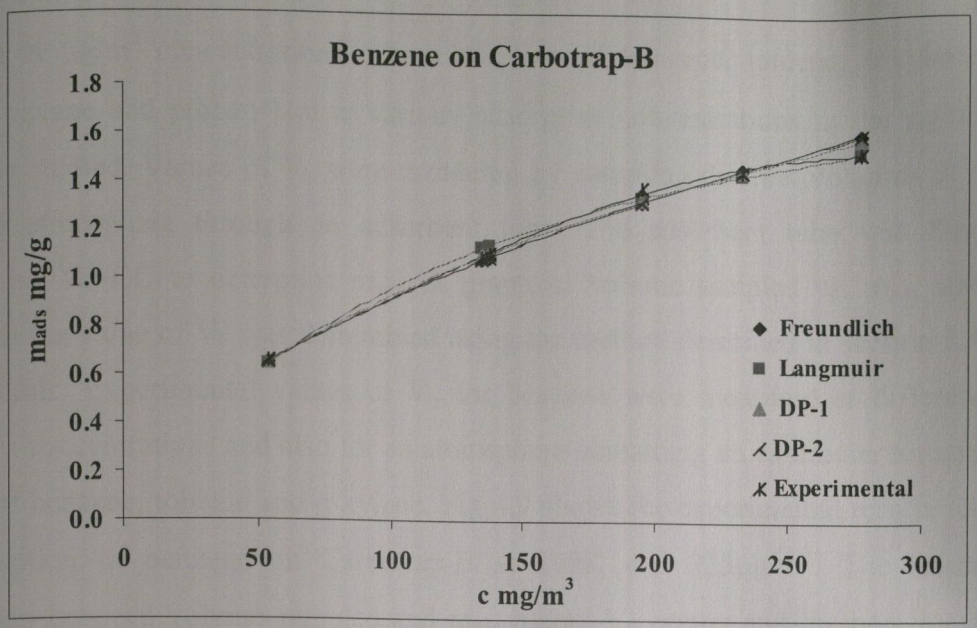


**Fig 4.8** **Non-linearised Experimental, Langmuir, Freundlich, DP-1 and DP-2 isotherms for the adsorption of benzene, in the mg/m$^3$ concentration range, on Carbotrap-B at 298K**

conditions. Comes *et al* (1993) calculated Langmuir adsorption parameters for the adsorption of benzene, toluene and styrene, at mg/m$^3$ concentrations, on Tenax GC. The authors made the assumption that these calculated parameters could be extrapolated to the μg/m$^3$ concentration range, i.e., $V_b$ at μg/m$^3$ concentrations could be calculated from adsorption parameters determined at mg/m$^3$ concentrations. This assumption was not tested at the time. Adsorption parameters were also calculated for the adsorption of binary and ternary mixtures of the compounds. Experimental values of $V_b$ for the multi-component atmospheres were compared to values of $V_b$ calculated using Eq. (2.36). The authors reported good agreement between calculated and experimental values and suggested Eq. (2.36) to be a useful tool for calculating values of $V_b$ for competitive adsorption.

If the assumption that $V_b$ in the μg/m$^3$ concentration range could be calculated from mg/m$^3$ adsorption parameters was true then the considerable volume of data in Table 4.4 could be used to cover the entire concentration range for ambient and occupational VOC sampling applications. To investigate the validity of the assumption that values of $V_b$ in the μg/m$^3$ range could be determined by extrapolating Langmuir, Freundlich and Dubinin-Polyani mg/m$^3$ isotherms, values of $V_b$ for a number of VOC were

measured at $\mu g/m^3$ concentrations. The adsorption of benzene, toluene, o-xylene, pentane, hexane and propan-1-ol at various adsorptive concentrations in the $\mu g/m^3$ range was studied. Values of $V_b$ were measured by sampling discreet volumes of a generated atmosphere through an adsorbent tube. The adsorbent tube was then analysed by TD-GC to determine $m_{ads}$. A graph of volume sampled vs. $m_{ads}$ was drawn and the value of $V_b$ was determined using the method described in section 3.4 of this thesis. Experimental values of $V_b$ for benzene were measured at different adsorptive concentrations and also for an atmosphere containing an equimolar ternary mixture of benzene, toluene and o-xylene. Fig 4.9 shows the experimental results for the adsorption of benzene on Carbotrap-B at 298K and $325\mu g/m^3$. The linear relationship between volume sampled and $m_{ads}$ before $V_b$ occurs and the non-linear relationship thereafter are evident in the graph. The corresponding graphs relating to the measurement of $V_b$ for the other VOC are shown in Appendix 6.

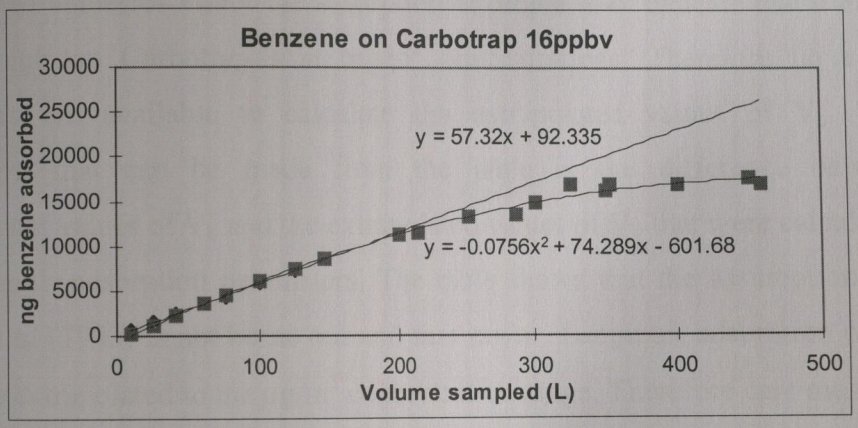


**Fig 4.9** **Graph showing the linear and non-linear relationships between volume sampled and mass of adsorbate for the determination of the value of $V_b$ for benzene on Carbotrap-B at 298K and at $60\mu g/m^3$(16ppbv).**

## 4.5 Values of $V_b$ for the adsorption of VOC on Carbotrap-B at $\mu g/m^3$ concentrations

The experimental results for the measurement of the values of $V_b$ at $\mu g/m^3$ concentrations are shown in Table 4.5. The asterisk beside benzene, toluene and o-xylene in the table refers to the value of $V_b$ for that particular VOC when measuring $V_b$ for the ternary mixture described above. The NA in the table in place of the

| Compound | Temperature of adsorption | Concentration | Experimentally measured $V_b$ | Extrapolated $V_b$ | | | |
|---|---|---|---|---|---|---|---|
| | | | | Freundlich | Langmuir | DP1 | DP2 |
| | K | µg/m$^3$ (ppbv) | L/g | L/g | L/g | L/g | L/g |
| benzene | 298 | 325 (88) | 169 | 120 | 16 | 39 | 122 |
| benzene | 298 | 220 (59) | 169 | 143 | 16 | 40 | 145 |
| benzene | 298 | 60 (16) | 171 | 257 | 17 | 40 | 260 |
| benzene* | 298 | 65 (18) | 165 | 247 | 17 | 40 | 251 |
| benzene* | 298 | 45 (12) | 169 | 292 | 17 | 39 | 296 |
| benzene | 261 | 45 (12) | > 440 | 519 | 53 | 26 | 518 |
| hexane | 298 | 56 (16) | 350 | 258 | 26 | 42 | 258 |
| hexane | 298 | 21 (6) | 346 | 374 | 26 | 36 | 374 |
| pentane | 298 | 47 (16) | 121 | 41 | 8 | 6 | 41 |
| propanol | 298 | 80 (33) | 13 | NA | NA | NA | NA |
| toluene* | 298 | 45 (12) | >600 | 898 | 70 | 59 | 897 |
| toluene | 298 | 76 (20) | 823 | 735 | 70 | 69 | 735 |
| o-xylene* | 298 | 52 (12) | >600 | 48993 | 508 | 12783 | 42780 |
| o-xylene | 298 | 48 (11) | >1850 | 52001 | 508 | 13210 | 45394 |

**Table 4.5 Experimentally measured $V_b$ for VOC in the µg/m$^3$ concentration range. Extrapolated isotherm values are also shown**

extrapolated values of $V_b$ for the adsorption of propan-1-ol indicate that it has instant breakthrough on Carbotrap-B at mg/m$^3$ concentrations. Therefore no adsorption parameters are available to calculate the extrapolated values of $V_b$. The first observation that can be made from the table is the difference between the experimental values of $V_b$ and the extrapolated values of $V_b$ that were calculated from the Langmuir adsorption parameters. The table shows that the assumption made by Comes *et al* (1993) is not borne out and that mg/m$^3$ Langmuir adsorption parameters cannot be extrapolated to the µg/m$^3$ concentration range. Therefore care must be taken to ensure that the calculated parameters are only used for the range of concentrations at which the values of $V_b$ from which they are calculated were measured and any previous assumptions regarding extrapolation should be ignored. There is however, one similarity between the values of $V_b$ from the extrapolated Langmuir isotherm and the experimental values of $V_b$ for benzene. Both sets are constant under isothermal conditions, and do not change with adsorptive concentration. Values of $V_b$ for benzene were calculated for adsorptive concentrations of between 45µg/m$^3$ and 325µg/m$^3$. The constant value for the extrapolated Langmuir $V_b$ may be explained by referring back to Eq. (2.34), which expresses $V_b$ in terms of b, $m_{max}$ and c the adsorptive concentration as:

$$V_b = \frac{bm_{max}}{1+bc}$$

As the adsorptive concentration decreases so to does the value of bc and eventually below a certain adsorptive concentration 1+bc approaches unity. The Langmuir isotherm is a Type I isotherm as classed by Brunauer *et al* (1938) and described in section 2.1.2 of this thesis. The typical shape of a Type I isotherm, as shown in Fig 2.2, exhibits a linear increase in adsorption at lower adsorptive concentrations which leads onto a gradual decline in the slope of adsorption as surface coverage increases to produce a typical plateau as adsorption approaches the formation of a monolayer of adsorbate. At low adsorptive concentrations $V_b=bm_{max}$ represents the linear portion of the Langmuir isotherm and the calculated values of $V_b$ are not concentration dependent. The values of $V_b$, calculated from the Freundlich adsorption parameters, decrease as the adsorptive concentration increases. This is due to the fact that the Freundlich isotherm resembles a Type II isotherm and does not show a saturation value. The amount of adsorbed species increases infinitely with increasing adsorptive concentration. However the initial part of the isotherm, unlike the Langmuir isotherm, does not show a linear relationship between the amount adsorbed and adsorptive concentration. Instead it remains convex to the concentration axis and this may explain the value of $V_b$ calculated using the Freundlich isotherm.

The experimental values of $V_b$ for benzene indicate that the adsorption process is not concentration dependent at $\mu g/m^3$ concentrations. There is a linear relationship between $m_{ads}$ and volume sampled. This relationship is analogous to the Henry's Law region for the absorption of VOC in liquids. Experimental values of $m_{ads}$ of benzene were calculated from the measured values of $V_b$. The extrapolated values of $V_b$, calculated for each of the model isotherms, were also used to calculate values of $m_{ads}$ for benzene for the adsorptive concentration range of $45\mu g/m^3$ and $325\mu g/m^3$. These calculated values of $m_{ads}$ were then used to draw the calculated non-linearised isotherms for the adsorption of benzene on Carbotrap-B at 298K at $\mu g/m^3$ concentrations. The corresponding experimental isotherm was drawn from the experimentally measured values of $V_b$ for the adsorption of benzene on Carbotrap-B at 298K at $\mu g/m^3$ concentrations. The non-linearised isotherms are shown in Fig. 4.10.

The results reported in Table 4.5, and those shown in Fig 4.10, demonstrate quite clearly that, at $\mu g/m^3$ levels, there is better quantitative agreement between the values of experimentally measured $V_b$ and those obtained by extrapolation of the Freundlich and DP-2 isotherms, than with those obtained by extrapolation of the Langmuir and DP-1 isotherms. The similarity between the Freundlich and DP-2 values of $V_b$ is related to the fact that the expressions for the linear Freundlich isotherm, Eq. (2.37), and the linear DP-2 isotherm. Eq. (2.40) are mathematically equivalent, i.e., they are of the generic form log a = b(c) + log d, and as such any adsorption parameters will yield similar results. The linear DP-1 isotherm was proposed for a microporous adsorbent. Carbotrap-B is not a microporous adsorbent and it seems the DP-1 adsorption parameters, although comparable to the other parameters for describing the adsorption behaviour of the VOC on Carbotrap-B at $mg/m^3$ levels, cannot be extrapolated to $\mu g/m^3$ levels where $V_b$ is independent of concentration.

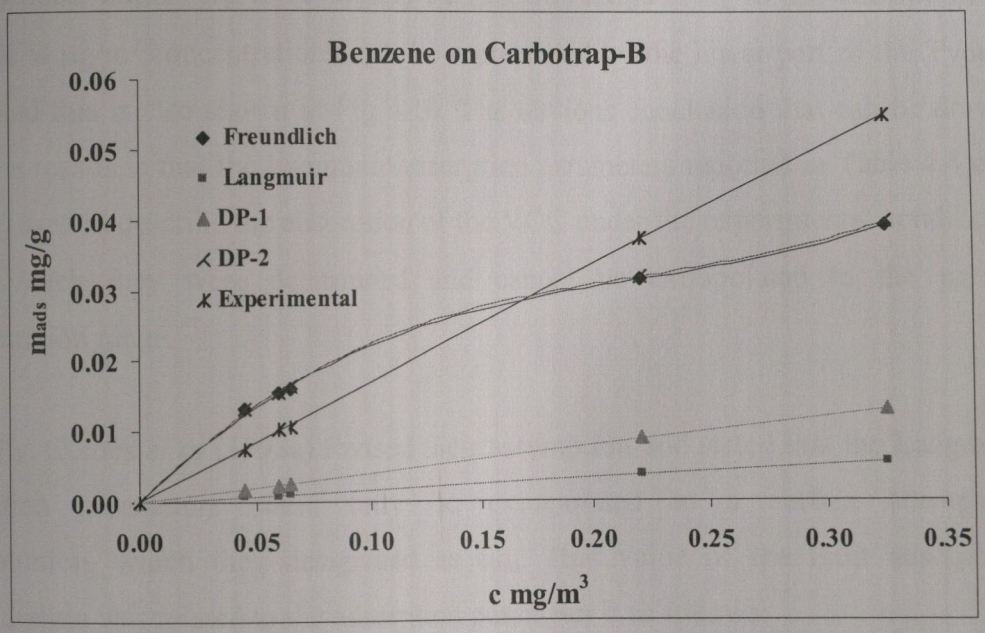


**Fig 4.10** **Non-linearised Experimental, Langmuir, Freundlich, DP-1 and DP-2 isotherms for the adsorption of benzene, in the $\mu g/m^3$ concentration range, on Carbotrap-B at 298K**

The poor agreement between the experimentally measured $V_b$ and those extrapolated from $V_b$ calculated from the Langmuir adsorption parameters may be explained by

considering $\Theta_L$ the surface coverage. As mentioned above the Langmuir isotherm is a Type I isotherm, The value of $\Theta_L$ may be calculated as follows:

$$\Theta_L = \frac{m_{ads}}{m_{max}} \qquad \text{Eq. (4.4)}$$

The Langmuir adsorption parameters were calculated for the adsorption of benzene at concentrations between 50mg/m$^3$ to 300mg/m$^3$. The range of calculated $\Theta_L$ from experimentally determined values of $V_b$ for these concentrations is 0.28 to 0.66. The range of $\Theta_L$ for the experimentally determined values of $V_b$ at μg/m$^3$ concentrations is 0.003 to 0.066. The Langmuir adsorption parameters were calculated for an adsorption system that could be represented by the portion of the Type I isotherm that is approaching the plateau section. This can be seen in the non-linear Langmuir curve in Fig 4.8, where the relationship between $m_{ads}$ and adsorptive concentration is not entirely linear but is seen to be slightly curved. The range of $\Theta_L$ for the adsorption of benzene at μg/m$^3$ concentrations may be represented by the linear part of the Type I curve and this is also shown in Fig 4.10. The obvious conclusion that can be drawn from the results is that the Langmuir adsorption parameters reported in Table 4.4 can only be used to describe the adsorption of the VOC under the experimental conditions under which they were determined and cannot be extrapolated to the μg/m$^3$ concentration range.

Recently, Comes *et al* (1998a) revised their assumption and stated that the Langmuir adsorption parameters could only be extrapolated to a certain adsorptive concentration, which they designated as $c_{lim}$. This value of the limit adsorptive concentration was related to the adsorption parameter b as follows:

$$c_{lim} = \frac{0.05}{b} \qquad \text{Eq. (4.5)}$$

The authors observed patterns, similar to the results reported in this thesis, for calculated values of b for homologous groups of compounds and concluded that b exhibited a remarkable uniformity for compounds of similar chemical nature to such

an extent that the inverse of b could determine the value of $c_{lim}$. They further concluded that the adsorptive concentration greatly affected the significance of b. The figure 0.05 was taken as the limit of acceptable relative error in measuring the adsorptive concentration. From the results reported in this thesis, $c_{lim}$ for the adsorption of benzene on Carbotrap-B was calculated to be 7.1mg/m$^3$. Using the calculated Langmuir adsorption parameters, $V_b$ for this concentration was calculated to be 15.3L/g. The corresponding $V_b$ from the Freundlich adsorption parameters was 30.1L/g. Values of $V_b$ for $c_{lim}$ were calculated for all VOC in Table 4.4. They were then compared to their corresponding calculated Freundlich $V_b$. The Freundlich value was always found to be greater, by factors of between 2 and 60. This would again suggest that the Langmuir adsorption parameters should not be extrapolated even in the mg/m$^3$ concentration range.

The values of $V_b$ obtained experimentally and also from extrapolation of the Freundlich and DP-2 isotherms are of the same order of magnitude as some of the reported $V_b$ values determined for the adsorption of benzene on Carbotrap B by elution chromatography, i.e., 350L/g, 490L/g (Bertoni and Tappa 1997) and 114L/g(Matrogiacomo *et al* 1995).

To summarise the results reported in Table 4.5: the experimental results show that the values of $V_b$ for the adsorption of benzene at μg/m$^3$ levels on Carbotrap B are independent of concentration and of the presence of other adsorbing species under isothermal conditions. The other adsorbing species present in this study were toluene and o-xylene and all three compounds were present in the generated atmospheres at equimolar concentrations. The value of $V_b$ also increased as the temperature of adsorption decreased and this will be discussed in more detail later. The Freundlich and DP-2 adsorption isotherms provide the better results when extrapolating from the μg/m$^3$ to the μg/m$^3$ concentration ranges. At mg/m$^3$ levels, however, all sets of adsorption parameters describe equally well the adsorption on Carbotrap B of the VOC studied.

Although the Freundlich and DP-2 adsorption parameters can be used to calculate $V_b$ at μg/m$^3$ levels that give good quantitative agreement with the experimental values of

$V_b$, care must be taken when using the calculated values for VOC sampling applications. As can be seen in Table 4.5, values of $V_b$ calculated from both models continually increase as adsorptive concentration decreases and calculated values can exceed the experimentally measured values. However, the experimental values of $V_b$ for all VOC in Table 4.5 provide a simple relationship that makes it possible to use the adsorption parameters of Table 4.4 to calculate values of $V_b$ for other VOC at $\mu g/m^3$ levels without having to extrapolate data from one concentration region to another. This will be explained more clearly with the help of Table 4.6.

| VOC | Conc Range $mg/m^3$ | | Ratio of measured $V_b$ | | Range of Calculated $V_b$ at $\mu g/m^3$ level L/g | | Measured value of $V_b$ at $\mu g/m^3$ level L/g |
|---|---|---|---|---|---|---|---|
| benzene | 53 | 278 | 1 | 1 | 170 | 170 | 170 |
| toluene | 54 | 272 | 5.1 | 6.0 | 861 | 1017 | 823 |
| o-xylene | 56 | 277 | 21.1 | 13.7 | 3579 | 2327 | >1850 |
| n-pentane | 34 | 188 | 0.6 | 0.7 | 94 | 124 | 121 |
| n-hexane | 34 | 208 | 1.9 | 2.1 | 320 | 355 | 348 |

**Table 4.6 Comparison of experimentally measured and calculated values of $V_b$ for the adsorption of VOC on Carbotrap-B to those measured for the adsorption of benzene.**

Table 4.6 reports the range of concentrations that were generated to measure the $V_b$ of each of the VOC on Carbotrap-B at $mg/m^3$ concentrations at 298K. They are in fact the same values reported in Table 4.3. The second column shows the ratio of experimentally measured values of $V_b$ in the $mg/m^3$ range for the adsorption of VOC on Carbotrap-B to those measured for the adsorption of benzene. In Table 4.5 it was shown that the experimental value of $V_b$ for benzene at $\mu g/m^3$ concentrations was constant under isothermal conditions and was not influenced by concentration effects or the presence of other adsorbing species. The experimental value of $V_b$ for benzene was measured to be 170L/g. The range of calculated values of $V_b$ for the other VOC, reported in the third column of Table 4.6 are the calculated ratios multiplied by this experimentally measured $V_b$ for benzene on Carbotrap-B at 298K in the $\mu g/m^3$ range. The final column of Table 4.6 shows the experimentally measured values of $V_b$ for the adsorption of each of the VOC on Carbotrap-B in the $\mu g/m^3$ range. It is evident

from the table that the experimentally measured $V_b$ for the other VOC compare favourably with the calculated range of $V_b$.

While the experimentally measured $V_b$ for both hexane and pentane fall into the top end of the calculated range, the experimentally measured value of $V_b$ for toluene is just below the bottom end of the calculated range. Propan-1-ol was found to have a value of $V_b$ of 13L/g on Carbotrap-B at $\mu g/m^3$ concentrations. Using the same assumptions that were used to calculate the range of $V_b$ above, propanol-1-ol would be expected to have values of $V_b$ within the range 0.4L/g to 0.9L/g at $mg/m^3$ concentrations. The results suggest that this could be a useful method for calculating values of $V_b$ at $\mu g/m^3$ concentrations from the parameters in Table 4.4 for VOC sampling applications using the relationship:

$$V_{b(VOC)}^{\mu gm^{-3}} = \frac{V_{b(VOC)}^{mgm^{-3}}}{V_{b(benzene)}^{mgm^{-3}}} * V_{b(benzene)}^{\mu gm^{-3}} \qquad \text{Eq. (4.6)}$$

Safe sampling volumes could be calculated from the value of $V_b$ at the lower end of the calculated range. The data set used for these calculations is however, quite small and further investigations need to be carried out to validate the proposed method.

## 4.6 Effect of temperature on experimentally measured values of $V_b$ and adsorption parameters in the $mg/m^3$ concentration range

Experimental values of $V_b$ for the adsorption of 13 VOC on Carbotrap-B were measured at different temperatures in the range 261K to 310K. This range of temperatures was chosen to represent the normal range of temperatures that may be encountered when sampling VOC in ambient air or workplace atmospheres. The concentration range for which $V_b$ were measured was $50mg/m^3$ to $650mg/m^3$. Table 4.7 lists the 13 VOC whose adsorption on Carbotrap-B at different temperatures was

| Compound | Temp K | Conc range mg/m3 | | Range of measured $V_b$ L/g | |
|---|---|---|---|---|---|
| benzene | 308 | 50 | 278 | 8.2 | 3.9 |
| | 298 | 53 | 278 | 12.0 | 5.5 |
| | 278 | 54 | 272 | 25.8 | 12.8 |
| | 263 | 52 | 274 | 42.0 | 23.1 |
| toluene | 308 | 53 | 264 | 29.8 | 18.2 |
| | 298 | 54 | 272 | 60.8 | 32.9 |
| | 278 | 51 | 264 | 130.7 | 64.0 |
| | 263 | 53 | 267 | 259.4 | 87.6 |
| o-xylene | 308 | 55 | 283 | 157.2 | 60.4 |
| | 298 | 56 | 277 | 252.6 | 75.3 |
| | 278 | 54 | 272 | 370.0 | 94.0 |
| | 263 | 54 | 273 | 440.0 | 110.0 |
| ethylbenzene | 308 | 54 | 269 | 65.5 | 42.3 |
| | 298 | 55 | 274 | 124.8 | 65.0 |
| | 278 | 53 | 266 | 293.4 | 100.9 |
| | 263 | 54 | 266 | 396.3 | 115.1 |
| propylbenzene | 308 | 78 | 239 | 177.5 | 86.2 |
| | 298 | 54 | 273 | 356.0 | 94.8 |
| | 278 | 78 | 238 | 308.6 | 117.2 |
| styrene | 308 | 56 | 282 | 122.1 | 51.9 |
| | 298 | 56 | 287 | 170.0 | 63.3 |
| | 278 | 56 | 281 | 306.1 | 89.7 |
| | 263 | 56 | 280 | 401.6 | 108.4 |
| 12dichloroethane | 261 | 111 | 559 | 15.7 | 6.7 |
| | 268 | 108 | 540 | 11.7 | 5.3 |
| | 278 | 105 | 525 | 7.6 | 3.6 |
| | 298 | 93 | 461 | 3.9 | 2.0 |
| 1122tetrachlororthane | 268 | 143 | 666 | 179.5 | 94.4 |
| | 278 | 130 | 639 | 99.8 | 58.1 |
| | 298 | 118 | 574 | 38.4 | 25.5 |
| hexane | 261 | 54 | 273 | 126.7 | 58.4 |
| | 270 | 51 | 265 | 70.0 | 33.1 |
| | 278 | 54 | 274 | 51.5 | 25.2 |
| | 298 | 34 | 208 | 22.6 | 11.5 |
| chlorobenzene | 261 | 96 | 484 | 252.4 | 90.6 |
| | 268 | 94 | 468 | 205.3 | 77.5 |
| | 278 | 90 | 453 | 159.3 | 61.4 |
| | 298 | 81 | 410 | 74.8 | 38.0 |
| pentanol | 288 | 66 | 324 | 187.9 | 72.6 |
| | 298 | 67 | 329 | 130.6 | 51.4 |
| | 310 | 61 | 296 | 84.5 | 40.0 |
| pentane | 261 | 51 | 263 | 22.1 | 11.5 |
| | 270 | 47 | 247 | 15.2 | 7.9 |
| | 278 | 45 | 245 | 12.3 | 6.7 |
| | 298 | 34 | 188 | 6.6 | 4.0 |
| hexanol | 288 | 66 | 328 | 353.6 | 111.2 |
| | 298 | 61 | 299 | 299.1 | 108.5 |
| | 310 | 61 | 297 | 157.7 | 74.1 |

**Table 4.7 Range of mg/m$^3$ VOC concentrations generated and measured $V_b$ for 13 VOC on Carbotrap-B at different temperatures**

measured. The table also shows the range of concentrations generated for each VOC and the range of measured $V_b$ for that concentration range at each temperature. For each of the VOC, the same concentration range was generated at each temperature. As expected the values of the range of $V_b$ for each of the VOC decreases as temperature increases. This is due to the fact that as the temperature at which adsorption takes place increases, the distribution of available adsorption sites decreases. This causes a decrease in the adsorption capacity of the adsorbent for the VOC resulting in lower values of $V_b$. The measured values of $V_b$ were used to draw linearised Langmuir, Freundlich, DP-1 and DP-2 isotherms for the adsorption of the 13 VOC on Carbotrap-B at each temperature studied. Again it would be impractical to include all of these isotherms in this discussion. Fig 4.11 shows the linearised Langmuir isotherms for benzene at the different temperatures studied. Fig 4.12 shows the linearised Freundlich isotherms while Fig 4.13 and Fig 4.14 show the linearised DP-1 and DP-2 isotherms, respectively, for the adsorption of benzene at the different temperatures. The isotherms relating to the adsorption of the other 12 VOC listed in Table 4.7 can be found in Appendix 7 (Langmuir), Appendix 8 (Freundlich), Appendix 9 (DP-1) and Appendix 10 (DP-2).

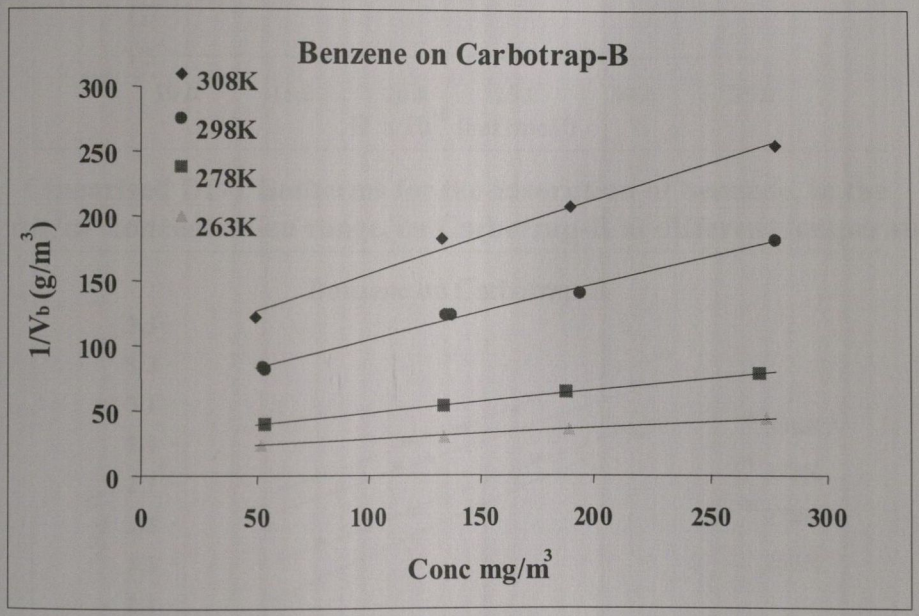


**Fig 4.11 Linearised Langmuir isotherms for the adsorption of benzene, in the mg/m$^3$ concentration range, on Carbotrap-B at different temperatures**

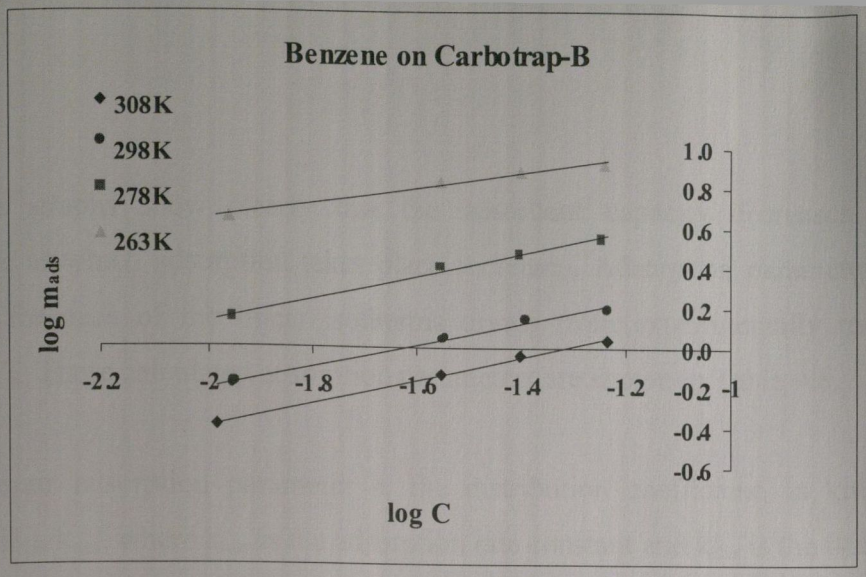


Fig 4.12 **Linearised Freundlich isotherms for the adsorption of benzene, in the mg/m$^3$ concentration range, on Carbotrap-B at different temperatures**

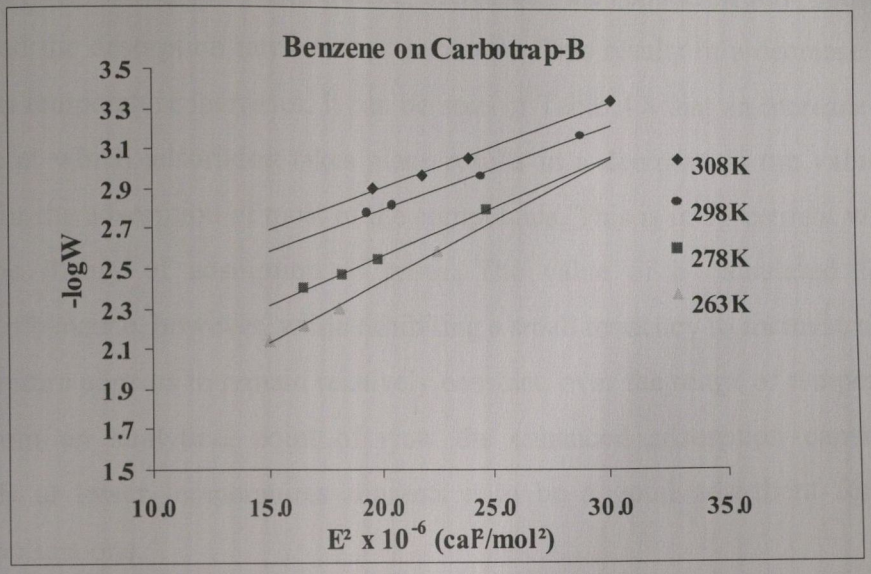


Fig 4.13 **Linearised DP-1 isotherms for the adsorption of benzene, in the mg/m$^3$ concentration range, on Carbotrap-B at different temperatures**

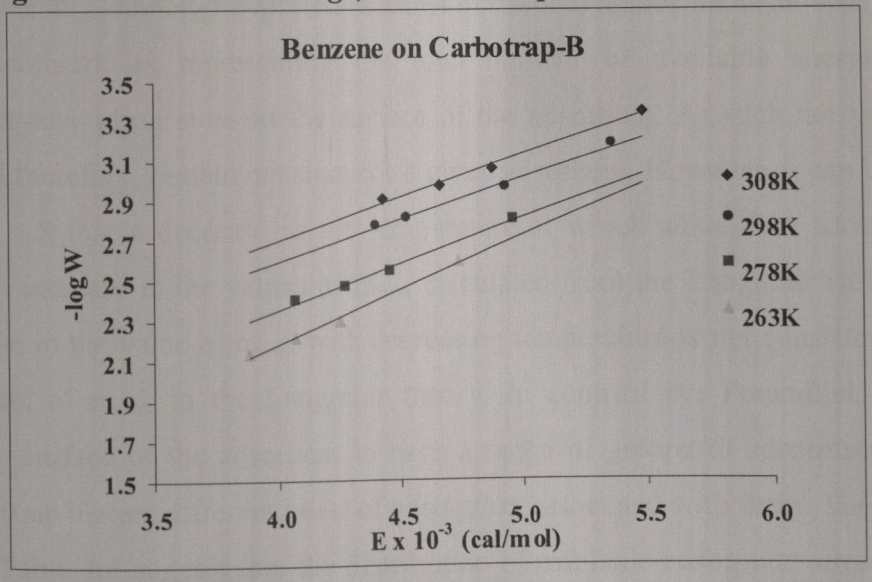


Fig 4.14 **Linearised DP-2 isotherms for the adsorption of benzene, in the mg/m$^3$ concentration range, on Carbotrap-B at different temperatures**

All of the graphs show clearly that the adsorbent capacity decreases as the temperature at which adsorption takes place increases. Adsorption parameters were calculated for each of the linear isotherms drawn from experimentally measured values of $V_b$. These calculated adsorption parameters are shown in Table 4.8.

The Langmuir adsorption parameter b, the distribution coefficient, is kinetically defined as $k_{ads}/k_{des}$, where $k_{ads}$ is the adsorption rate constant and $k_{des}$ is the desorption rate constant of the adsorptive molecule as defined in Eq. (2.14). According to this equation, as the adsorption temperature increases, the condensation coefficient decreases and the desorption rate constant increases. This results in a decrease in the value of b as temperature increases. It can be seen in Table 4.8 that an increase in the temperature at which adsorption takes place results in a decrease in the value of b calculated for the adsorption of most of the compounds. This is in agreement with the basic kinetic theory of adsorption of gases. The value of b calculated for the adsorption of benzene, however, while exhibiting a small tendency to increase slightly with temperature appears to remain relatively constant, over the range of temperatures studied. From an analytical point of view the enhanced adsorption capacity of Carbotrap B at lower temperatures suggests it to be a good adsorbent for VOC sampling applications.

The parameter $m_{max}$ although reported in terms of mass of adsorbate, is defined by the Langmuir isotherm as representing the total number of available energetically homogenous adsorption sites on the surface of the adsorbent. As such the value of $m_{max}$ should therefore, remain constant for a given adsorbent. However, it can be seen from Table 4.8 that a decrease in the temperature at which adsorption takes place results in an increase in the values of $m_{max}$ calculated from the Langmuir isotherms. This increase in the value of $m_{max}$ with decreasing temperature is not consistent with the definition of $m_{max}$ in the Langmuir theory. In contrast the Freundlich theory assumes the surface of the adsorbent to have a range of groups of adsorption sites, with each group having different heats of adsorption associated with them. The values of $m_{max}$ in Table 4.8 suggest that the distribution of available adsorption sites on the surface of the adsorbent, and not the actual total number of adsorption sites as suggested by the Langmuir $m_{max}$, changes with temperature. As the temperature is

| Compound | Temp | Langmuir Parameters | | | Freundlich Parameters | | | DP-1Parameters | | | DP-2 Parameters | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | K | b (m3/mg) | $M_{max}$ (mg/g) | $R^2$ | n | $k_F$ | $R^2$ | $logW_{o(DP1)}$ | $k_{(DP1)}*10^8$ | $R^2$ | $logW_{o(DP2)}$ | $k_{(DP2)}*10^4$ | $R^2$ |
| benzene | 263 | 0.005 | 11.29 | 0.986 | 1.542 | 1.63 | 0.999 | -1.42 | 7.75 | 0.995 | -0.49 | 5.39 | 0.989 |
| benzene | 278 | 0.006 | 5.51 | 0.997 | 1.744 | 1.27 | 0.994 | -1.68 | 5.59 | 0.997 | -0.78 | 4.51 | 0.993 |
| benzene | 298 | 0.007 | 2.31 | 0.999 | 1.815 | 0.89 | 0.993 | -1.97 | 4.15 | 0.997 | -0.87 | 4.27 | 0.995 |
| benzene | 308 | 0.006 | 1.76 | 0.998 | 1.713 | 0.77 | 0.998 | -2.04 | 3.96 | 0.999 | -0.95 | 4.14 | 0.998 |
| toluene | 263 | 0.011 | 31.25 | 0.992 | 2.274 | 1.96 | 0.994 | -1.27 | 5.63 | 0.997 | -0.70 | 3.65 | 0.991 |
| toluene | 278 | 0.006 | 26.60 | 0.969 | 1.792 | 1.96 | 1.000 | -1.24 | 5.86 | 0.997 | -0.44 | 4.39 | 0.997 |
| toluene | 298 | 0.004 | 16.31 | 0.956 | 1.614 | 1.77 | 0.997 | -1.17 | 5.90 | 0.997 | -0.31 | 4.55 | 0.999 |
| toluene | 308 | 0.003 | 10.46 | 0.999 | 1.419 | 1.64 | 0.991 | -1.16 | 6.08 | 0.997 | -0.23 | 4.85 | 0.995 |
| o-xylene | 263 | 0.048 | 31.95 | 0.999 | 7.299 | 1.66 | 0.992 | -1.44 | 1.86 | 0.999 | -1.31 | 1.07 | 0.995 |
| o-xylene | 278 | 0.042 | 27.62 | 0.993 | 6.549 | 1.62 | 0.983 | -1.43 | 2.33 | 0.995 | -1.28 | 1.20 | 0.999 |
| o-xylene | 298 | 0.021 | 24.15 | 0.999 | 3.945 | 1.67 | 0.999 | -1.39 | 2.72 | 0.977 | -1.08 | 1.86 | 0.983 |
| o-xylene | 308 | 0.011 | 22.52 | 0.998 | 2.365 | 1.82 | 0.989 | -1.29 | 4.02 | 0.997 | -0.73 | 3.00 | 0.992 |
| styrene | 263 | 0.029 | 33.33 | 0.979 | 5.432 | 1.72 | 0.999 | -1.40 | 3.35 | 0.984 | -1.23 | 1.53 | 0.981 |
| styrene | 278 | 0.026 | 28.49 | 0.996 | 4.122 | 1.74 | 0.989 | -1.38 | 3.57 | 0.997 | -1.13 | 1.91 | 0.991 |
| styrene | 298 | 0.012 | 23.87 | 0.990 | 2.502 | 1.81 | 0.981 | -1.32 | 4.40 | 0.995 | -0.85 | 2.93 | 0.989 |
| styrene | 308 | 0.008 | 20.49 | 0.995 | 2.134 | 1.80 | 0.991 | -1.28 | 4.53 | 0.998 | -0.67 | 3.32 | 0.999 |
| ethylbenzene | 263 | 0.027 | 34.25 | 0.980 | 4.521 | 1.79 | 0.986 | -1.33 | 4.22 | 0.987 | -1.14 | 1.88 | 0.991 |
| ethylbenzene | 278 | 0.017 | 32.15 | 0.998 | 3.058 | 1.88 | 0.995 | -1.27 | 4.65 | 0.991 | -0.91 | 2.58 | 0.989 |
| ethylbenzene | 298 | 0.006 | 29.15 | 0.999 | 1.649 | 2.10 | 1.000 | -1.09 | 6.09 | 0.998 | -0.28 | 4.45 | 0.995 |
| ethylbenzene | 308 | 0.003 | 26.32 | 0.994 | 1.359 | 2.08 | 0.999 | -1.07 | 6.43 | 0.998 | -0.03 | 5.22 | 0.999 |
| propylbenzene | 278 | 0.046 | 30.12 | 0.998 | 7.962 | 1.63 | 0.991 | -1.43 | 2.02 | 0.981 | -1.33 | 0.88 | 0.989 |
| propylbenzene | 298 | 0.032 | 28.65 | 0.997 | 5.241 | 1.69 | 0.984 | -1.36 | 2.14 | 0.980 | -1.13 | 1.40 | 0.984 |
| propylbenzene | 308 | 0.013 | 26.81 | 0.997 | 2.851 | 1.84 | 0.984 | -1.28 | 3.05 | 0.999 | -0.86 | 2.49 | 0.997 |

| Compound | Temp K | Langmuir Parameters | | | Freundlich Parameters | | | DP-1Parameters | | | DP-2 Parameters | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | b (m3/mg) | $M_{max}$ (mg/g) | $R^2$ | n | $k_F$ | $R^2$ | $logW_{o(DP1)}$ | $k_{(DP1)}*10^8$ | $R^2$ | $logW_{o(DP2)}$ | $k_{(DP2)}*10^4$ | $R^2$ |
| 12dichloroethane | 261 | 0.005 | 5.25 | 0.999 | 2.059 | 1.12 | 0.981 | -1.93 | 5.79 | 0.989 | -1.22 | 4.07 | 0.981 |
| 12dichloroethane | 268 | 0.004 | 4.13 | 0.998 | 1.965 | 1.02 | 0.995 | -1.99 | 5.38 | 0.999 | -1.19 | 4.15 | 0.995 |
| 12dichloroethane | 278 | 0.004 | 2.86 | 0.997 | 1.853 | 0.89 | 0.981 | -2.05 | 5.00 | 0.988 | -1.16 | 4.24 | 0.981 |
| 12dichloroethane | 298 | 0.003 | 1.52 | 0.992 | 1.688 | 0.63 | 0.997 | -2.19 | 4.23 | 0.999 | -1.08 | 4.34 | 0.997 |
| 1122tetrachlororthane | 268 | 0.002 | 104.17 | 0.995 | 1.675 | 2.56 | 0.981 | -1.17 | 14.94 | 0.996 | -0.79 | 4.87 | 0.981 |
| 1122tetrachlororthane | 278 | 0.002 | 70.42 | 0.992 | 1.486 | 2.43 | 0.986 | -1.16 | 10.36 | 0.995 | -0.50 | 5.29 | 0.986 |
| 1122tetrachlororthane | 298 | 0.001 | 33.56 | 0.991 | 1.343 | 2.11 | 0.993 | -1.40 | 8.44 | 0.998 | -0.52 | 5.46 | 0.993 |
| hexane | 261 | 0.007 | 23.98 | 0.998 | 1.870 | 1.94 | 0.989 | -1.01 | 6.47 | 0.994 | -0.24 | 4.48 | 0.989 |
| hexane | 270 | 0.007 | 13.35 | 0.999 | 1.801 | 1.70 | 0.989 | -1.18 | 5.79 | 0.995 | -0.30 | 4.53 | 0.989 |
| hexane | 278 | 0.006 | 10.75 | 0.995 | 1.772 | 1.59 | 0.991 | -1.21 | 5.13 | 0.995 | -0.26 | 4.44 | 0.991 |
| hexane | 298 | 0.006 | 4.1 | 0.987 | 1.608 | 1.25 | 1.000 | -1.46 | 4.27 | 1.000 | -0.25 | 4.56 | 1.000 |
| chlorobenzene | 261 | 0.008 | 54.35 | 0.995 | 2.753 | 2.09 | 0.994 | -1.12 | 10.12 | 0.996 | -1.08 | 3.04 | 0.994 |
| chlorobenzene | 268 | 0.008 | 46.30 | 0.999 | 2.489 | 2.07 | 0.975 | -1.12 | 5.49 | 0.986 | -0.63 | 3.28 | 0.975 |
| chlorobenzene | 278 | 0.007 | 35.84 | 0.993 | 2.464 | 1.94 | 0.993 | -1.20 | 4.70 | 0.995 | -0.66 | 3.19 | 0.993 |
| chlorobenzene | 298 | 0.004 | 25.06 | 0.962 | 1.702 | 1.93 | 0.989 | -1.23 | 5.68 | 0.995 | -0.42 | 4.31 | 0.989 |
| pentanol | 288 | 0.011 | 30.58 | 0.999 | 2.396 | 1.91 | 0.970 | -1.30 | 7.08 | 0.987 | -0.96 | 3.17 | 0.970 |
| pentanol | 298 | 0.010 | 22.03 | 0.993 | 2.402 | 1.74 | 0.981 | -1.38 | 5.36 | 0.988 | -0.95 | 3.05 | 0.981 |
| pentanol | 310 | 0.007 | 17.83 | 0.998 | 1.872 | 1.75 | 0.994 | -1.42 | 6.05 | 0.999 | -0.85 | 3.77 | 0.994 |
| pentane | 261 | 0.006 | 5.03 | 0.998 | 1.637 | 1.28 | 0.988 | -1.42 | 5.96 | 0.993 | -0.33 | 5.11 | 0.988 |
| pentane | 270 | 0.006 | 3.30 | 0.990 | 1.642 | 1.08 | 0.999 | -1.58 | 5.28 | 0.995 | -0.43 | 4.93 | 0.999 |
| pentane | 278 | 0.005 | 2.90 | 0.995 | 1.552 | 1.06 | 0.991 | -1.53 | 5.02 | 0.995 | -0.25 | 5.06 | 0.991 |
| pentane | 298 | 0.005 | 1.5 | 0.997 | 1.383 | 0.88 | 0.995 | -1.59 | 4.39 | 0.997 | 0.01 | 5.30 | 0.995 |
| hexanol | 288 | 0.018 | 42.55 | 0.999 | 3.560 | 1.93 | 0.994 | -1.28 | 7.47 | 1.000 | -1.14 | 2.13 | 0.994 |
| hexanol | 298 | 0.014 | 40.82 | 0.997 | 2.631 | 2.04 | 0.965 | -1.14 | 5.44 | 0.981 | -0.79 | 2.79 | 0.965 |
| hexanol | 310 | 0.007 | 33.22 | 0.998 | 1.852 | 2.07 | 0.983 | -1.10 | 5.77 | 0.992 | -0.48 | 3.81 | 0.983 |

**Table 4.8** Adsorption parameters calculated from the linearised isotherms drawn from the $V_b$ measured for the adsorption of VOC in the mg/m$^3$ concentration range at different temperatures on Carbotrap-B

decreased the number of available sites increases and this is consistent with an increase in the Langmuir b parameter. The $m_{max}$ value, as calculated from the Langmuir isotherm, is therefore defined as a measure of the number of available adsorption sites at a certain temperature and not the total number of adsorption sites that are actually present on the surface of the adsorbent.

The Freundlich parameter n is also found to be temperature dependent. An interpretation of this can be based on the hypothesis that the reciprocal of this parameter, 1/n, corresponds with the $RT/\Delta H_o$ term in Eq. (2.21) assuming that $q_o$ is equivalent to the enthalpy of adsorption. As the temperature at which adsorption takes place increases, so does RT. As a result $RT/\Delta H_o$ should increase with temperature, and the calculated Freundlich parameter n for the adsorption should decrease accordingly, if the hypothesis holds true. Looking at Table 4.8 this is seen to be the case for the adsorption of twelve out of thirteen of the compounds studied. By contrast, however, the calculated n for benzene appears to increase slightly with increasing temperature.

The DP-1 and DP-2 adsorption parameter, $k_{DP-1}$ and $k_{DP-2}$, respectively, are related to $\beta$, the adsorption affinity coefficient. The parameter $k_{DP-1}$ is related to $\beta^{-2}$ as defined by Eq. (2.41) while $k_{DP-2}$ is related to $\beta^{-1}$ as defined by Eq. (2.42). Because of the difference in the relationship of each parameter with $\beta$ it is difficult to compare the effect of temperature on the adsorption parameters of both models from a simple inspection of Table 4.8. The value of $\beta$ for each VOC can be calculated for both the DP-1 and DP-2 isotherms using Eq. (2.43) and Eq. (2.44), respectively. The values for $k_{ref}$ for each VOC were taken to be the $k_{DP1}$ and $k_{DP2}$ values, respectively, that were obtained from the study of the adsorption of each of the VOC at 298K. The $k_{DP1}$ and $k_{DP2}$ values obtained for the other temperatures studied were then compared to the values obtained at 298K. In this way both the DP-1 and DP-2 isotherms can be compared. The calculated values of $\beta$, for each of the 13 VOC and for each model are reported in Table 4.9. As explained already, as the temperature at which adsorption takes place increases the potential for adsorption of the adsorptive molecules decrease. The reduction in the potential for adsorption of a VOC should be reflected by an analogous decrease in the value of $\beta$ for the VOC. Taking the value of 298K as

| Compound | Temp K | $\beta_{(DP1)}$ | $\beta_{(DP2)}$ |
|---|---|---|---|
| benzene | 263 | 0.73 | 0.79 |
| benzene | 278 | 0.86 | 0.95 |
| benzene | 298 | 1.00 | 1.00 |
| benzene | 308 | 1.02 | 1.03 |
| toluene | 263 | 1.02 | 1.25 |
| toluene | 278 | 1.00 | 1.04 |
| toluene | 298 | 1.00 | 1.00 |
| toluene | 308 | 0.99 | 0.94 |
| o-xylene | 263 | 1.21 | 1.74 |
| o-xylene | 278 | 1.08 | 1.55 |
| o-xylene | 298 | 1.00 | 1.00 |
| o-xylene | 308 | 0.82 | 0.62 |
| styrene | 263 | 1.15 | 1.92 |
| styrene | 278 | 1.11 | 1.53 |
| styrene | 298 | 1.00 | 1.00 |
| styrene | 308 | 0.99 | 0.88 |
| ethylbenzene | 263 | 1.20 | 2.37 |
| ethylbenzene | 278 | 1.14 | 1.72 |
| ethylbenzene | 298 | 1.00 | 1.00 |
| ethylbenzene | 308 | 0.97 | 0.85 |
| propylbenzene | 278 | 1.03 | 1.59 |
| propylbenzene | 298 | 1.00 | 1.00 |
| propylbenzene | 308 | 0.84 | 0.56 |
| 12dichloroethane | 261 | 0.85 | 1.07 |
| 12dichloroethane | 268 | 0.89 | 1.05 |
| 12dichloroethane | 278 | 0.92 | 1.02 |
| 12dichloroethane | 298 | 1.00 | 1.00 |
| 1122tetrachlororthane | 268 | 0.75 | 1.12 |
| 1122tetrachlororthane | 278 | 0.90 | 1.03 |
| 1122tetrachlororthane | 298 | 1.00 | 1.00 |
| hexane | 261 | 0.81 | 1.02 |
| hexane | 270 | 0.86 | 1.01 |
| hexane | 278 | 0.91 | 1.03 |
| hexane | 298 | 1.00 | 1.00 |
| chlorobenzene | 261 | 0.75 | 1.42 |
| chlorobenzene | 268 | 1.02 | 1.32 |
| chlorobenzene | 278 | 1.10 | 1.35 |
| chlorobenzene | 298 | 1.00 | 1.00 |
| pentanol | 288 | 0.87 | 0.96 |
| pentanol | 298 | 1.00 | 1.00 |
| pentanol | 310 | 0.94 | 0.81 |
| pentane | 261 | 0.86 | 1.04 |
| pentane | 270 | 0.91 | 1.08 |
| pentane | 278 | 0.94 | 1.05 |
| pentane | 298 | 1.00 | 1.00 |
| hexanol | 288 | 0.85 | 1.31 |
| hexanol | 298 | 1.00 | 1.00 |
| hexanol | 310 | 0.97 | 0.73 |

Table 4.9 **Calculated values of DP-1 β and DP-2 β for the adsorption of VOC on Carbotrap-B at different temperatures**

the reference temperature, calculated values of β should relate to the increase or decrease in the adsorption capacity of the adsorbent for the VOC as temperature changes.

As already seen with the Langmuir and Freundlich adsorption parameters, the adsorption capacity of Carbotrap-B for the VOC decreases as the adsorption temperature increases. Analogously, the value of β would be expected to be lower than 1 when calculated for temperatures greater than 298K and greater than 1 for temperatures below 298K. The changes in the calculated values of β for the DP-2 isotherm, like the Langmuir adsorption parameter b and Freundlich adsorption parameter n, reflect the changes in the adsorption capacity of the adsorbent for the VOC as the adsorption temperature changes. The calculated adsorption capacity, $m_{max}$, of Carbotrap-B, for benzene and the rest of the VOC increase as the adsorption temperature decreases. The values of β, calculated for the DP-1 isotherm, do not consistently reflect the change in adsorption capacity resulting from the change in the temperature at which adsorption takes place. This may again be explained by the fact that the DP-2 isotherm equation was proposed for non-porous adsorbents while the DP-1 isotherm equation was proposed for microporous adsorbents, and so would not be expected to fit well with the experimental data for Carbotrap-B.

Values of $V_b$ for the adsorption of each of the 13 VOC were measured at a minimum of three different temperatures. The temperature range studied was from 260K to 310K. Similar ranges of VOC concentration were generated at each temperature studied. The effect of a change of temperature on the experimentally measured values of $V_b$ for each VOC was quantified by calculating the differences in the values of $V_b$ that were measured for the same adsorptive concentration but at different temperatures. The values of $V_b$ measured at 298K were taken as reference values. For each of the VOC, a percentage difference in the value of measured $V_b$ from the 298K values, which was due to the change in temperature, was calculated for each adsorptive concentration generated. The calculated differences were expressed in percentage difference per 1K change in temperature. For each of the VOC, the differences in the values of $V_b$ were found to be similar for the different adsorptive concentrations under isothermal conditions: i.e., the differences in the measured

values of $V_b$ due to the change in temperature were found to be similar irrespective of which adsorptive concentration was used for the calculation. Therefore, for each of the VOC, an average difference in measured values of $V_b$ was calculated for each of the different temperatures at which adsorption was measured. The calculated average differences and the temperatures at which they were measured are shown in Table 4.10.

The overall average percentage difference in the values of $V_b$ measured at different temperatures from those measured at 298K for each of the VOC is 4.8%±4.9% $K^{-1}$ change in the temperature of adsorption. The range of calculated average percentage differences for $V_b$, measured at temperatures lower than 298K, is 2.5% to 7.5% $K^{-1}$ change in the temperature of adsorption. There appears to be a linear relationship between the calculated average percentage differences in measured $V_b$ $K^{-1}$ with the change in temperature of adsorption. A plot of these two confirms this and is shown in Fig 4.15. Two linear relationships are evident. Firstly the calculated average differences $K^{-1}$ for values of $V_b$ that were measured between 260K and 298K indeed

| Compound | % difference per 1K of measured $V_b$ at the following temperatures from $V_b$ measured at 298K | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 261K | 263K | 268K | 271K | 278K | 288K | 308K | 310K |
| pentane | 5.7 | | | 4.0 | 3.8 | | | |
| hexane | 12.0 | | | 7.5 | 6.3 | | | |
| hexan-1-ol | | | | | | 0.6 | | 3.2 |
| pentan-1-ol | | | | | | 4.4 | | 5.6 |
| chlorobenzene | 4.7 | | 4.4 | | 3.9 | | | |
| 1,2-dichloroethane | 7.4 | | 6.0 | | 5.5 | | | |
| 1,1,2,2-tetrachloroethane | | | 10.6 | | 7.2 | | | |
| toluene | | 6.1 | | | 5.0 | | 4.5 | |
| styrene | | 2.5 | | | 2.7 | | 2.6 | |
| propylbenzene | | | | | 0.3 | | 3.8 | |
| o-xylene | | 1.6 | | | 1.7 | | 2.6 | |
| ethylbenzene | | 3.6 | | | 4.2 | | 4.1 | |
| benzene | | 8.4 | | | 6.2 | | 3.1 | |
| Average% diff | 7.4 | 4.5 | 7.0 | 5.8 | 4.3 | 2.5 | 3.4 | 4.4 |

Table 4.10 **Percentage differences, per 1K change in the temperature of adsorption, for values of $V_b$ measured at different temperatures from those measured at 298K on Carbotrap-B**

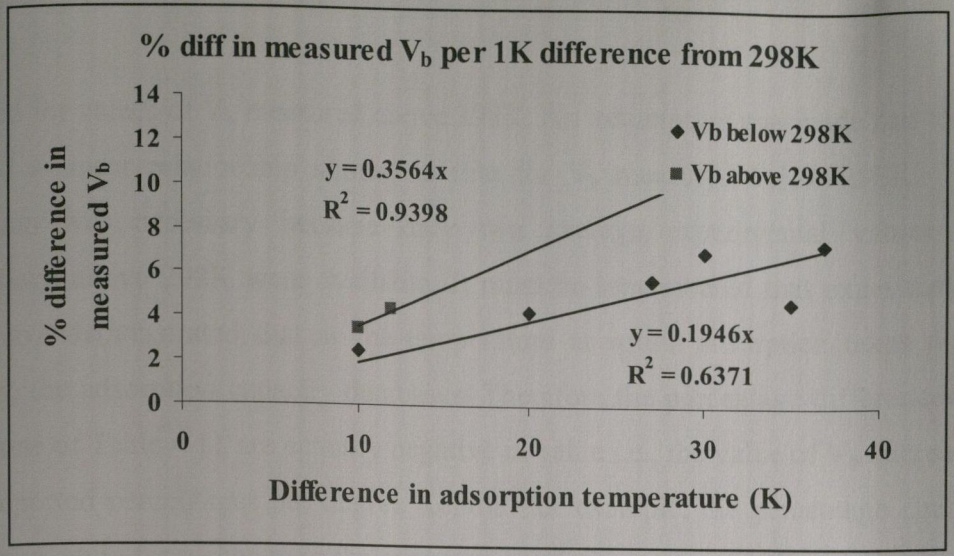


**Fig 4.15** **Values of the average calculated percentage difference per 1K in the values of measured $V_b$ from those measured at 298K plotted against the difference form 298K of the temperature at which $V_b$ was measured**

show a linear relationship with a change in adsorption temperature. $V_b$ were only measured at two temperatures above 298K, so that it was necessary to assume that the relationship between the average calculated percentage differences per degree Kelvin is also linear with the differences in adsorption temperature. The relationships shown in Fig 4.15 can be used to calculate a table of percentage differences $K^{-1}$ for measured $V_b$ for the adsorption of VOC on Carbotrap-B over a range of concentrations. This table is reported here as Table 4.11.

| Diff in K from 298K | % diff per 1K change for $V_b$ above 298K | % diff per 1K change for $V_b$ below 298K |
|---|---|---|
| 1 | 0.4 | 0.2 |
| 5 | 1.8 | 1.0 |
| 10 | 3.6 | 1.9 |
| 15 | 5.3 | 2.9 |
| 20 | 7.1 | 3.9 |
| 25 | 8.9 | 4.9 |
| 30 | 10.7 | 5.8 |
| 35 | 12.5 | 6.8 |

**Table 4.11** **Percentage differences in value of $V_b$ per 1K change in the temperature of adsorption from those measured at 298K as a function of the change in the temperature of adsorption.**

The percentage differences have been calculated from the linear relationships expressed in Fig 4.15. The first column gives percentage differences that have been

calculated for values of $V_b$ measured above 298K. An assumption was made that there is indeed a linear relationship similar to that for $V_b$ measured below 298K. This assumption was necessary because only two average experimental values for temperatures above 298K were available. It must be remembered that experimental results have demonstrated that as the temperature at which adsorption takes place increases, the adsorption capacity decreases. Therefore the percentage differences in column one of Table 4.11 are actually negative in value i.e., the value of $V_b$ decreases by the reported percentages per degree Kelvin. For example, the percentage change per degree Kelvin for a change in the temperature of adsorption of 10K is 3.6% for $V_b$ measured above 298K. Therefore the percentage decrease in the value of $V_b$ at 308K from that measured at 298K would be predicted to be 36%.

The second column shows the calculated percentage difference $K^{-1}$ in the value of $V_b$ measured at temperatures below 298K. Again it has been shown that as the temperature at which adsorption takes place decreases the adsorption capacity increases. So the percentage difference $K^{-1}$ in column two are positive differences i.e., $V_b$ measured at 288K would be 19% greater than those measured at 298K. Table 4.11 is not a definitive guide for evaluating the effect of temperature on measured values of $V_b$ for the adsorption of VOC on Carbotrap-B. A study involving a greater range of VOC and temperatures would have to be conducted to validate Table 4.11. However, it does provide a useful means of establishing Safe Sampling Volumes for sampling applications over the temperature range of 260K to 310K for the adsorption of the 44 VOC whose adsorption on Carbotrap-B has been studied during this project.

### 4.6.1 Calculation of isosteric enthalpies of adsorption.

The ranges of the measured values of $V_b$ for the adsorption of 13 VOC on Carbotrap-B over the temperature range 260K to 310K are reported in Table 4.7. Using these experimental values of $V_b$, the enthalpies of adsorption ($-\Delta H_{ads}$) for each of the compounds were calculated by the van't Hoff expression (Eq. 2.49). For each of the VOC the calculated enthalpies were found to be dependent on concentration. The value of $m_{ads}$ was then calculated for each of the adsorptive concentrations. Values of $m_{ads}$ were then used to calculate $\Theta_L$, the Langmuir fractional surface coverage, for

each adsorptive concentration. Calculated values of $\Theta_L$ ranged from 0.05-0.3mmol/g or in percentage terms 25 to 80% of the monolayer capacities calculated from the linear Langmuir isotherms. Fig 4.16 shows the relationship between the experimental values of $-\Delta H_{ads}$ and $\Theta_L$ for the adsorption of toluene on Carbotrap-B over the range of temperatures 260K to 310K. A linear relationship between the calculated values of $-\Delta H_{ads}$ and the calculated values of $\Theta_L$ was observed for each of the compounds. The isosteric enthalpy of adsorption, $-\Delta H^{st}$, or near zero surface coverage enthalpy of adsorption, for each of the VOC was determined by extrapolating to zero $\Theta_L$ the plot of calculated $-\Delta H_{ads}$ against calculated $\Theta_L$. The resulting isosteric enthalpy adsorption and the coefficient of linear regression, $R^2$, for each compound are shown in Table 4.12. Also shown in the table are the molar heats of vaporisation as reported in the CRC Handbook of Chemistry and Physics (1986) and the calculated value of $k_{TEMP}$ from Eq. (2.49)

The values of $-\Delta H^{st}$ for the 13 VOC show that compounds within an homologous group containing the same number of carbons have similar results. This is consistent with other reported studies that have shown similar relationships between $-\Delta H^{st}$ and

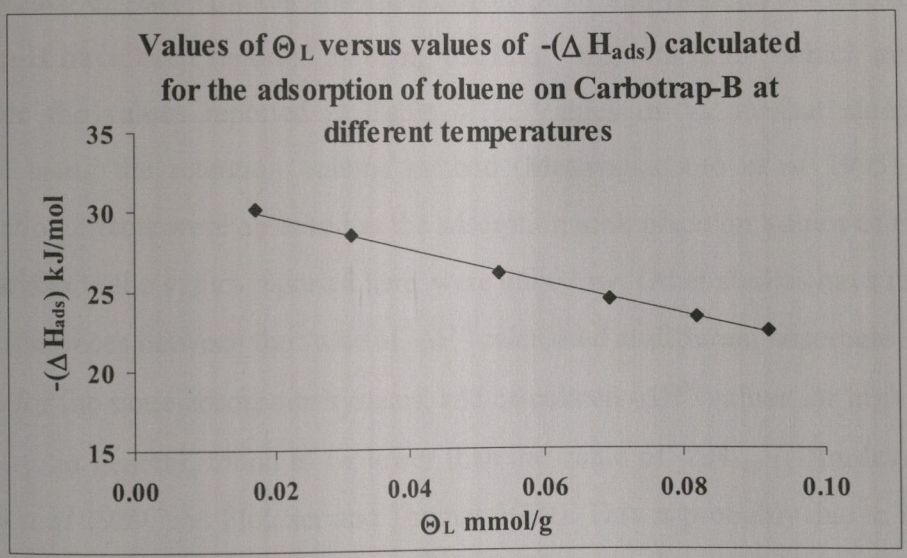


**Fig 4.16 Determination of $-\Delta H^{st}$ of from calculated values of $\Theta_L$ and $-\Delta H_{ads}$ for the adsorption of toluene on Carbotrap-B at different temperatures**

| compound | $-\Delta H^{st}$ $kJmol^{-1}$ | $-\Delta H_{vap}$ $kJmol^{-1}$ | $k_{TEMP}$ | $R^2$ |
|---|---|---|---|---|
| pentane | 22.6 | 27.6 | -7.31 +/- 0.14 | 0.999 |
| hexane | 32.9 | 31.9 | -10.24 +/- 0.16 | 0.999 |
| pentan-1-ol | 34.9 | 52.3 | -6.06 +/- 0.65 | 0.994 |
| hexan-1-ol | 41.5 | 53.2 | -3.67 +/- 2.74 | 0.999 |
| chlorobenzene | 25.5 | 42.3 | -4.19 +/- 0.90 | 0.998 |
| 1,2-dichloroethane | 27.1 | 33.3 | -9.08 +/- 0.22 | 0.999 |
| 1,1,2,2-tetrachloroethane | 36.9 | 41.5 | -10.46 +/- 0.32 | 0.999 |
| toluene | 31.7 | 38.1 | -6.83 +/- 1.82 | 0.998 |
| styrene | 25.1 | 40.3 | -1.34 +/- 2.23 | 0.998 |
| propylbenzene | 30.8 | 43.6 | 0.89 +/- 2.51 | 0.998 |
| o-xylene | 25.0 | 43.4 | 0.14 +/- 1.96 | 0.999 |
| ethylbenzene | 34.2 | 42.2 | -4.17 +/- 3.98 | 0.994 |
| benzene | 24.1 | 33.8 | -8.39 +/- 1.02 | 0.999 |

**Table 4.12 Calculated values of $-\Delta H^{st}$, literature values of $-\Delta H_{vap}$, $k_{TEMP}$ and values of $R^2$ from the linear plots of $\Theta_L$ and $-\Delta H_{ads}$ for the adsorption of 13 VOC on Carbotrap-B at different temperatures**

the carbon number or the molecular weight of adsorbate. (Helmig 1996, Bruner *et al* 1976). Values of $-\Delta H^{st}$ for the adsorption of benzene and hexane, respectively, on Carbotrap-B have been reported as being $62kJmol^{-1}$ and $66kJmol^{-1}$ which are more than twice the values reported in Table 4.16. Values of $V_b$ in that study were measured using the retention volume method (Mastrogiacomo *et al* 1995) so no concentration effects were observed as the adsorption took place for values of $\Theta_L$ that, in comparison to the values reported here, were quite low. Other studies have reported similar differences between the value of $-\Delta H^{st}$ calculated at different adsorbate surface coverage for the same adsorption systems, and calculated $-\Delta H^{st}$ values for high values of $\Theta_L$ were, in general, found to be lower than the value of $-\Delta H_{vap}$ ((Djordevic *et al* 1986, Lu *et al* 1989, and Fletcher and Thomas 1999). This is probably due to the fact that as the surface coverage approaches the monolayer capacity of the adsorbent for a particular adsorbate, the adsorbed molecules interact between one another similarly to the analogous interactions in the adsorbate in its pure liquid phase.

Other reported values for the adsorption of these compounds on GCB that have been determined by the retention volume method are benzene 38-40kJmol$^{-1}$ (Vidal-Madjar and Guiochon 1971, Vidal-Madjar *et al* 1975), toluene 48kJmol$^{-1}$, ethylbenzene 52kJmol$^{-1}$, o-xylene 53kJmol$^{-1}$, propylbenzene 59kJmol$^{-1}$, pentane 34kJmol$^{-1}$, hexane 44kJmol$^{-1}$ (Kouznetsov *et al* 1969) and for $C_6$-$C_8$ hydrocarbons 32-43kJmol$^{-1}$ (Domingo-Garcia *et al* 1984, Carrott and Sing 1987). The results in Table 4.16 are of the same order of magnitude, although slightly lower than the reported values. Nevertheless they are in the range of values normally measured for physisorption processes. While the frontal chromatography method used to determine $V_b$ in this study is ideal for determining the effects of environmental parameters such as temperature and concentration on the adsorption of VOC in 'real' sampling application situations, it is less able to provide precise data from which accurate thermodynamic properties of the adsorbent can be determined. However, they are very useful for the comparison of adsorbents for practical applications and can be used to calculate, along with the calculated values of $k_{TEMP}$, the values of $V_b$ at different temperatures using Eq. (2.49).

## 4.7 Effect of humidity on values of measured $V_b$ for adsorption on Carbotrap-B in the mg/m$^3$ concentration range

As stated in section 2.2 Carbotrap-B is claimed to be a hydrophobic adsorbent. However, Helmig and Vierling (1995) reported that small amounts of water are adsorbed by Carbotrap-B at high humidities. Matney *et al* (2000) used Carbotrap-B for sampling trace amounts, μg/m$^3$ concentration range, of VOC. They reported a 98% recovery of methanol that had been adsorbed onto Carbotrap-B at 80%RH. However, methanol like propan-1-ol has instant breakthrough on Carbotrap-B at mg/m$^3$ concentrations. To determine the effect of humidity on $V_b$ at mg/m$^3$ concentrations, the values of $V_b$ for the adsorption of six VOC on Carbotrap-B were measured at 20%RH and 80%RH. The values of $V_b$ reported in Table 4.3 and Table 4.7 were measured experimentally at ambient conditions. The value of %RH under the experimental conditions ranged from 40%RH to 60%RH. For the experiments carried out to determine the effects of humidity on the values of $V_b$, atmospheres with 20%RH and 80%RH respectively were generated using the method described in

section 3.2.4. VOC concentrations in each of the atmospheres were verified using TD-GC analysis.

To ensure that the measured $V_b$ were consistent with those already reported here in this thesis, $V_b$ was measured for an atmosphere containing 198mg/m$^3$ of hexane at 50%RH. A difference of 4.5% between the value previously measured for hexane at 198mg/m$^3$ was observed. Considering that the uncertainty in measurement of $V_b$ on Carbotrap-B has been calculated to be 10.1%, this difference was deemed to be acceptable. Table 4.13 reports the percentage differences between the $V_b$ for the adsorption of six VOC on Carbotrap-B measured at 20%RH and 80%RH, top half and bottom half of the table respectively, from those measured under ambient conditions. The adsorptive concentrations at which the $V_b$ were measured are also reported in the

| Compound | Conc mg/m$^3$ | $V_b$ (L/g) at 20%RH measured | expected | %difference |
|---|---|---|---|---|
| toluene | 129 | 44 | 45 | 2.3 |
| toluene | 261 | 31 | 33 | 5.2 |
| chlorobenzene | 333 | 45 | 43 | -5.6 |
| hexane | 197 | 12 | 12 | -6.3 |
| hexane | 96 | 17 | 16 | -2.4 |
| 1,1,2,2-tetrachoroethane | 475 | 25 | 28 | 7.3 |
| hexanol | 244 | 137 | 129 | -6.5 |
| **Compound** | **Conc mg/m$^3$** | **$V_b$ (L/g) at 80%RH measured** | **expected** | **%difference** |
| toluene | 159 | 43 | 42 | -3.3 |
| toluene | 246 | 32 | 34 | 5.2 |
| chlorobenzene | 314 | 45 | 44 | -2.1 |
| hexane | 121 | 14 | 15 | 7.3 |
| hexane | 187 | 11 | 12 | 5.9 |
| 1,1,2,2-tetrachoroethane | 436 | 29 | 28 | -1.8 |
| hexanol | 228 | 139 | 136 | -6.8 |
| hexanol | 115 | 225 | 218 | -8.4 |

Table 4.13 **Percentage difference in the values of $V_b$ measured for the adsorption of six VOC on Carbotrap-B at 20%RH and 80%RH, respectively, from those values measured under ambient conditions.**

table. As can be seen, the values of $V_b$ measured at both 20%RH and 80%RH differ by less than 10.1% from the values measured under ambient conditions. The calculated differences are both negative and positive in value. From the results reported in Table 4.13 it can be assumed that %RH has no effect on the measured values of $V_b$ for the adsorption of the VOC on Carbotrap-B at $mg/m^3$ concentrations.

## 4.8 Adsorption of benzene on Carbotrap-B

Carbotrap-B is a synthetic GCB with an adsorbent surface area of $100m^2/g$. Like most other synthetic GCB it consists of a two-dimensional structure in which graphitic sheets are randomly orientated to one another. The graphitic sheets are composed of rings of six carbon atoms resulting in a high amount of free surface electrons with the charges being uniformly distributed around the carbon atom centres. The surface charge of Carbotrap-B is highly delocalised (Warren 1941, Supelco 1986, Hrouzkova *et al* 1997). The benzene ring is also a stable ring structure containing six carbon atoms with a delocalised $\pi$ electron ring. The electron charge is evenly distributed around the ring. As a result benzene is a lot less polarisable than analogous compounds. The structure of benzene is quite similar to the structure of the carbon rings on the adsorbent surface. The stability of the benzene ring structure, and the presence of both delocalised electron fields, may explain the low values of measured $V_b$ for benzene that are reported in Table 4.3 The uncharacteristic patterns of the calculated adsorption parameters for the adsorption of benzene at different temperatures reported in Table 4.8 may also be a result of this.

The experimentally measured $V_b$ of benzene are quite low when compared to those of similar compounds such as toluene, hexane and hexene. The differences cannot be explained by a difference in the calculated polarisabilities of the compounds, the values of which for benzene is 26.3, toluene 31.1, hexane 29.9 and hexene 29.2. The increased polarisability of toluene is due to the presence of the methyl group and the measured $V_b$ reflect this increased polarisability. However, the polarisabilities of both hexane and hexene are quite similar, yet the measured values of $V_b$ for both are quite different. The measured values of $V_b$ for hexene are lower than those for hexane and

are similar in quantity to those measured for benzene. These results, as previously stated, may suggest a negative specific effect for the adsorption of compounds containing π electrons. Carbotrap-B has been classed, as a Class I adsorbent under the Kislev classification and as such should not exhibit specific adsorption effects. The values of the $V_b$ measured for trichloroethylene and tetrachloroethylene, when compared to the measured $V_b$ for the tri- and tetra- chloroethanes seem to contradict the results of benzene and hexene, i.e. there is no negative specific effect exhibited by Carbotrap-B for VOC containing π electrons. Because the available data set is small further study is required to answer this question.

Fig 4.16 showed the relationship between values of $-\Delta H_{ads}$ and $\Theta_L$ that were calculated from experimentally measured values of $V_b$ for the adsorption of toluene over the temperature range of 260K to 310K. Values of $-\Delta H_{ads}$ were shown to decrease linearly as $\Theta_L$ increased. The calculated values of $-\Delta H_{ads}$ and $\Theta_L$ for 12 of the 13 VOC whose adsorption at different temperatures was studied all exhibited the same relationship. The calculated values of $-\Delta H_{ads}$ for the adsorption of benzene, however, increased linearly as $\Theta_L$ increased. This can be seen in Fig 4.17. Similar graphs for the adsorption of the other VOC can be found in Appendix 11.

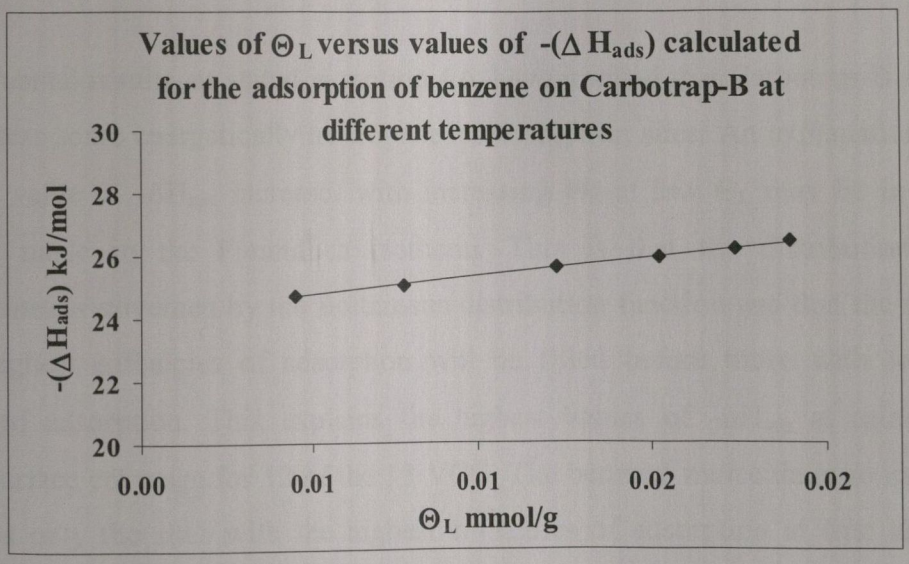


Fig 4.17 **Relationship of calculated values of $\Theta_L$ and $-\Delta H_{ads}$ for the determination of $-\Delta H^{st}$ for the adsorption of benzene on Carbotrap-B at different temperatures**

Djordevic *et al* (1986) studied the adsorption of benzene on Poropak Q, a porous polymer adsorbent. They also found that the calculated value of $-\Delta H_{ads}$ initially increased as $\Theta_L$ increased. At a certain fractional surface coverage the value of $-\Delta H_{ads}$ reached a maximum from where it decreased linearly with increasing $\Theta_L$. Djordevic *et al* were unable to explain the reason for this and cited another study which had reported similar behaviour but did not explain it.

The Langmuir and Freundlich adsorption parameters, b and n, respectively, are both related to the adsorption rate coefficient. As such, both decrease in value as the temperature of adsorption increases. As can be seen from Table 4.8, the values of the calculated b and n parameters for 12 of the 13 VOC do decrease as the temperature is increased. The calculated values of b and n however, seem to remain constant or increase just slightly as the temperature is increased. The values of $V_b$, $m_{max}$, that are reported in Tables 4.7. 4.8 and 4.9, respectively, however, follow the same pattern as those for the other VOC i.e., they decrease as the temperature of adsorption increases. This implies that the adsorption capacity increases as the adsorption temperature decreases. The constancy of the b and n parameters may be due to the stability of the benzene molecule and perhaps is also a function of the interaction of the two delocalised electron fields.

The experimental results, as stated in section 4.6, have implied that Carbotrap-B may indeed possess some energetically heterogeneous adsorption sites. An explanation as to why the value of $-\Delta H_{ads}$ increases with increasing $\Theta_L$ at low $\Theta_L$ may lie in the assumption made in the Freundlich isotherm. This is that the distribution of adsorption sites is governed by the Boltzmann distribution function and that the sites with the highest enthalpies of adsorption will be filled before those with lower enthalpies of adsorption. This explains the highest values of $-\Delta H_{ads}$ at minimal fractional surface coverage for 12 of the 13 VOC. The benzene molecule is so stable that perhaps only the sites with the highest enthalpies of adsorption at first allow adsorption of benzene. In order for other molecules to adsorb on adsorption sites containing low enthalpies of adsorption a source of activation energy or enthalpy is required. This activation enthalpy may be supplied by the enthalpy released from the adsorption of the first benzene molecules on the sites possessing the highest

enthalpies. Therefore the measured value of $-\Delta H_{ads}$ at the lowest surface coverage is equivalent to the enthalpy released when the first molecules adsorb, minus the activation enthalpy required for other molecules to adsorb.

Eventually as more molecules adsorb, resulting in an increase in $\Theta_L$, more enthalpy is released and the value of the measured $-\Delta H_{ads}$ increases until the value of $\Theta_L$ reaches a certain point at which the measured enthalpy starts to decrease. This decrease in the measured enthalpy may be due to the fact that the remaining adsorption sites do not possess as much enthalpy and the overall measured enthalpy decreases with $\Theta_L$.

## 4.9 Adsorption of VOC on Carbosieve SIII

Carbosieve SIII was the second adsorbent chosen for this study of adsorbents for VOC sampling applications. Carbosieve SIII is a carbon molecular sieve that exhibits weak Class III, approaching Class I adsorption characteristics according to the Kislev classification of adsorbents. The use of Carbosieve SIII as an adsorbent for certain applications has already been discussed in section 2.2.5 As discussed earlier in this chapter, Carbosieve SIII is reported to cover the $C_1$ to $C_5$ hydrocarbon adsorption range. However, due to concerns regarding recovery of adsorbed VOC, Carbosieve SIII was applied to the $C_1$ to $C_4$ range in this study. Also due to time constraints only the $mg/m^3$ concentration range was studied using Carbosieve SIII.

Typically adsorbent bed weights of about 0.08g were used. To ensure that this bed weight was above the critical bed weight, the values of $V_b$ were measured for the adsorption of butane at two different adsorptive concentrations, $56mg/m^3$ and $169mg/m^3$, respectively, and also for methanol at two different adsorptive concentrations, $60mg/m^3$ and $290mg/m^3$. Two different adsorbent bed weights, 0.08g and 0.125g, were used. The differences between the measured values of $V_b$ for the two different bed weights were found to be less than 6%. Carbosieve SIII was found to be less reproducible than Carbotrap-B for measurements of $V_b$. Again at least one repeat measurement was made for each of the VOC. The relative uncertainty for repeat measurements using the same tube under the same experimental conditions was calculated to be 7.6%. Three different tubes were used to measure the $V_b$ for the

adsorption of butane on Carbosieve SIII at an adsorptive concentration of 169mg/m$^3$. Three different measurements were made for each tube. The overall uncertainty for measuring $V_b$ on Carbosieve SIII using different tubes was calculated using Eq. (4.1) to be 9.4%. Using Eq. (4.2) the overall uncertainty in measuring $V_b$ on Carbosieve SIII at mg/m$^3$ concentrations was calculated to be 10.7%. This value incorporates the uncertainty of 5.2% already calculated for the determination of the VOC concentration.

The adsorption of 19 VOC, with adsorptive concentrations in the mg/m$^3$ range, on Carbosieve SIII was studied at 298K. The 19 VOC are listed above in section 4.1. Of the 19 VOC, only 15 were found to have $V_b$ greater than 1L/g. The first three compounds listed, ethane, ethene and ethyne, all exhibited instant breakthrough on Carbosieve SIII at 298K, even when the adsorbent bed weight was increased to 0.2g. Betz *et al* (1989) reported a value of 0.98g/L for the adsorption of ethane on Carbosieve SIII. This value was obtained by the retention volume method. Schwarze and Sollars (1995) also report similar values for ethane. Although ethyne had instant breakthrough on Carbosieve SIII, the FID response to the concentration of ethyne in the effluent of the adsorbent tube was only 60% that of the response of the FID to the ethyne adsorptive concentration at the tube inlet. This suggested that some sort of reaction was taking place between the adsorbent and ethyne perhaps resulting in the breakdown of ethyne. Dettmer *et al* (2000) and Peters and Bakkeren (1994) also report breakdown of reactive compounds on Carbosieve SIII. The fourth VOC that had instant breakthrough was carbon tetrachloride. This was a surprising result as both dichloromethane and chloroform had high values of measured $V_b$ under the same experimental conditions. The FID response for the concentration at both the tube inlet and outlet were the same suggesting that no breakdown of the VOC was taking place. To ensure that there was nothing wrong with the solvent a separate new bottle was procured and new tubes prepared. Carbon tetrachloride still exhibited instant breakthrough on Carbosieve SIII.

For the other 15 compounds values of $V_b$ greater than 1L/g were obtained. The measured values of $V_b$ and the corresponding range of adsorptive concentrations are shown in Table 4.14. The first observation that can be made is that the values of

measured $V_b$ are far greater than those measured for the adsorption of similar VOC on Carbotrap-B.

| Compound | Conc range mg/m$^3$ | | Range of measured $V_b$ L/g of adsorbent | |
|---|---|---|---|---|
| **methanol** | **57** | **290** | **35** | **25** |
| **ethanol** | **62** | **311** | **341** | **165** |
| **chloroform** | **161** | **543** | **829** | **316** |
| **bromoform** | **1011** | **164** | **2810** | **645** |
| **bromoethane** | **103** | **522** | **567** | **270** |
| **bromochloromethane** | **144** | **695** | **893** | **267** |
| **dichloromethane** | **95** | **480** | **319** | **173** |
| **propene** | **43** | **128** | **64** | **45** |
| **propane** | **45** | **134** | **77** | **51** |
| **butane** | **56** | **169** | **482** | **241** |
| **isobutene** | **57** | **171** | **447** | **222** |
| **1,3-butadiene** | **55** | **165** | **599** | **303** |
| **trans-but-2-ene** | **54** | **170** | **519** | **232** |
| **cis-but-2-ene** | **56** | **172** | **583** | **255** |
| **but-1-ene** | **57** | **171** | **483** | **240** |

**Table 4.14 Range of mg/m$^3$ VOC concentrations generated and measured $V_b$ for 15 VOC on Carbosieve SIII at 298K**

There is also an almost tenfold increase in the value of measured $V_b$ each time the carbon number within a homologous series is increased by one. This is observed for both the alcohol and the alkane series. Propan-1-ol had instant breakthrough on Carbotrap-B at mg/m$^3$ concentrations and a value of 13L/g at μg/m$^3$ concentrations. 1,2-dichloroethane had values of $V_b$ of 2L/g to 4L/g on Carbotrap-B at mg/m$^3$ concentrations. Both of these are the next step up in the series for ethanol and dichloromethane, both of which have values of $V_b$ in the hundreds of litres per gram.

Carbosieve SIII is a far stronger adsorbent than is Carbotrap-B and for this reason it is limited in its use for VOC sampling applications that use TD-GC for analysis. The stronger the adsorbent the more difficult the desorption process. Normally when used for sampling applications, the adsorbents only collect small amounts of VOC. In this study the adsorbents were saturated each time that a $V_b$ was measured. This created problems for the use of Carbosieve SIII as some of the more strongly retained

compounds proved very difficult to remove while cleaning the tubes. Cleaning times of up to 24hrs were required in some cases at temperatures approaching the limit of thermal stability of the adsorbent. For this reason there was a higher turnover rate of Carbosieve SIII tubes than Carbotrap-B for measurement purposes. This is, of course, a disadvantage of using Carbosieve SIII for such studies.

The measured values of $V_b$ for the adsorption of each of the 15 VOC were used to draw linear Langmuir, Freundlich, DP-1 and DP-2 isotherms. These linear isotherms are similar in nature to those already reported for the adsorption of VOC on Carbotrap-B. The linear isotherms for the adsorption of the 15 VOC on Carbosieve SIII can be found in Appendices 12 (Langmuir), 13 (Freundlich), 14 (DP-1) and 15 (DP-2). Adsorption parameters for the adsorption of the 15 VOC were calculated from each of the linearised isotherms. These are reported in Table 4.15. The same patterns emerge from Table 4.14 as did from Table 4.4. The Langmuir parameters b and $m_{max}$ and the Freundlich parameter n increase as adsorption increases in line with the measured values of $V_b$. Similarly to the study of adsorption of VOC on Carbotrap-B, calculated values of experimental $\beta$ for the adsorption of the 15 VOC on Carbosieve SIII yielded no relevant information on a relationship between physical properties of the VOC and the measured values of $V_b$.

Also shown in Table 4.15 are the values of $R^2$, the regression coefficients for the linear isotherms. Again this parameter is a measure of the adherence of the data to theoretical basis. Values of $R^2$ range from 0.97 to 0.99 are found indicating that each of the model isotherms describes equally well the adsorption behaviour of the VOC on Carbosieve SIII under the experimental conditions. The calculated adsorption parameters provide a useful tool from which $V_b$ can be evaluated for sampling procedures.

The effect of humidity on the values of measured $V_b$, for the adsorption of VOC in the $mg/m^3$ concentration range, on Carbosieve SIII, was investigated. As previously stated in section 2.2.5, Carbosieve SIII has been reported to adsorb up to 400mg/g of water at high %RH. As the values of $V_b$, reported in Table 4.14, were measured for VOC at ambient conditions (liquid VOC) and dry conditions (gaseous VOC), the

| Compound | Langmuir Parameters | | | Freundlich Parameters | | | DP Eq 1 parameters | | | DP Eq 2 parameters | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | b (m3/mg) | $M_{max}$ (mg/g) | $R^2$ | n | $k_F$ | $R^2$ | $\log W_{o(DP-1)}$ | $k_{(DP-1)}*10^8$ | $R^2$ | $\log W_{o(DP-2)}$ | $k_{(DP-2)}*10^4$ | $R^2$ |
| methanol | 0.002 | 20.2 | 0.988 | 1.25 | 1.5 | 0.997 | -1.02 | 6.7 | 1.000 | 0.26 | 5.9 | 0.998 |
| ethanol | 0.006 | 80.0 | 0.993 | 1.76 | 2.3 | 0.976 | -0.50 | 5.1 | 0.985 | 0.35 | 4.2 | 0.985 |
| chloroform | 0.012 | 196.1 | 0.997 | 4.76 | 2.5 | 0.985 | -0.61 | 1.6 | 0.983 | -0.23 | 1.5 | 0.985 |
| bromoform | 0.010 | 714.3 | 0.999 | 5.20 | 3.0 | 0.973 | -0.51 | 2.4 | 1.000 | -0.31 | 1.4 | 0.997 |
| bromoethane | 0.003 | 217.4 | 0.984 | 1.83 | 2.7 | 1.000 | -0.10 | 3.6 | 0.999 | 1.02 | 4.0 | 1.000 |
| bromochloromethane | 0.010 | 208.3 | 0.997 | 4.31 | 2.5 | 0.993 | -0.68 | 1.8 | 0.996 | -0.27 | 1.7 | 0.993 |
| dichloromethane | 0.003 | 149.3 | 0.990 | 1.57 | 2.6 | 0.995 | -0.16 | 4.3 | 0.997 | -1.10 | 4.7 | 0.995 |
| propene | 0.006 | 12.8 | 0.997 | 1.48 | 1.7 | 0.997 | -0.34 | 3.5 | 0.998 | 1.42 | 5.0 | 0.997 |
| propane | 0.007 | 14.0 | 0.994 | 1.57 | 1.7 | 0.995 | -0.43 | 3.3 | 0.996 | 1.21 | 4.7 | 0.995 |
| butane | 0.018 | 54.2 | 0.993 | 2.73 | 2.1 | 0.981 | -0.34 | 2.1 | 0.993 | -0.56 | 2.7 | 0.991 |
| isobutene | 0.016 | 52.6 | 0.980 | 2.63 | 2.1 | 0.978 | -0.37 | 2.1 | 0.979 | 0.54 | 2.8 | 0.978 |
| 1,3-butadiene | 0.017 | 67.6 | 1.000 | 2.64 | 2.2 | 0.995 | -0.27 | 2.1 | 0.997 | 0.63 | 2.8 | 0.995 |
| trans-but-2-ene | 0.026 | 47.8 | 0.997 | 3.77 | 1.9 | 0.997 | -0.63 | 1.5 | 0.995 | -0.01 | 1.9 | 0.997 |
| cis-but-2-ene | 0.033 | 51.0 | 0.999 | 4.19 | 2.0 | 0.988 | -0.65 | 1.4 | 0.990 | -0.10 | 0.2 | 0.988 |
| but-1-ene | 0.017 | 54.3 | 0.997 | 2.78 | 2.1 | 0.996 | -0.39 | 2.0 | 1.000 | 0.47 | 2.6 | 1.000 |

**Table 4.15** Adsorption parameters calculated from the linearised isotherms drawn from the values of $V_b$ measured for the adsorption of VOC in the mg/m$^3$ concentration range at 298K on Carbosieve SIII

effect of humidity on the reported values of $V_b$ needs to be known. Atmospheres were generated from liquid VOC using the dynamic atmosphere generator described in section 3.2. The diluant air used for these atmospheres was ambient air so that ambient conditions prevailed. Values of $V_b$ measured for these VOC and reported in Table 4.14 were measured under experimental conditions where the humidities ranged from 40%RH to 60%RH. Atmospheres were generated from gaseous VOC using the experimental set-up outlined in section 3.2.3. The diluant air was dry cylinder air and so the values of $V_b$ reported for the gaseous VOC were measured under experimental conditions where the %RH was zero. The generation of atmospheres with varying degrees of %RH has already been discussed in section 3.2.4. The effect of humidity on the measured values of $V_b$ for the adsorption of ethanol, propane and 1,3-butadiene are reported in Table 4.16.

| Compound | %RH | Conc | $V_b$ (L/g) | | |
|---|---|---|---|---|---|
| | | $mg/m^3$ | measured | expected | %difference |
| ethanol | 20 | 242 | 128 | 197 | 35 |
| ethanol | 20 | 48 | 267 | 375 | 29 |
| ethanol | 20 | 247 | 123 | 194 | 37 |
| ethanol | 80 | 181 | 266 | 231 | -15 |
| ethanol | 80 | 142 | 311 | 261 | -19 |
| propane | 80 | 98 | 40 | 59 | 32 |
| propane | 80 | 57 | 38 | 72 | 48 |
| 1,3-butadiene | 80 | 121 | 23 | 378 | 94 |
| propane | 50 | 125 | 35 | 53 | 35 |
| propane | 50 | 72 | 36 | 67 | 47 |
| 1,3-butadiene | 50 | 110 | 324 | 403 | 20 |

**Table 4.16 Percentage differences in measured $V_b$ due to changes in %RH for the adsorption of ethanol, propane and 1,3 butadiene on Carbosieve SIII**

The expected value of $V_b$ for ethanol is the value measured for the corresponding adsorptive concentrations under ambient conditions. For propane and 1,3-butadiene it is the corresponding value measured at 0%RH. Percentage differences of measured $V_b$ range from –15% to 94%. These differences are far greater than the 10.7% calculated for $V_b$ measurements on Carbosieve SIII so it appears that %RH does affect the value of $V_b$ for the adsorption of these VOC on Carbosieve SIII. For non-polar propane, the measured values of $V_b$ are between 30% and 40% less than those measured at 0%RH. There appears to be no significant difference between the values measured at 50%RH

and 80%RH. However for 1,3-butadiene the differences increase as %RH increases. Measured values at 50%RH are 20% less than those measured at 0%RH while those measured at 80%RH are almost 100% less.

The results obtained from the adsorption of ethanol seem to suggest that the presence of an adsorbed layer of water enhance the adsorption of polar compounds, probably due to hydrogen bonding. Measured values of $V_b$ at 20%RH are between 25 to 40% less than those measured at 50%RH. Values measured at 80%RH are approximately 20% greater than those measured at 50%RH. The values of measured $V_b$ are still quite high and suggest that Carbosieve SIII is a good adsorbent for C1 to C4 VOC sampling applications. However, care must be taken when sampling VOC from atmospheres with a high humidity content. Safe sampling volumes need to be adjusted accordingly to the value of %RH under which sampling is being carried out.

## 4.10 Application of calculated Freundlich and Langmuir adsorption parameters to the modelling of diffusive sampling behaviour of benzene and toluene on Carbotrap-B

The Freundlich and Langmuir adsorption parameters calculated from the values of $V_b$ measured for the adsorption of benzene and toluene on Carbotrap-B have been successfully used to model the adsorption behaviour of a Radiello-Perkin-Elmer diffusion tube. (Fondazione Salvatore Maugeri, Padova, Italy) The diffusion tube consists of a Radiello adsorption cartridge inserted into a Perkin-Elmer stainless steel 0.4mm I.D. tube with a diffusion cap fitted onto the open end of the tube. The Radiello cartridge is commercially available and widely used throughout Europe for diffusive sampling applications. The model used was developed at the Environmental Institute of the JRC Ispra. It considers a non-steady-state diffusion inside the adsorbent bed. The mass balance equation is written as follows (Perez Ballesta 2001):

$$D\varepsilon\gamma\frac{d^2C}{dx^2} = \varepsilon\frac{dC}{dt} + (1-\varepsilon)\frac{dC_{ads}}{dt} \qquad \text{Eq. (4.6)}$$

where C is the concentration of the pollutant in the gas phase, $C_{ads}$ is the corresponding equilibrium concentration in the adsorbent as described by the

Freundlich isotherm. ε and γ correspond to porosity and tortuosity values respectively, and D is the diffusivity of the pollutant in air.

The inlet boundary condition at the adsorbent bed (x=0) is linked with the equation described by Fick's second law, which describes the diffusion along the free diffusion path. Downstream, different boundary conditions apply ($x=L_{ads}$) and the adsorbent acts as an infinite sink for the pollutant. This is shown graphically in Fig 4.18.

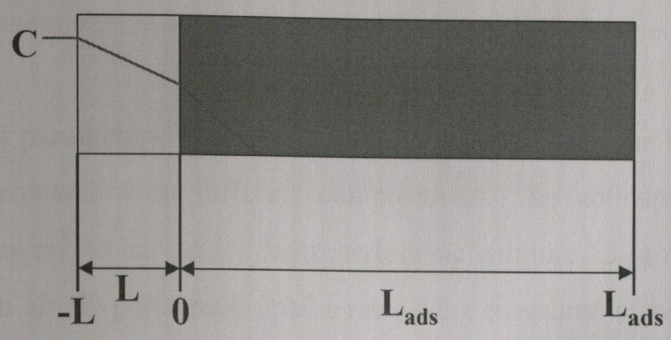


**Fig 4.18 Graphical representation showing adsorbent acting as infinite sink in the diffusion tube**

The equations can be solved numerically by the Crank and Nicolson finite difference method. Freundlich adsorption parameters were needed for the model that described the adsorption of benzene on Carbotrap-B at an adsorptive concentration of 5μg/m$^3$ and also the adsorption of benzene, at the same adsorptive concentration, from a mixture containing toluene at an adsorptive concentration of 105μg/m$^3$. For the adsorption of benzene on its own the calculated adsorption parameters reported in Table 4.4 were used. For benzene in a mixture with toluene the following procedure was used.

The calculated Freundlich adsorption parameters for the adsorption of benzene and toluene on Carbotrap-B that are reported in Table 4.4 were used to calculate values of $V_b$ for both at the required adsorptive concentrations i.e., benzene 5μg/m$^3$ and for toluene 100μg/m$^3$. Eq. (2.37) was used for the calculation.

From the calculated values of $V_b$, Langmuir adsorption constants, b and $m_{max}$ for both toluene and benzene were calculated using Eq. (2.35). Using the calculated values of b and $m_{max}$ for benzene and toluene, Eq. (2.36) was used to calculate the value of $V_b$ from a mixture containing 5μg/m$^3$ benzene and 100μg/m$^3$ of toluene. From these calculated values of $V_b$ for benzene, Freundlich parameters, n and $k_F$, were calculated for the adsorption of benzene from a benzene/toluene mixture at an adsorptive concentration of 5μg/m$^3$ were calculated using Eq. (2.37). The calculated Freundlich parameters in Table 4.4 are related to $m_{ads}$ which is expressed in terms of mg/g. For application of the model to $m_{ads}$ was converted to μg/m$^3$ of adsorbent.

The calculated parameters were used to model uptake rates for benzene from two different atmospheres with different compositions. The atmospheres tested were benzene at 5μg/m$^3$ in air and a benzene/toluene mixture, 5μg/m$^3$ and 100μg/m$^3$, respectively, in air. Experimental uptake rates were measured at NPL laboratories in the UK. The model and experimental uptake rates were determined for five day sampling periods for atmospheres with different compositions. A good agreement was observed between modelled and experimental results. From the results obtained the theoretical uptake rate of benzene by the Perkin-Elmer tube was calculated to be 4.8ng/(μg/m$^3$*week) while the experimental uptake rate was found to be 6.2ng/(μg/m$^3$*week). Fig. 4.19 shows the sampling efficiencies of the tube for benzene from both the single component atmosphere and the benzene/toluene mixture. The sampling efficiencies predicted by the model, after the above parameters were inputted, and the experimental results are all shown. The lines represent the modelled results while the points are the experimental results. Experimentally a drop of 10% in sampling efficiency was observed for benzene alone over the 120hr period while the sampling efficiency for benzene from the benzene/toluene mixture was found to drop by 32% over the same period. The analogous decreases in sampling efficiencies predicted by the model are 16% and 28%, respectively. The values of experimentally measured $V_b$ reported in Table 4.3 show that Carbotrap-B has a higher affinity for toluene than for benzene: $V_b$ for toluene is five times higher than that for benzene. The results suggest that the presence of compounds with a higher affinity for

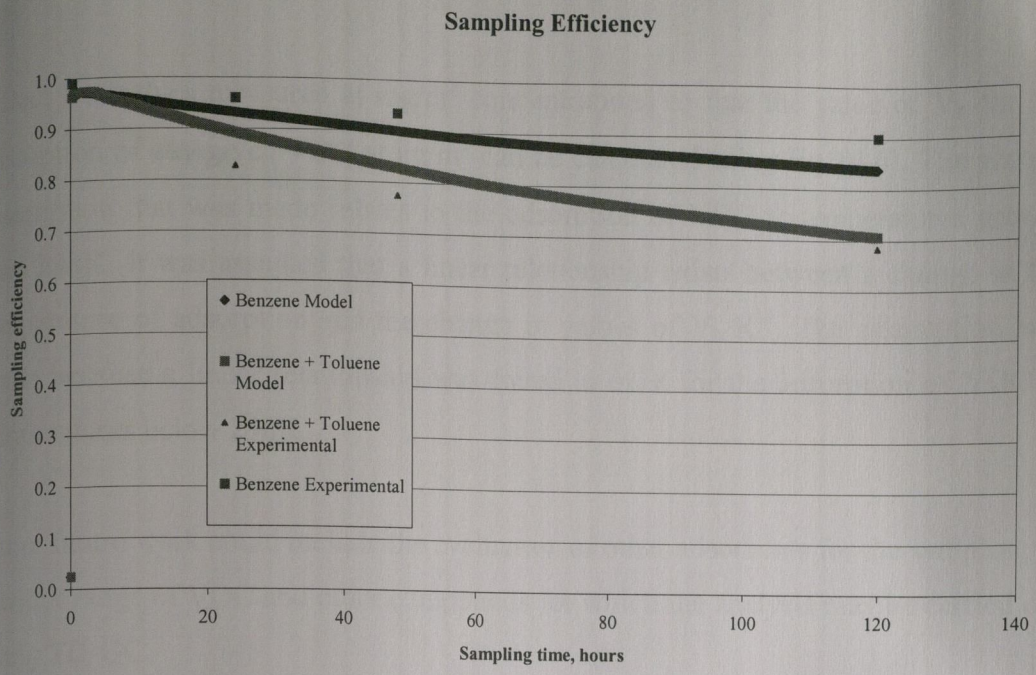


**Fig. 4.19** **Sampling efficiencies calculated from the model (solid lines) and experimental results.**

an adsorbent could induce a drop in the uptake rate of weakly adsorbed compounds. The good agreement between modelled and experimental results show that the model could be a useful tool in determining these effects and the calculated adsorption parameters a good tool for modelling purposes.

## 4.11 Future Work

Due to technical and time constraints the study of the adsorption of VOC such as ethane on Carbosieve SIII at $\mu g/m^3$ concentrations was not carried out. The technical constraint being that the atmosphere generation systems used and developed during this thesis were only effective for $C_4$ hydrocarbons and above as this was the limit for the activated charcoal filter which produced the zero air. An exposure chamber that could be used for the study of the adsorption of these VOC on Carbosieve SIII has just been developed in the laboratory. Unfortunately the completion of this chamber came too late to include its use in the work reported in this thesis. Also, due to time constraints it was not possible to include a study of the effects of temperature on the adsorption of VOC on Carbosieve SIII. Further study on the adsorption of VOC on Carbotrap-B is necessary to evaluate two assumptions that were made in this thesis. The first assumption was that the values of $V_b$ for the VOC at $\mu g/m^3$ concentrations

reflect the values measured at $mg/m^3$ concentrations so that the value of $V_b$ for the adsorption of any given VOC at $\mu g/m^3$ can be calculated using Eq. (4.6). The second assumption that was made relates to the adsorption of VOC at temperatures greater than 298K. It was assumed that a linear relationship exists between a change in the temperature of adsorption and the change in values of $V_b$ $K^{-1}$. The assumption was made because a linear relationship was found to exist for the adsorption of VOC at temperatures below 298K.

Other future work could include the evaluation of other adsorbents for the sampling of a wider range of VOC and other compounds for which the analysis may be carried out using TD-GC.

# CONCLUSIONS

The main aim of the work reported in this thesis was to evaluate two solid adsorbents Carbotrap-B and Carbosieve SIII, for VOC sampling applications with TD-GC as the analysis method. A dynamic sampling technique was chosen to evaluate both adsorbents. This dynamic technique involved measuring experimental values of $V_b$ for the adsorption of VOC on both adsorbents. In total the adsorption of 44 VOC on Carbotrap-B and 19 VOC on Carbosieve SIII was measured. Methods for the generation of atmospheres containing known VOC adsorptive concentrations were developed and used in the lab. Using the generated atmospheres, the effects of adsorptive concentration, temperature and atmospheric humidity on the experimentally measured values of $V_b$ for the adsorption of the VOC on Carbotrap-B were investigated. The effects of adsorptive concentration and atmospheric humidity on the measured values of $V_b$ for the adsorption of VOC on Carbosieve SIII were also measured. The principal conclusions from the study are:

- The adsorptive concentration and temperature of adsorption both have an inverse effect on the measured values of $V_b$. However, out of the total of 63 VOC for which the adsorption on either adsorbent was measured, only five were found to have values of $V_b$ of less than 1L/g at $mg/m^3$ concentrations. The range of VOC covered by both adsorbents was the $C_1$ to $C_{12}$ VOC.

- From the experimentally measured values of $V_b$ at $mg/m^3$ concentrations, linear Langmuir, Freundlich, and Dubinin-Polyani isotherms have been drawn. Adsorption parameters were calculated for each of these isotherms. The calculated adsorption parameters characterise the adsorption system for which they were calculated and can be used to calculate the effects of temperature and or concentration on the values of $V_b$ for specific adsorption systems. These adsorption parameters are useful tools for VOC sampling applications and some of the calculated parameters have been successfully applied to diffusive sampler modelling applications.

- It is evident from the measured values of $V_b$ for the adsorption of benzene on Carbotrap-B at both $\mu g/m^3$ and $mg/m^3$ concentrations that the Langmuir adsorption parameters can only be used to describe the adsorption of the VOC under the

experimental conditions under which they were determined and cannot be extrapolated to the $\mu g/m^3$ concentration range or even the $mg/m^3$ concentration range.

• Values of $V_b$ at $\mu g/m^3$ levels are independent of concentration and experimental data provide a simple relationship that makes it possible to use the $mg/m^3$ adsorption parameters to calculate values of $V_b$ for other VOC at $\mu g/m^3$ levels without having to extrapolate data from one concentration region to another.

• The experimental data also provided a simple relationship from which the change in measured $V_b$ due to a change in the temperature of adsorption could be calculated.

• Atmospheric humidity does not affect the measured values of $V_b$ on Carbotrap-B but adsorption of VOC on Carbosieve SIII, an increase in humidity appears to have a negative effect on the values of $V_b$ for non-polar VOC and a positive effect for those of polar VOC.

• Carbotrap-B is a Class one adsorbent. The experimental data however, suggests specific adsorption effects with benzene. Carbosieve SIII is a weak Class III adsorbent. The experimental data also suggests specific adsorption effects with VOC that contain a concentrated negative charge such as a $\pi$-bond.

• Carbosieve SIII has been shown to be a much stronger adsorbent than Carbotrap-B. For this reason care must be taken when saturating the adsorbent with strongly retained adsorbents as these compounds greatly affect the reusability of the Carbosieve SIII tubes for TD-GC analysis methods.

• The experimental data suggest that the process of adsorption of the VOC on Carbotrap-B is physisorption: an increase in adsorption temperature results in a decrease in adsorption capacity, the adsorption capacity increase with increasing molecular polarisability of the adsorbate and the calculated values of $\Delta H^{st}$ are typical of those for physisorption.

• Both dynamic sampling and passive sampling of VOC onto an adsorbent bed have been chosen as reference sampling methods for the EU daughter directive for benzene. Consequently a full knowledge of solid adsorbents with regard to VOC adsorption at a wide range of concentrations and environmental conditions will be necessary to fully implement this directive. The calculated adsorption parameters reported in this thesis describe the adsorption behaviour of the VOC studied on either Carbotrap-B or Carbosieve SIII assuming that the models used accurately describe the adsorption process involved. Adsorption parameters have been calculated for a range of concentrations and temperatures. By calculating the adsorption parameters for a range of compounds over a range of different environmental conditions, the adsorption behaviour of similar compounds can be predicted. These parameters can be used practically as an efficient tool for optimising and developing an effective sampling strategy for monitoring VOC concentrations in the ambient atmosphere over a wide range of environmental conditions using the reference methods chosen for the directive.

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# PUBLICATIONS

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# An Investigation of the Adsorption of $C_5$-$C_{12}$ Hydrocarbons in the ppmv and ppbv Ranges on Carbotrap B

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The effects of concentration and temperature on the breakthrough volumes ($V_b$) of 23 volatile organic compounds on Carbotrap B have been determined using the frontal chromatography method. From the measured $V_b$, original isotherms have been produced and adsorption parameters based on the Langmuir, Freundlich, and Dubinin-Polyani adsorption models have been calculated. The calculated adsorption parameters describe the behavior of these VOC on Carbotrap B under the experimental conditions and are useful data for VOC sampling applications including adsorption modeling of pumped and diffusive sampling. Each of the adsorption models give similar results and are in good agreement with the experimental data in the ppmv concentration range. It will be shown that contrary to previous assumptions the Langmuir adsorption parameters obtained at ppmv concentrations cannot be used to predict $V_b$ at ppbv concentrations and the calculated parameter $m_{max}$ does not represent the maximum adsorbent capacity. The Freundlich and Dubinin-Polyani models are shown to be more successful in describing the adsorption behavior of the VOC at ppbv levels where $V_b$ is independent of concentration. The isosteric heats of adsorption ($-\Delta H^{st}$) for some of the compounds have been determined using the Van't Hoff equation which can be used to predict the effect of temperature on $V_b$.

## Introduction

Volatile organic compounds (VOC) are ubiquitous atmospheric species that can be attributed to both biogenic and anthropogenic emissions (*1*). Many of these compounds cause adverse health effects in humans after short term and/or chronic exposure and they account for a large proportion of the 189 hazardous air pollutants (HAP) listed in the 1990 U.S. EPA Clean Air Amendment Act (*2*). Historically the monitoring of these compounds has concentrated on short-term exposure to VOC in the workplace. It is only recently that effects of chronic exposure to ambient atmospheric levels of these compounds have been taken into consideration. In 1996 the World Health Organization (WHO) published air quality guidelines for Europe (*3*) that along with those for the classical pollutants also contained guidelines for VOC such as benzene, toluene, and styrene. Unfortunately very few data exist that can be used to quantify the population exposure to VOC. Although urban background concentrations of compounds such as BTX (benzene, toluene, and xylenes) are often continuously monitored, recent work has shown that the levels measured by fixed stations do not reflect those to which the population is exposed (*4*). To determine the real exposure of the population, widespread multisite sampling campaigns incorporating both indoor and outdoor monitoring as well as personal exposure monitoring are necessary. These campaigns can also be used to validate pollutant dispersion models in addition to providing population exposure models (*5*). The measurement of population exposure will become even more important as the European Ambient Air Framework directive (*6*) is put in place. This directive intends to establish exposure limits for compounds in ambient air and other environments, e.g. 5 $\mu g/m^3$ for benzene in ambient air (*7*).

Over the years a popular sampling technique employed for assessing workplace VOC concentrations has been the adsorption of VOC on to solid adsorbents via either pumped tubes or diffusive sampling (*8–11*). Most modern analytical apparatus used in the determination of VOC incorporates a preconcentration step in the analytical chain. Solid adsorbents have been extensively employed, and one can expect further expansion in and development of their use. At European level, a Standardization Committee working group (CEN/TC264/WG13) has been given the task of preparing a standard reference method for the measurement of benzene in ambient air. This method is to be based on the use of solid adsorbents through pumped/diffusive tubes and BTX monitors. Consequently a full knowledge of solid adsorbents with regard to VOC adsorption at a wide range of concentrations and environmental conditions will be necessary. Although a considerable amount of information in this area can be found in the literature (*12–16*), information dealing with breakthrough volumes of complex atmospheres under various environmental conditions is hardly ever available.

The breakthrough volume is defined as the volume of a gaseous sample that passes through an adsorbent bed before a given fraction of the analyte is eluted from the adsorbent, it is an important parameter in defining the applicability of a solid adsorbent for active sampling. In the early applications of solid adsorbents this parameter was determined by means of elution chromatography and was calculated as a function of the retention volume and the number of theoretical plates in a chromatographic system using the adsorbent as the stationary phase (*17*, *18*). As a result, extensive accounts of retention volumes have appeared as guidelines in the use of adsorption systems (*19*, *20*). An implicit assumption of this retention volume model was that the retention volume did not depend on the concentration of the VOC. Breakthrough volumes have also been determined by frontal chromatography. In a previous study carried out in this laboratory (*21*), Langmuir adsorption isotherms for the adsorption of VOC in the ppmv range on Tenax at ambient temperatures were determined using breakthrough volumes determined by the frontal chromatography method. This work showed clearly that breakthrough volumes depended on VOC concentrations. Langmuir equations for the prediction of solid adsorbent breakthrough volumes for single and multicomponent mixtures were also derived. An assumption, not tested at the time, was made that these equations could be used to determine breakthrough volumes in the ppbv range by simple extrapolation of the ppmv range isotherm to lower concentrations (*21*).

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In this paper measurements of the breakthrough volumes of VOC in both the ppmv and ppbv ranges on Carbotrap B at different temperatures are reported. The results indicate that there is no dependence of the breakthrough volumes on the VOC concentrations at ppbv levels. This is in agreement with the earlier retention volume theory. However, it will also be seen that breakthrough volumes at ppbv levels cannot be predicted by simple extrapolation of a Langmuir isotherm obtained at ppmv levels. This result is supported by the experimental determination of Langmuir and Freundlich and Dubinin-Polyani isotherms for 23 hydrocarbons over a wider range of concentrations and temperatures. The experimentally measured breakthrough volumes are also used to calculate the values of the isosteric enthalpies of adsorption ($-\Delta H^{st}$) for some of the hydrocarbons on Carbotrap B which can be used to predict the effect of temperature on $V_b$. The isotherms and adsorption parameters presented in this paper are useful data for pumped tube sampling applications as well as adsorption modeling applications for diffusive samplers because they provide calculated values of $V_b$ that are very close to experimental results and allow the effects of concentration and temperature to be taken into account. As new regulations and sampling methods for VOC concentrations in ambient and workplace atmospheres are put into place, more data on the behavior of solid adsorbents as well as improved modeling techniques will be required.

## Theory

When sampling atmospheric VOC using solid adsorbents, the adsorption process most appropriate for analytical purposes is physisorption as it is a reversible process that allows up to 100% of the sampled compound to be recovered. When chemisorption or chemical reactions occur between the analyte and the adsorbent or between adsorbed compounds they are seen as an adverse effect leading to a deterioration of the quality of the sample (*22, 23*). Extensive reports explaining these adsorption processes from thermodynamic (*24*), statistical (*25*), kinetic (*26*), and potential theory (*27*) approaches are widely available in the literature. However, for analytical or other applications, adsorption isotherms, derived either experimentally or from one of several models, are hardly ever available even though they are extremely useful tools. The earliest model developed was that of Langmuir, and this has been successfully used to describe the adsorption process on several adsorbents (*28, 29*). In this theory $\Theta$, the fraction of occupied adsorption sites on the surface of the adsorbent, can be expressed as

$$\Theta = \frac{bc}{1 + bc} \tag{1}$$

where $b$ is the distribution coefficient and is defined kinetically as the adsorption rate constant, $k_{ads}$ ($m^3\ mg^{-1}\ s^{-1}$) is divided by the desorption rate constant $k_{des}$ ($s^{-1}$), and $c$ is the adsorptive concentration. The Langmuir model can also be expressed as a linear equation relating breakthrough volumes, $V_b$, to the adsorption parameters $b$ and $m_{max}$ as

$$\frac{1}{V_b} = \frac{1}{bm_{max}} + \frac{c}{m_{max}} \tag{2}$$

where $m_{max}$ is defined as the maximum adsorbent capacity (*21*). This equation is used to calculate the parameters $b$ and $m_{max}$, and the linear regression coefficient of the plot of $1/V_b$ vs $c$ gives an indication of the Langmuirian behavior of the adsorption system. In earlier work carried out in this laboratory this model was used to derive adsorption parameters $b$ and $m_{max}$ from experimentally measured breakthrough volumes to describe the adsorption of single and multicomponent VOC mixtures on Tenax GC (*21*). The Langmuir equation was also used to describe the isotherms of multicomponent VOC mixtures and allowed the calculation of breakthrough volumes of any one compound, j, in a mixture of i compounds. This is given by

$$V_b^j = \frac{m_{max}{}^j b^j}{1 + \sum(b^i c^i)} \tag{3}$$

and the equation has been used to show that the adsorbent capacity of an adsorbent for a compound is significantly affected by the presence of other adsorbing species.

A second approach, known as the Freundlich model, similar in nature to the Langmuir model is expressed empirically as

$$\Theta = K' C^{1/n} \tag{4}$$

where $K'$ and $1/n$ are empirical constants. $C$ represents $c/c_{ref}$ where $c$ is the adsorptive concentration, and $c_{ref}$ is an arbitrarily chosen value. In this work $c_{ref}$ was chosen to be 1500 ppmv as previously reported by van den Hoed et al. (*30*). Expressing $\Theta$ in terms of mass of adsorbate, $m$ (calculated from experimental $V_b$), a linear response should be obtained from eq 4 by plotting $\log(m)$ as a function of $\log(C)$ as follows

$$\log(m) = \frac{1}{n}\log(C) + k \tag{5}$$

where $k$ represents $\log(K' \cdot m_{max})$. Breakthrough volumes can therefore be used to calculate the empirical Freundlich parameters for an adsorbent–adsorbate pairing. The Freundlich model gives a concise analytical expression for the experimental facts rather than a clear-cut picture of the mechanism of adsorption (*26, 31*). One of the more successful attempts at giving a theoretical interpretation of the Freundlich isotherm is the work done by Zeldowitsh (*31, 32*).

A final approach investigates the Dubinin-Polyani (DP) equations which have been reported by Reucroft et al. (*33*) both of which have the form

$$\log W = \log W_o - \frac{B}{2.303}\left[\frac{T}{\beta}\log\frac{P_o}{P}\right]^n \tag{6}$$

where $W$ is the volume of condensed adsorbate expressed in $cm^3$ of adsorbate per gram of adsorbent, $P$ is the equilibrium pressure of adsorbate vapor, $P_o$ is the saturated vapor pressure of the liquid adsorbate at $T$ in K, $W_o$ and $B$ are constants related to the pore volume and structure of the adsorbent, $\beta$ is a constant known as the adsorption affinity coefficient, and $n$ is an integer. It was proposed that $n = 2$ for adsorbents whose pore structure was of comparable dimensions to the size of the adsorbate molecules i.e., microporous adsorbents and that $n = 1$ for adsorbents with macroporous structures. Both forms of eq 6 can be written in terms of two parameters from which linearized log–log isotherms can be drawn. For microporous adsorbents ($n = 2$) and macroporous adsorbents ($n = 1$), respectively, eq 6 becomes

$$\log W = \log W_o - K'\epsilon^2 \tag{7}$$

$$\log W = \log W_o - K''\epsilon \tag{8}$$

where

$$\epsilon = RT\ln\frac{P_o}{P} \tag{9}$$

and

$$K' = \frac{B}{\beta^2(2.303)^3R^2} \quad (10)$$

$$K''' = \frac{B}{\beta(2.303)^2R} \quad (11)$$

$R$ is the gas constant and $\epsilon$ is the adsorption potential expressed in calories per mole. $W$ can be calculated from experimental $V_b$ values, and $\epsilon$ can be calculated from the concentration at which $V_b$ was measured. Equation 7 from here on will be called the DP1 equation with adsorption parameters log $W_o$ and $K'$, and eq 8 will be called the DP2 equation with adsorption parameters $W_o$ and $K'''$.

**$V_b$ at Low Concentrations.** At low concentrations adsorption varies directly with concentration, and in such a diluted system Henry's Law has been proposed to describe the adsorption process by analogy to the solution of gases in liquids (*26, 31*). The mass adsorbed, $m$, is a measure of adsorption and is related to $V_b$ as follows

$$m = V_b c \quad (12)$$

where $m$ and $c$ vary proportionately giving a constant value for $V_b$. This will be shown experimentally later on.

**Relationship of $V_b$ and $-\Delta H_{ads}$.** Adsorption of a gaseous molecule onto a solid adsorbent results in the release of heat. The change in enthalpy during the adsorption process can be related to experimentally measured breakthrough volumes by means of a van't Hoff type equation of the form (*34*)

$$\ln(V_b) = \frac{-\Delta H}{RT} + K'''' \quad (13)$$

where $-\Delta H_{ads}$ is the enthalpy of adsorption and $K''''$ is a constant. Equation 11 shows a linear relationship between $V_b$ and $1/T$. $-\Delta H_{ads}$ is given by the slope of the plot of $V_b$, measured over a small range of temperatures.

## Experimental Section

**Generation of Atmospheres Containing VOC.** Atmospheres containing VOC at ppmv levels were generated using a ppmv Dynamic Atmosphere Generator that was developed at INERIS and which is described in detail in previous publications (*21, 35*). This generator has been further developed to allow the generation of atmospheres with VOC at ppbv levels. This is also described in detail in the literature (*36*). Both of these atmosphere generators were employed to create atmospheres containing VOC at the concentrations required for these experiments. The concentrations of VOC in the generated atmospheres could be calculated from the working parameters of the generator, which were recorded in real time. The VOC used in the generation of atmospheres were analytical grade solvents purchased from Carlo-Erba, Italy.

**Verification of the VOC Concentrations in the Generated Atmospheres.** For atmospheres at ppmv levels a Hamilton 1001LTN gastight syringe was used to collect 800 $\mu$L samples of the generated atmospheres. These samples were injected into the tube desorption chamber of a Dynatherm Model 890 Thermal Desorber (TDU) in the preparative mode (Dynatherm Analytical Instruments Inc. produced for Supelco Inc., Bellefonte, PA). The desorption chamber contained an empty Supelco glass tube and was heated to 573 K for 7 min after injection. The VOC were trapped on an adsorbent tube containing Carbotrap B (Supelco Inc.) at the side port exit of the TDU.

The adsorption tubes containing the trapped VOC were then analyzed by thermal desorption-gas chromatography (TD-GC) analysis. The analytical chain consisted of another Dynatherm Model 890 TDU connected to a Carlo Erba HRGC 5300 Mega Series GC by a fused silica transfer line maintained at 473 K. The GC was equipped with a flame ionization detector (FID) and a Chrompack WCOT fused silica CP-SIL 5CB column (25m × 0.25 mm i.d.). The adsorbent tubes were desorbed at 573 K for 7 min under a stream of helium. The flow rate of helium was 12.5 mL/min. During this desorption step the part of the analytical column immediately after the connection to the transfer line was placed in a paste of dry ice/acetone (~183 K) to cryrofocus the desorbed VOC. This paste was removed as the GC temperature program was started.

The GC oven temperature program was as follows: start temperature of 308 K followed by a temperature ramp rate of 3.5 K/min. The ramp rate changed to 5 K/min and then 25 K/min immediately after the column temperature reached 343 K and 348 K, respectively. Once at 548 K the temperature was held constant for 1 min before cooling to 308 K. The total analysis time was 20 min. The carrier gas used was helium with a flow rate of 1.5 mL/min through the analytical column. The FID response was recorded using Chrompack Maestro (Ver. 2.3).

External calibration of the GC was carried out by injecting different volumes of a methanol solution containing known concentrations of the VOC of interest into the tube desorption chamber of the TDU and collecting the VOC onto a Carbotrap B tube as described above. VOC concentrations in atmospheres at ppbv levels were determined by active sampling onto adsorbent tubes containing Carbotrap B. The samples were drawn through the tubes by Gillian dual mode low flow rate samplers at a flow rate of 100 mL/min. The flow rates were verified using a Gillian Gilibrator-2 placed between the tube and the pump. The contents of the adsorbent tubes were then analyzed as described above. A difference of 10% between measured and calculated concentrations of VOC in the generated atmospheres was set as the performance criteria for the generators. This difference of 10% was to incorporate all errors in the generation, sampling, and analysis of the atmospheres.

**Adsorbent.** The adsorbent used was Carbotrap B, a graphitized carbon black (GCB) commercially available from Supelco Inc. Carbotrap B has a 20/40 mesh and a surface area of 100 $m^2/g$ (*37*). Carbotrap B can be conditioned thermally up to 673 K and has good thermal desorption efficiencies (*10, 17, 38–43*). It also has good storage stability and low blank values and does not have a high affinity for water (*37, 41, 44, 45*).

**Adsorbent Tubes.** The adsorbent tubes used were Supelco glass tubes that contained a bed of Carbotrap B held in place by two plugs of silanized glass wool. The dimensions of the tubes were 115 mm in length with an i.d. of 4 mm and an o.d. of 6 mm. Typical Carbotrap B loading was 80 mg for the $V_b$ determined at low temperatures and ppbv levels and 150–180 mg for $V_b$ determined at temperatures of 298 K and above as well as ppmv levels. The adsorbent tubes were conditioned for 12 h on a Dynatherm Model 60 tube conditioner at a temperature of 623 K while being flushed with helium at a flow rate of 100 mL/min. Ideally GCB do not have any surface active sites. However, some studies have suggested that ineffective heating in the preparation of the adsorbent may result in some sites of this type being present (*43, 46*). Therefore, before any $V_b$ measurements were carried out on Carbotrap B, all new adsorbent tubes were saturated with toluene in order to block off any active sites that might give rise to chemisorption. After saturation the tubes were desorbed, under helium, at 623 K for 24 h at a flowrate of 100 mL/min.

**Method of Measurement of $V_b$ of VOC on Carbotrap B at ppmv Levels.** Breakthrough volumes were measured directly by drawing the atmospheres generated in the ppmv Dynamic Atmosphere Generator through an adsorbent tube and monitoring the VOC concentrations in the effluent with

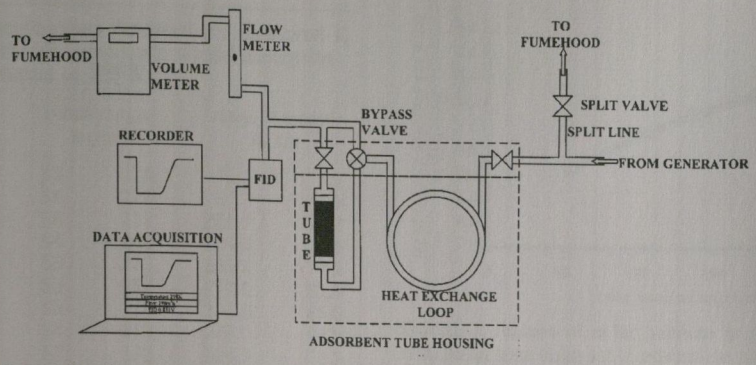


**FIGURE 1. Experimental setup for the determination of $V_b$ at ppmv concentrations.**

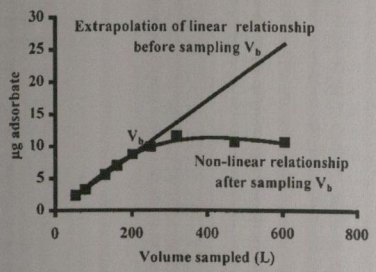


**FIGURE 2. Linear and nonlinear relationships between sampled volume and mass of adsorbate before and after $V_b$ at ppbv concentrations.**

a FID. The generated atmospheres were sampled by means of a membrane pump. The adsorbent tube was situated in a thermally controlled adsorbent tube housing with different tube housings being used depending on the temperature required for the $V_b$ determination. Figure 1 shows the experimental set up for the determination of $V_b$ at ppmv levels. The split line valve was adjusted to permit a flow through the adsorbent tube housing of 100 mL/min without causing any back-pressure at the tube entrance. By turning a three-way valve, situated at the tube inlet and labeled bypass valve in Figure 1, this flow of 100 mL/min was either directed through the adsorbent tube ($V_b$ measurement) or instead directed straight to the outlet flow of the adsorbent tube housing (while tube was being heated or cooled to required temperature for $V_b$ determination). Two milliliters of the outlet flow were directed toward a FID detector to enable monitoring of the VOC concentration. The other 98 mL of the flow passed through a glass bead flow meter and then a Schlumberger precision volume meter. These devices allowed for the measurement of the total flow through the adsorbent tube during a $V_b$ determination.

**Method of Measurement of $V_b$ of VOC on Carbotrap B at ppbv Levels.** The atmospheres generated in the ppbv Dynamic Atmosphere generator were actively sampled onto adsorbent tubes containing Carbotrap B at a flow rate of 100 mL/min using Gillian samplers. Different volumes of each atmosphere were sampled, and the tubes were analyzed by TD-GC to determine the adsorbate loading for each volume sampled. A linear relationship between the volume sampled and the amount of adsorbate exists until breakthrough occurs as shown in Figure 2 (*47*). The equation of the curve representing the linear relationship is calculated by the least mean squares method as is the equation representing the nonlinear relationship. $V_b$ is then determined by calculating the points of intersection of these two curves.

**Adsorption Tube Housing.** For $V_b$ determinations at 298 K and higher temperatures the adsorbent tube was housed in the oven of a Girdel 30 GC. A heat exchange loop made from 1.5 m of stainless steel tubing ensured isothermal conditions. For $V_b$ determinations below ambient temperatures the adsorbent tube was housed in an Engel 10 Portable Fridge. Again a heat exchange loop was used to ensure isothermal conditions. A glass tube, cooled to 267 K, was also used as a simple trap to condense any water vapor present in the generated atmospheres during $V_b$ determinations below 277 K. All adsorbent tubes were heated or cooled to the required temperatures for an hour before any measurements of $V_b$ were carried out.

## Results and Discussion.

**Performance Characteristics.** The concentration of VOC in each atmosphere generated used to draw the linear Langmuir and Freundlich isotherms were calculated from experimental working parameters. The experimental standard deviation of these calculated concentrations was determined from 130 GC analyses in the ppmv range and 51 GC analyses in the ppbv range according to ISO-GUM (*48*). The resulting percentage experimental standard deviations were calculated to be 4.7% at ppmv concentrations and 4.4% at ppbv concentrations. $V_b$ at ppmv levels is measured as a function of adsorbate, temperature, adsorptive concentration, and mass of adsorbent. By repeat measurements at constant temperature and changing the other parameters one at a time the experimental standard deviation in the measurement of $V_b$ at ppmv levels was calculated to be 1.9% with $n = 52$. The uncertainty of $V_b$ at ppbv levels was taken to be 5% in accordance with the specification (*49*) of the samplers used to draw the samples across the adsorbent tubes. Therefore the overall experimental uncertainty associated with each point used to construct the linear isotherms at ppmv levels was calculated to be 5.1%, while for those at ppbv levels the uncertainty was calculated to be 6.7%.

**Values of $V_b$ Measured at ppmv Concentrations on Carbotrap B at 298 K.** In total the adsorption of 23 VOC on Carbotrap B was studied at 298 K. For each compound the value of $V_b$ was measured for a minimum of four different concentrations using the earlier described method. The range of measured $V_b$ for the adsorption of each compound on Carbotrap B as well as the range of concentrations produced is shown in Table 1. The $V_b$ reported in Table 1 are per unit gram of adsorbent and are obtained from extrapolation of the experimental values measured on adsorbent loading of between 150 and 180 mg. To check that the mass of adsorbent was above the critical bed-depth (*15*, *50*, *51*) and that no bias resulted because of the extrapolation $V_b$, at both ends of the concentration ranges given in Table 1, were measured for five compounds using different loading of adsorbent ranging from 90 to 190 mg. No effect due to the critical bed-depth was observed for the five compounds and less than 2% difference was found between the values of $V_b$ per unit gram extrapolated from the measured values of $V_b$ at both 90 mg and 190 mg mass of adsorbent. Our experimental values for the $V_b$ of toluene and *n*-hexane at 50 and 100 ppmv were

**TABLE 1: Range of Concentrations Produced and Measured $V_b$ Per Sorbent Mass for the 23 Compounds Whose Adsorption on Carbotrap B Was Studied at 298 K**

| compd | concn range, mg/m³ | | range of measd $V_b$, L/g | |
|---|---|---|---|---|
| benzene | 53 | 278 | 12.0 | 5.5 |
| toluene | 54 | 272 | 60.8 | 32.9 |
| *o*-xylene | 56 | 277 | 252.6 | 75.3 |
| *p*-xylene | 54 | 269 | 224.6 | 77.6 |
| *m*-xylene | 55 | 275 | 235.2 | 71.2 |
| styrene | 56 | 287 | 170.0 | 63.3 |
| ethylbenzene | 55 | 274 | 124.8 | 65.0 |
| propylbenzene | 54 | 273 | 356.0 | 94.8 |
| 1,2,3-tmb[a] | 67 | 335 | 320.5 | 73.9 |
| 1,3,5-tmb[a] | 64 | 371 | 314.7 | 63.3 |
| 1,2,4-tmb[a] | 54 | 293 | 397.5 | 83.2 |
| cyclohexane | 47 | 239 | 6.4 | 3.5 |
| methylcyclohexane | 45 | 238 | 20.1 | 14.1 |
| *n*-pentane | 34 | 188 | 6.6 | 4.0 |
| *n*-hexane | 34 | 208 | 22.6 | 11.5 |
| *n*-hexene | 39 | 227 | 17.6 | 8.9 |
| *n*-heptane | 43 | 218 | 137.5 | 52.5 |
| *n*-octane | 52 | 252 | 302.6 | 80.0 |
| isooctane | 50 | 257 | 51.6 | 22.9 |
| *n*-nonane | 53 | 261 | 406.2 | 89.5 |
| *n*-decane | 54 | 269 | 449.7 | 96.8 |
| *n*-undecane | 45 | 311 | 594.5 | 135.4 |
| *n*-dodecane | 47 | 310 | 735.3 | 173.5 |

[a] tmb = trimethylbenzene.

within ±5% of those calculated from the Wheeler equation parameters reported by Vahdat et al. (*42*) for the adsorption of these compounds on Carbotrap B.

**Adsorption Parameters for Individual VOC at ppmv Concentrations.** The measured $V_b$ were used to draw Langmuir, Freundlich, and Dubinin-Polyani isotherms for each adsorption system investigated. Langmuir and Freundlich adsorption parameters were calculated from each isotherm, and these calculated parameters are shown in Table 2. The values of the linear regression coefficients, $R^2$, for the linear adsorption isotherms derived from the measured $V_b$ give a measure of the abilities of each model to relate $V_b$ to the calculated adsorption parameters. As stated in the Introduction, $V_b$ was calculated as a function of the retention volume as determined by elution chromatography in the early applications of solid adsorbents (*17–20*). There are, however, large differences in the values for $V_b$ determined using the frontal and elution chromatography methods (*21, 52–54*). These differences can be explained by the fact that at ppmv concentrations $V_b$ is dependent on several parameters. The $V_b$ of VOC at ppmv levels is concentration dependent (see eq 2). Also the presence of other adsorbing species affect the $V_b$ of individual VOC in a mixture as shown in eq 3. The effects of these factors on the values of $V_b$ can be determined by the frontal chromatography method but are not revealed by the elution chromatography method. For pumped tube sampling applications the values of $V_b$ under various experimental conditions need to be known. For this reason the adsorption parameters in Table 1 as well as the isotherms from which they were derived provide an extremely useful tool from which $V_b$ can be evaluated. Up to 100 such adsorption parameters have now been produced by this method in this laboratory to define the adsorption of VOC on adsorbents such as Tenax GC, Carbotrap B, and Carbosieve SIII (*21, 52, 53, 54*).

Figure 3 shows the Langmuir, Freundlich, and Dubinin-Polyani isotherms, derived from the measured $V_b$, for the adsorption of benzene on Carbotrap B in the ppmv concentration range. Each model describes equally well the adsorption behavior of benzene on Carbotrap B at ppmv

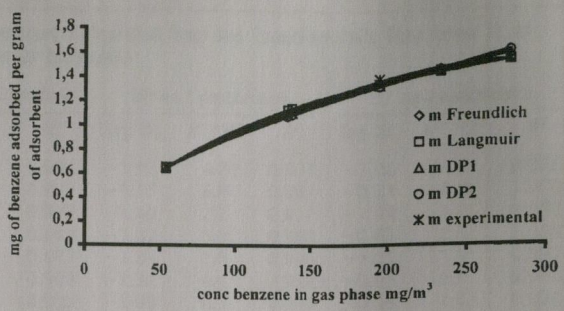


**FIGURE 3. Values of *m* for benzene in the mg/m³ (ppmv) range calculated from each set of adsorption parameters determined at mg/m³ concentrations. Experimentally measured values of *m* also shown.**

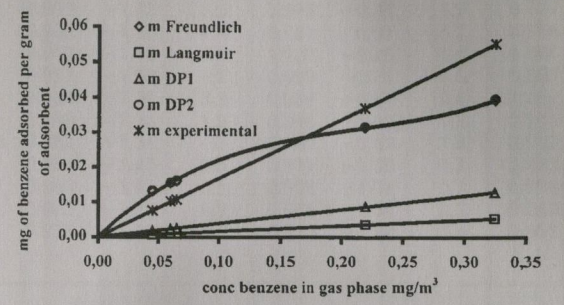


**FIGURE 4. Values of *m* for benzene in the μg/m³ (ppbv) range calculated from each set of adsorption parameters determined in the mg/m³ (ppmv) range. Experimentally measured *m* values at ppbv concentrations also shown.**

levels. In a previous paper (*21*), it was suggested that the $V_b$ of VOC at ppbv levels could be determined by simple extrapolation to the ppbv range of the isotherm derived at ppmv levels.

**Experimental Values of $V_b$ for the Adsorption of Benzene on Carbotrap B at ppbv Concentrations.** To investigate the validity of the $V_b$ obtained when extrapolating Langmuir, Freundlich, and DP ppmv isotherms to the ppbv range, the values of $V_b$ of benzene at various adsorptive concentrations in the ppbv range were determined using the method described in the Experimental Section. Values of $V_b$ were determined using both the single compound and multicomponent mixtures, and the results are shown in Table 3. In addition to the values of the experimentally measured $V_b$, the extrapolated Langmuir, Freundlich, and DP isotherms are shown for comparison in Figure 4. The Langmuir isotherm predicts $V_b$ to be independent of concentration under isothermal conditions at low concentrations. This can be explained by referring back to eq 1. The experimental values of $V_b$ confirm that this is indeed the case for the adsorption of benzene on Carbotrap B. Quantitatively, however, there is a much greater agreement between the experimentally measured $V_b$ at ppbv levels and those obtained by extrapolation of the Freundlich and DP2 isotherms than for those obtained by extrapolation of the Langmuir isotherm. The values of $V_b$ obtained experimentally and also from extrapolation of the Freundlich and DP2 isotherms are of the same order of magnitude as some of the reported $V_b$ values determined for the adsorption of benzene on Carbotrap B by elution chromatography, i.e., 350 L/g (*12*), 490 L/g (*12*), and 114 L/g (*55*), which is not surprising since eqs 5 and 8 are mathematically equivalent. The experimental results reported here also show that the $V_b$ values for the adsorption of benzene at ppbv levels on Carbotrap B are independent of the presence of other adsorbing species under isothermal conditions. The other adsorbing species present in this study

**TABLE 2: Langmuir, Freundlich, and Dubinin-Polyani Adsorption Parameters Calculated from the Experimentally Measured $V_b$ at 298 K with the Value of the Linear Regression Coefficient of the Linear Isotherms**

| | Langmuir parameters | | | Freundlich parameters | | | DP eq 1 parameters | | | DP eq 2 parameters | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| compd | $b$, m³/mg | $m_{max}$, mg/g | $R^2$ | $n$ | $k$ | $R^2$ | log $W_o$ | $K'' *10^8$ | $R^2$ | log $W_o$ | $K''' *10^4$ | $R^2$ |
| benzene | 0.007 | 2.3 | 0.997 | 1.81 | 0.9 | 0.994 | −1.97 | 4.2 | 0.997 | −1.00 | 4.0 | 0.995 |
| toluene | 0.004 | 16.3 | 0.969 | 1.61 | 1.8 | 0.992 | −1.17 | 5.9 | 0.997 | −0.31 | 4.5 | 1.000 |
| *o*-xylene | 0.021 | 24.2 | 0.993 | 3.94 | 1.7 | 0.983 | −1.40 | 2.7 | 0.977 | −1.08 | 1.9 | 0.983 |
| *p*-xylene | 0.017 | 25.3 | 0.999 | 2.92 | 1.8 | 0.969 | −1.27 | 3.5 | 0.980 | −0.83 | 2.5 | 0.969 |
| *m*-xylene | 0.023 | 22.6 | 0.999 | 3.78 | 1.7 | 0.987 | −1.39 | 2.8 | 0.995 | −1.05 | 1.9 | 0.987 |
| styrene | 0.012 | 23.9 | 0.998 | 2.51 | 1.8 | 0.989 | −1.33 | 4.4 | 0.996 | −0.85 | 2.9 | 0.989 |
| ethylben | 0.006 | 29.2 | 0.996 | 1.65 | 2.1 | 0.995 | −1.09 | 6.1 | 0.999 | −0.28 | 4.4 | 0.995 |
| propylbenzene | 0.032 | 28.7 | 0.997 | 5.24 | 1.7 | 0.984 | −1.36 | 2.1 | 0.998 | −1.13 | 1.4 | 0.984 |
| 1,2,3-tmb[a] | 0.066 | 25.8 | 0.991 | 11.15 | 1.5 | 0.996 | −1.,49 | 1.1 | 0.996 | −1.40 | 0.7 | 0.996 |
| 1,3,5-tmb[a] | 0.084 | 24.3 | 0.989 | 11.64 | 1.5 | 0.977 | −1.50 | 0.9 | 0.988 | −1.41 | 0.6 | 0.992 |
| 1,2,4-tmb[a] | 0.089 | 25.0 | 0.997 | 12.56 | 1.5 | 0.992 | −1.50 | 1.0 | 0.990 | −1.40 | 0.6 | 0.977 |
| cyclohexane | 0.005 | 1.5 | 0.992 | 1.57 | 0.9 | 0.996 | −2.04 | 4.7 | 0.998 | −0.89 | 4.7 | 0.997 |
| methylcyclohexane | 0.003 | 7.7 | 0.967 | 1.49 | 1.5 | 0.997 | −1.43 | 5.6 | 0.995 | −0.36 | 4.9 | 0.997 |
| *n*-pentane | 0.005 | 1.5 | 0.997 | 1.38 | 0.9 | 0.995 | −1.59 | 4.4 | 0.997 | 0.01 | 5.3 | 0.995 |
| *n*-hexane | 0.006 | 4.1 | 0.987 | 1.61 | 1.3 | 0.992 | −1.46 | 4.3 | 1.000 | −0.25 | 4.6 | 1.000 |
| *n*-hexene | 0.007 | 3.2 | 0.983 | 1.62 | 1.1 | 0.997 | −1.56 | 4.2 | 0.999 | −0.34 | 4.5 | 0.997 |
| *n*-heptane | 0.015 | 14.9 | 0.989 | 2.43 | 1.7 | 0.984 | −1.20 | 3.3 | 0.989 | −0.51 | 3.0 | 0.982 |
| *n*-octane | 0.043 | 21.9 | 0.999 | 6.07 | 1.5 | 0.998 | −1.36 | 1.5 | 0.998 | −1.12 | 1.2 | 0.998 |
| isooctane | 0.009 | 8.6 | 0.998 | 1.92 | 1.5 | 0.982 | −1.34 | 4.1 | 0.990 | −0.47 | 3.8 | 0.982 |
| *n*-nonane | 0.148 | 23.7 | 0.999 | 18.69 | 1.5 | 0.994 | −1.45 | 0.5 | 0.971 | −1.39 | 0.3 | 0.983 |
| *n*-decane | 0.173 | 26.5 | 0.995 | 22.52 | 1.5 | 0.995 | −1.41 | 0.5 | 0.998 | −1.36 | 0.3 | 0.998 |
| *n*-undecane | 0.180 | 29.8 | 0.993 | 24.27 | 1.5 | 0.963 | −1.38 | 0.6 | 0.955 | −1.34 | 0.3 | 0.963 |
| *n*-dodecane | 0.200 | 38.5 | 0.986 | 20.24 | 1.7 | 0.953 | −1.27 | 0.7 | 0.973 | −1.22 | 0.4 | 0.953 |

[a] tmb = trimethylbenzene.

**TABLE 3: Comparison of Experimentally Determined Values of $V_b$ for Benzene on Carbotrap B at ppbv Concentrations with Those Given by Extrapolation of the Corresponding Langmuir, Freundlich, and Dubinin-Polyani Isotherms Measured in the ppmv Range**

| compd | temp of adsorption, K | concn, $\mu$g/m³ (ppbv) | experimentally measured $V_b$, L/g | extrapolated $V_b$, L/g | | | |
|---|---|---|---|---|---|---|---|
| | | | | Freund | Lang | DP1 | DP2 |
| benzene | 298 | 325 (88) | 169 | 120 | 16 | 39 | 122 |
| benzene | 298 | 220 (59) | 169 | 143 | 16 | 40 | 145 |
| benzene | 298 | 60 (16) | 171 | 257 | 17 | 40 | 260 |
| benzene[a] | 298 | 65 (18) | 165 | 247 | 17 | 40 | 251 |
| benzene[a] | 298 | 45 (12) | 169 | 292 | 17 | 39 | 296 |
| benzene | 261 | 45 (12) | >440 | 519 | 53 | 26 | 518 |

[a] $V_b$ of benzene in a BTX mixture.

were toluene and *o*-xylene and all three compounds were present in the generated atmospheres at equimolar concentrations. These results would seem to suggest that contrary to previous assumptions, Langmuir adsorption parameters calculated from $V_b$ measured at ppmv concentrations cannot be used to predict $V_b$ at ppbv concentrations. The extrapolated DP1 isotherm also fails to describe the adsorption behavior of benzene on Carbotrap B at ppbv concentrations. This can be explained by the fact that this isotherm was proposed for microporous adsorbents which is not the case for Carbotrap B. The Freundlich and DP2 adsorption isotherms provide the better results when extrapolating from the ppmv to the ppbv concentration ranges. At ppmv levels, however, all sets of adsorption parameters describe equally well the adsorption on Carbotrap B of the VOC studied.

**Values of $V_b$ and Calculated Adsorption Parameters at Different Temperatures.** The adsorption of different concentrations in the ppmv range of benzene, toluene, *o*-xylene, styrene, ethylbenzene, and propylbenzene on Carbotrap B was studied at different temperatures in the range 263−308 K. Table 4 shows the range of $V_b$ measured and concentration range studied for each compound at the respective temperatures. Langmuir and Freundlich isotherms for these compounds were then drawn from the measured $V_b$ for each temperature studied. For each of these isotherms Langmuir and Freundlich adsorption parameters were calculated, and these parameters are shown in Table 5. It is seen in Tables 3 and 4 that the experimentally measured $V_b$ at both ppbv and ppmv levels increase with decreasing temperature.

**TABLE 4: Range of Concentrations Produced and Measured $V_b$ Per Sorbent Mass for the Compounds Whose Adsorption Was Studied at Different Temperatures**

| compd | temp, K | concn range, mg/m³ | | range of measd $V_b$, L/g | |
|---|---|---|---|---|---|
| benzene | 308 | 50 | 278 | 8.2 | 3.9 |
| | 278 | 54 | 272 | 25.8 | 12.8 |
| | 263 | 52 | 274 | 42.0 | 23.1 |
| toluene | 308 | 53 | 264 | 29.8 | 18.2 |
| | 278 | 51 | 264 | 130.7 | 64.0 |
| | 263 | 53 | 267 | 259.4 | 87.6 |
| *o*-xylene | 308 | 55 | 283 | 157.2 | 60.4 |
| | 278 | 54 | 272 | 370.0 | 94.0 |
| | 263 | 54 | 273 | 440.0 | 110.0 |
| ethylbenzene | 308 | 54 | 269 | 65.5 | 42.3 |
| | 278 | 53 | 266 | 293.4 | 100.9 |
| | 263 | 54 | 266 | 396.3 | 115.1 |
| propylbenzene | 308 | 78 | 239 | 177.5 | 86.2 |
| | 278 | 78 | 238 | 308.6 | 117.2 |
| styrene | 308 | 56 | 282 | 122.1 | 51.9 |
| | 278 | 56 | 281 | 306.1 | 89.7 |
| | 263 | 56 | 280 | 401.6 | 108.4 |

**Effect of Temperature on the Calculated Langmuir and Freundlich Adsorption Parameters.** The Langmuir adsorp-

**TABLE 5: Langmuir, Freundlich, and Dubinin-Polyani Adsorption Parameters for the Compounds for the Compounds Whose Adsorption Was Studied at Different Temperatures**

| | | Langmuir parameters | | | Freundlich parameters | | | DP eq 1 parameters | | | DP eq 2 parameters | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| compd | temp, K | $b$, m³/mg | $m_{max}$, mg/g | $R^2$ | $n$ | $k$ | $R^2$ | log $W_o$ | $K''$ *10⁸ | $R^2$ | log $W_o$ | $K'''$ *10⁴ | $R^2$ |
| benzene | 263 | 0.005 | 11.29 | 0.986 | 1.542 | 1.63 | 0.999 | −1.42 | 7.75 | 0.995 | −0.49 | 5.39 | 0.989 |
| benzene | 278 | 0.006 | 5.51 | 0.997 | 1.744 | 1.27 | 0.994 | −1.68 | 5.59 | 0.997 | −0.78 | 4.51 | 0.993 |
| benzene | 298 | 0.007 | 2.31 | 0.999 | 1.815 | 0.89 | 0.993 | −1.97 | 4.15 | 0.997 | −0.87 | 4.27 | 0.995 |
| benzene | 308 | 0.006 | 1.76 | 0.998 | 1.713 | 0.77 | 0.998 | −2.04 | 3.96 | 0.999 | −0.95 | 4.14 | 0.998 |
| toluene | 263 | 0.011 | 31.25 | 0.992 | 2.274 | 1.96 | 0.994 | −1.27 | 5.63 | 0.997 | −0.70 | 3.65 | 0.991 |
| toluene | 278 | 0.006 | 26.60 | 0.969 | 1.792 | 1.96 | 1.000 | −1.24 | 5.86 | 0.997 | −0.44 | 4.39 | 0.997 |
| toluene | 298 | 0.004 | 16.31 | 0.956 | 1.614 | 1.77 | 0.997 | −1.17 | 5.90 | 0.997 | −0.31 | 4.55 | 0.999 |
| toluene | 308 | 0.003 | 10.46 | 0.999 | 1.419 | 1.64 | 0.991 | −1.16 | 6.08 | 0.997 | −0.23 | 4.85 | 0.995 |
| *o*-xylene | 263 | 0.048 | 31.95 | 0.999 | 7.299 | 1.66 | 0.992 | −1.44 | 1.86 | 0.999 | −1.31 | 1.07 | 0.995 |
| *o*-xylene | 278 | 0.042 | 27.62 | 0.993 | 6.549 | 1.62 | 0.983 | −1.43 | 2.33 | 0.995 | −1.28 | 1.20 | 0.999 |
| *o*-xylene | 298 | 0.021 | 24.15 | 0.999 | 3.945 | 1.67 | 0.999 | −1.39 | 2.72 | 0.977 | −1.08 | 1.86 | 0.983 |
| *o*-xylene | 308 | 0.011 | 22.52 | 0.998 | 2.365 | 1.82 | 0.989 | −1.29 | 4.02 | 0.997 | −0.73 | 3.00 | 0.992 |
| styrene | 263 | 0.029 | 33.33 | 0.979 | 5.432 | 1.72 | 0.999 | −1.40 | 3.35 | 0.984 | −1.23 | 1.53 | 0.981 |
| styrene | 278 | 0.026 | 28.49 | 0.996 | 4.122 | 1.74 | 0.989 | −1.38 | 3.57 | 0.997 | −1.13 | 1.91 | 0.991 |
| styrene | 298 | 0.012 | 23.87 | 0.990 | 2.502 | 1.81 | 0.981 | −1.32 | 4.40 | 0.995 | −0.85 | 2.93 | 0.989 |
| styrene | 308 | 0.008 | 20.49 | 0.995 | 2.134 | 1.80 | 0.991 | −1.28 | 4.53 | 0.998 | −0.67 | 3.32 | 0.999 |
| ethylbenzene | 263 | 0.027 | 34.25 | 0.980 | 4.521 | 1.79 | 0.986 | −1.33 | 4.22 | 0.987 | −1.14 | 1.88 | 0.991 |
| ethylbenzene | 278 | 0.017 | 32.15 | 0.998 | 3.058 | 1.88 | 0.995 | −1.27 | 4.65 | 0.991 | −0.91 | 2.58 | 0.989 |
| ethylbenzene | 298 | 0.006 | 29.15 | 0.999 | 1.649 | 2.10 | 1.000 | −1.09 | 6.09 | 0.998 | −0.28 | 4.45 | 0.995 |
| ethylbenzene | 308 | 0.003 | 26.32 | 0.994 | 1.359 | 2.08 | 0.999 | −1.07 | 6.43 | 0.998 | −0.03 | 5.22 | 0.999 |
| propylbenzene | 278 | 0.046 | 30.12 | 0.998 | 7.962 | 1.63 | 0.991 | −1.43 | 2.02 | 0.981 | −1.33 | 0.88 | 0.989 |
| propylbenzene | 298 | 0.032 | 28.65 | 0.997 | 5.241 | 1.69 | 0.984 | −1.36 | 2.14 | 0.980 | −1.13 | 1.40 | 0.984 |
| propylbenzene | 308 | 0.013 | 26.81 | 0.997 | 2.851 | 1.84 | 0.984 | −1.28 | 3.05 | 0.999 | −0.86 | 2.49 | 0.997 |

tion parameter $b$, the distribution coefficient, is kinetically defined as $k_{ads}/k_{des}$, where $k_{ads}$ is the adsorption rate constant and $k_{des}$ is the desorption rate constant of the adsorptive molecule. It can be seen in Table 5 that a decrease in temperature results in an increase in the value of $b$ calculated for the adsorption of most of the compounds which is in agreement with the basic kinetic theory of adsorption of gases. The value of $b$ calculated for the adsorption of benzene, however, while exhibiting a slight tendency to increase slightly with temperature appears to remain relatively constant, over the range of temperatures studied. From an analytical point of view the enhanced adsorption capacity of Carbotrap B at lower temperatures suggests it to be a good adsorbent for VOC sampling applications. The parameter $m_{max}$ was defined in the earlier theoretical section as the maximum adsorbent capacity and can be calculated from experimentally measured $V_b$ using the linear Langmuir isotherm, eq 2. This parameter, although reported in terms of mass of adsorbate, is defined by the Langmuir isotherm as representing the total number of adsorption sites available on the surface of the adsorbent. As such the value of $m_{max}$ should, therefore, remain a constant for a given adsorbent. However, it can be seen from Table 5 that a decrease in the temperature at which adsorption takes place results in an increase of the $m_{max}$ values calculated from the Langmuir isotherms. This increase in the value of $m_{max}$ with decreasing temperature is not consistent with the definition of $m_{max}$ in the Langmuir theory. The Langmuir theory assumes that all adsorption sites on the surface of the adsorbent are energetically homogeneous.

The Freundlich parameter $n$ is also temperature dependent. An interpretation of this can be based on the hypothesis that the reciprocal of this parameter, $1/n$, is linearly dependent on temperature (*32*). As the temperature at which adsorption takes place increases so does $1/n$. As temperature increases there are less available adsorption sites within the range of lower energies resulting in fewer molecules being adsorbed. Looking at Table 5 this is seen to be the case for the adsorption of five out of six of the compounds studied. By contrast, however, the calculated $n$ for benzene appears to increase slightly with increasing temperature.

The Freundlich theory assumes the surface of the adsorbent to have a range of adsorption sites each having different adsorbate–adsorbent heats of adsorption associated with them. The values of $m_{max}$ in Table 5 suggest that the distribution of available adsorption sites on the surface of the adsorbent, and not the actual total number of adsorption sites as suggested by the Langmuir $m_{max}$, changes with temperature. As temperature decreases the number of available sites increases, and this is consistent with an increase in the Langmuir $b$ parameter. The $m_{max}$ value calculated from the Langmuir isotherm is defined as a measure of the number of available adsorption sites at a certain temperature and not the total number of adsorption sites that are actually present on the surface of the adsorbent. Since $\Theta = m/m_{max}$ the value of $k$ in Table 5 equates to the value of $\log(K m_{max})$ where $K$ is an empirical constant (see eqs 4 and 5). Thus if the $m_{max}$ parameter used in the Freundlich isotherm represents the total number of adsorption sites, then the value of $k$ should remain constant over the range of temperatures at which the adsorption occurred. As is seen in Table 3, the value of $k$ remains relatively constant over the range of temperatures studied. The Langmuir parameters remain as useful tools for certain applications, but the Freundlich isotherm appears to be a more accurate representation of the actual adsorption behavior.

The parameter log $W_o$ of the DP equations is related to the adsorbent pore structure. The relationship between this parameter and temperature is quite complex and beyond the scope of this paper. However, the values of log $W_o$ calculated from the experimental $V_b$ values which are shown in Table 5 are of the same magnitude as those reported by Reucroft et al. (*33*). The DP1 and DP2 adsorption parameters, $K'$ and $K''$, are proportional to the reciprocals of $\beta^2$ and $\beta$, respectively. $\beta$ is the parameter which expresses the adsorption affinity of the adsorption system being studied. Therefore as temperature increases, $\beta$ decreases accordingly as is seen to be the case in Table 5 for five of the six compounds.

**Calculation of Isosteric Heats of Adsorption.** Tables 1 and 4 show the ranges of measured $V_b$ for the adsorption of benzene, toluene, *o*-xylene, ethylbenzene, styrene, and propylbenzene on Carbotrap B at 263, 278, 298, and 303 K. Using these measured $V_b$ the enthalpies of adsorption ($-\Delta H_{ads}$) for each concentration studied are calculated by the van't Hoff expression (eq 11). This equation is reported

**TABLE 6: $-\Delta H_{vap}$, Calculated $-\Delta H^{st}$, and $R^2$ for the Adsorption at ppmv Concentrations on Carbotrap B[a]**

| compd | $-\Delta H^{st}$, kJ mol$^{-1}$ | $-\Delta H_{vap}$, kJ mol$^{-1}$ | $R^2$ |
|---|---|---|---|
| benzene | 24.1 | 33.8 | 0.999 |
| toluene | 31.7 | 38.1 | 0.998 |
| *o*-xylene | 25.0 | 43.4 | 0.999 |
| styrene | 25.1 | 40.3 | 0.998 |
| ethylbenzene | 34.2 | 42.2 | 0.994 |
| propylbenzene | 30.8 | 43.6 | 0.998 |

[a] The value $R^2$ relates to the linear relationship between calculated $-\Delta H_{ads}$ and surface coverage of adsorbate.

to be limited to a temperature range of approximately 5 K due to the temperature dependence of $-\Delta H_{ads}$ (*18*). For each adsorbate the calculated enthalpies were concentration dependent. The surface coverage for each adsorbate was also calculated at the different concentrations studied using the measured $V_b$. Calculated surface coverage ranged from 0.05 to 0.3 mmol g$^{-1}$ or in percentage terms 25−80% of the monolayer capacities calculated from the linear Langmuir isotherms. A linear relationship between the calculated $-\Delta H_{ads}$ and surface coverage was observed for each compound and the isosteric heat of adsorption, $-\Delta H^{st}$, or near zero surface coverage heat of adsorption, for each adsorbate was determined by extrapolating to zero the plot of calculated $-\Delta H_{ads}$ against mmol g$^{-1}$ of adsorbate. The resulting isosteric heats of adsorption and the coefficient of linear regression, $R^2$, for each compound are shown in Table 6 as well as the molar heats of vaporization reported in the literature (*56*). The values of $-\Delta H^{st}$ for the six compounds show that compounds containing the same number of carbons have similar results. This is consistent with other reported studies that have shown similar relationships between $-\Delta H^{st}$ and carbon number or molecular weight of adsorbate (*57*, *58*). The $-\Delta H^{st}$ for the adsorption of benzene on Carbotrap B has been reported as being 62 kJ mol$^{-1}$, over twice the value shown in Table 6, when measured by the retention volume method (*55*). Other studies have shown similar differences between the values of $-\Delta H^{st}$ calculated at different adsorbate surface coverage for the same adsorption systems. Calculated $-\Delta H^{st}$ values for high surface coverage are in general lower than the $-\Delta H_{vap}$ (*59*−*61*). This is probably due to the fact that as the surface coverage approaches the monolayer capacity of the adsorbent for a particular adsorbate, the adsorbed molecules interact between themselves similarly to the adsorbate in its pure liquid phase. Other reported values for the adsorption of these compounds on GCB that have been determined by the retention volume method are benzene 38−40 kJ mol$^{-1}$ (*62*, *63*), toluene 48 kJ mol$^{-1}$ (*27*), ethylbenzene 52 kJ mol$^{-1}$ (*27*), *o*-xylene 53 kJ mol$^{-1}$ (*27*), propylbenzene 59 kJ mol$^{-1}$ (*27*), and $C_6$−$C_8$ hydrocarbons 32−43 kJ mol$^{-1}$ (*64*, *65*). The results in Table 6 are of the same order of magnitude, although slightly lower than the reported values. While the frontal chromatography method used to determine $V_b$ in this study is ideal for determining the effects of environmental parameters such as temperature and concentration on the adsorption of VOC in "real" sampling application situations, it is less able to provide precise data for which accurate thermodynamical properties of the adsorbent can be determined. However, they are very useful for the comparison of adsorbents for practical applications especially for the determination of $V_b$ at different temperatures.

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# The use of adsorption parameters in the prediction of effects of multicompound atmospheres on the uptake rates of benzene on Carboptrap-B.

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## Introduction

Over the years diffusive sampling has been and continues to be a popular technique for assessing workplace volatile organic compound (VOC) concentrations and measuring population exposure. As new regulations for VOC concentrations in ambient and workplace atmospheres are put into place, more data on the behaviour of solid adsorbents as well as improved modelling techniques will be required. Breakthrough volumes of VOC on an adsorbent, as measured by the frontal chromatography method, can be used to calculate Langmuir and Freundlich adsorption parameters that describe the adsorption behaviour of the VOC on the adsorbent. These parameters are useful data for modelling applications for diffusive sampling. We report here a direct application for determining uptake rates. Isotherm parameters, obtained from experimentally measured breakthrough volumes for benzene adsorbed onto Carbotrap-B[(1)], were used in a non-steady-state diffusion model to predict uptake rates in a Radiello-Perkin Elmer tube. The modelled results were then compared to experimental uptake rates.

## Theory

### Breakthrough Volume

The breakthrough volume ($V_b$) is defined as the volume of a gaseous sample that passes through an adsorbent bed before a given fraction of the analyte is eluted from the adsorbent.

### Langmuir Adsorption Parameters.

The Langmuir adsorption model assumes that only a single layer of adsorbate is formed, that the surface of the adsorbent is homogenous and that no interactions occur between adsorbed molecules. It can be expressed mathematically as :

$$V_b = \frac{bm_{max}}{1+bc} \qquad (1)$$

This can then be transformed into the linear expression :

$$\frac{1}{V_b} = \frac{1}{b m_{max}} + \frac{c}{m_{max}} \qquad (2)$$

C is the adsorptive concentration, $m_{max}$ is the adsorbent capacity and b is the distribution coefficient. A plot of $1/V_b$ vs c is used to calculate the parameters b and $m_{max}$. The breakthrough volume of any one compound, j, in a mixture of i compounds can be calculated from the competitive Langmuir adsorption equation which is expressed as :

$$V_b^{\,j} = \frac{m_{max}{}^{j} b^{j}}{1 + \Sigma\left(b^{i} c^{i}\right)} \qquad (3)$$

This equation has been used to show that the adsorbent capacity of an adsorbent for a compound is significantly affected by the presence of other adsorbing species[2].

**Freundlich Adsorption Parameters**

The Freundlich model, which is similar in nature to the Langmuir model, is expressed empirically as :

$$\Theta_F = k' C^{\frac{1}{n}} \qquad (4)$$

where the Freundlich parameters k' and 1/n are empirical constants. $\Theta_F$ is the proportion of occupied sites. C represents $c/c_{ref}$ where c is the adsorptive concentration and $c_{ref}$ is an arbitrarily chosen value. In this work $c_{ref}$ was chosen to be 1500ppmv, as previously used by van den Hoed et al[3]. $\Theta_F$ can be expressed in terms of mass of adsorbate, m, which is calculated from experimental $V_b$ using Eq 1. The Freundlich parameters can be calculated from a plot of log(m) versus log(C) according to the following expression

$$\log(m) = \frac{1}{n}\log(C) + k \qquad (5)$$

where k represents log ($k'.m_{max}$). Breakthrough volumes can therefore be used to calculate the empirical Freundlich parameters for an adsorbent-adsorbate pairing.

**Modelling Diffusive Sampler Behaviour**

The model applied here has been developed at the Environmental Institute of the JRC Ispra[4]. It considers a non-steady-state diffusion inside the adsorbent bed. The mass balance equation is written as follows :

$$D\varepsilon\gamma \frac{d^2C}{dx^2} = \varepsilon \frac{dC}{dt} + (1-\varepsilon)\frac{dC_{ads}}{dt} \qquad (6)$$

where C is the concentration of the pollutant in the gas phase, $C_{ads}$ is the corresponding equilibrium concentration in the adsorbent as described by the Freundlich isotherm. $\varepsilon$ and $\gamma$ correspond to porosity and tortuosity values respectively, and D is the diffusivity of the pollutant in air.The inlet boundary condition at the adsorbent bed (x=0) is linked with the equation described by Fick's second law, which describes the diffusion along the free diffusion path. Downstream, different

boundary conditions apply ($x=L_{ads}$) and the adsorbent acts as an infinite sink for the pollutant. This is shown graphically in Fig 1.

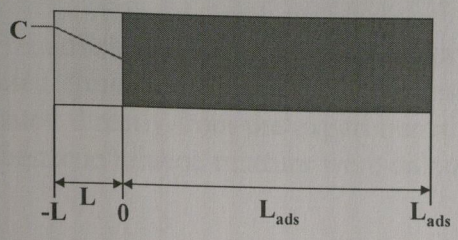


**Figure 1 : Graphical representation of model showing the adsorbent acting as a sink in a diffusive tube**

The equations can be solved numerically by the Crank and Nicolson finite difference method.

Experimentally measured $V_b$ were used to calculate the Freundlich adsorption parameters that were used to model the adsorption behaviour of the single component atmosphere. The values of $V_b$ that were used to calculate the Freundlich parameters for the benzene/toluene mixture were calculated using Eq (3). The Langmuir parameters used in Eq (3) were themselves calculated from experimental $V_b$ using Eq (2).

## Experimental

### Measurement of $V_b$

Atmospheres containing known concentrations of benzene and toluene were generated using a Dynamic Atmosphere Generator, which has been developed at INERIS. The concentrations were verified by sampling discreet volumes of the generated atmospheres and analysing by TD-GC. The breakthrough volumes were measured directly by drawing the generated atmospheres through an adsorbent tube and monitoring the benzene/toluene concentrations in the effluent of the tube with a FID. The adsorbent used was Carbotrap B™, a graphitized carbon black commercially available from Supelco. The atmosphere generator, analysis methods and breakthrough volume methods are described in detail in previous publications [1,2].

### Experimental Uptake Rates

Experiments were carried out at the National Physics Laboratory (NPL) in the UK. Atmospheres containing the VOC at known concentrations were generated in the NPL Controlled Test Atmosphere Facility (CATFAC). A Carlo Erba Trace Gas Analyser was used for continuous on-line monitoring of the generated atmosphere.

The design of the CATFAC ensured a laminar air flow of uniform velocity, wind speed was set to approximately $1ms^{-1}$ and temperature was maintained at 293±1K for the duration of the experiment. The tubes used were Perkin-Elmer diffusion tubes containing a Radiello Cartridge packed with approximately 100mg of Carbotrap B™ adsorbent. These tubes have been described in more detail in a previous publication[5]. The tubes were fitted with Perkin Elmer diffusion caps during the exposure period.

Tubes were exposed for 120 hours periods with additional tubes remaining sealed to be used as blanks.

**Results**

Table 1 shows the Freundlich adsorption parameters for the adsorption of benzene on Carbotrap B calculated from the experimentally measured $V_b$. The parameters for benzene were calculated directly from the experimentally measured $V_b$ using Eq. (5) while those for the benzene/toluene mixture were calculated using Eq's. (2), (3) and (5).

| Freundlich Parameters | Units | Benzene | Benzene/Toluene |
|---|---|---|---|
| k' | $\mu g/m^3$ | 3338197047 | 636124 |
| $C_{ref}$ | $\mu g/m^3$ | 4785764 | 4785764 |
| n | | 1.77 | 12.24 |

Table 1 : Calculated Freundlich adsorption parameters used in model

Table 2 shows the physical parameters of the adsorbent tubes that must also be inputted into the model. The table contains the physical parameters of the adsorbent tube and bed. The tortuosity is a property of a packed column that indicated the unevenness of the path followed by a gaseous molecule as it passes down the column. Benzene was injected into a Girdel 30 GC, which had as its column an adsorbent tube packed with Carbotrap B™. Retention times were measured for different carrier gas flow rates and the tortuosity was calculated from the results obtained. The porosity was calculated from the average particle and adsorbent bed volumes.

| Sampler Parameters | Units | Value |
|---|---|---|
| Diffusion Length | cm | 2.1 |
| Adsorbent Length | cm | 2 |
| Diameter of Diffusion Area | cm | 0.49 |
| Diffusivity | $cm^2/s$ | benzene in air |
| Porosity | (0-1) | 0.48 |
| Tortuosity | (0-1) | 0.81 |

Table 2: Parameters of adsorbent tube and bed inputted into model.

The model and experimental uptake rates were determined for five day sampling periods for atmospheres with different compositions. The atmospheres tested were benzene at $5\mu g/m^3$ in air and a benzene/toluene mixture, $5\mu g/m^3$ and $100\mu g/m^3$, respectively, in air. A good agreement was observed between modelled and experimental results. From the results obtained the theoretical uptake rate of benzene by the Perkin-Elmer tube was calculated to be 4.8ng/($\mu g/m^3$*week) while the experimental uptake rate was calculated to be 6.2ng/($\mu g/m^3$*week). Figure 2 shows the sampling efficiencies of the tube for benzene from both the single component atmosphere and the benzene/toluene mixture. The sampling efficiencies predicted by the model, after the above parameters

were inputted, and the experimental results are all shown. The lines represent the modelled results while the points are the experimental results. Experimentally a drop of 10% in sampling efficiency was observed for benzene alone over the 120hr period while the sampling efficiency for benzene from the benzene/toluene mixture was found to drop by 32% over the same period. The analogous decreases in sampling efficiencies predicted by the model are 16% and 28%, respectively. Recently published results show that toluene has a higher affinity for Carbotrap B than benzene: $V_b$ for toluene is five times higher than that for benzene[1]. The results suggest that the presence of compounds with a higher affinity for an adsorbent could induce a drop in the uptake rate of weakly adsorbed compounds. The good agreement between modelled and experimental results show that the model could be a useful tool in determining these effects.

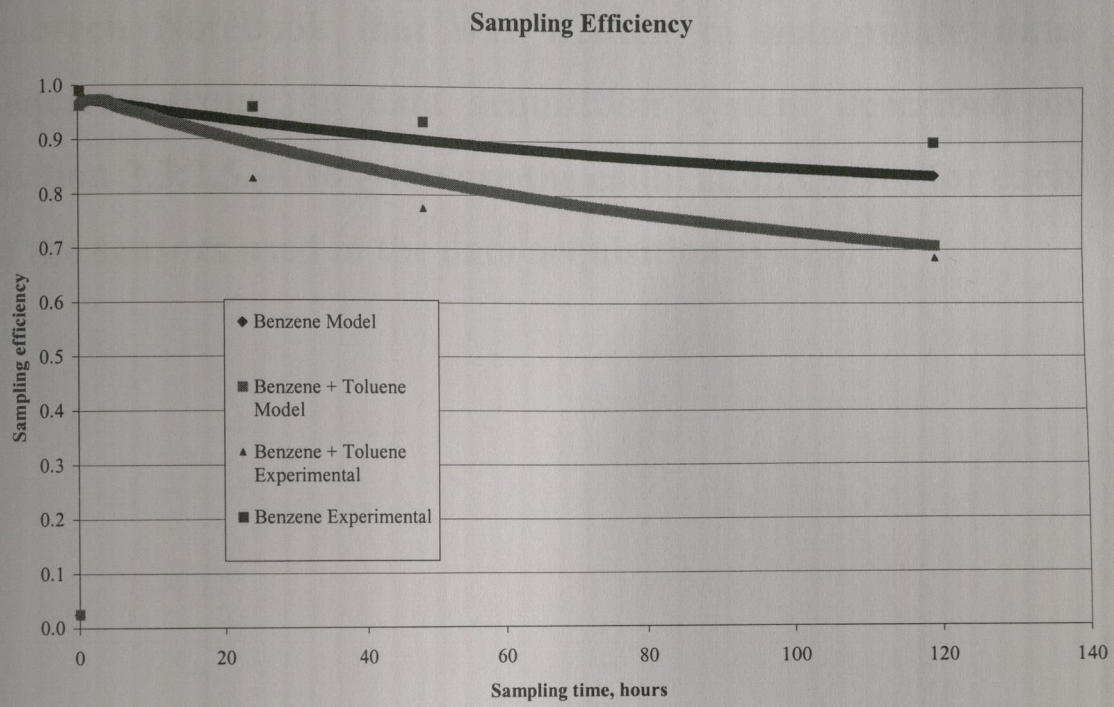


**Figure 2. Sampling efficiencies calculated from the model (solid lines) and experimental results.**

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# APPENDIX I

**Flow chart of various channels in the programme based on Labtech Notebook that was written to manipulate data acquired from the data acquisition system described in Section 3.3.2.5. Also given are the calibration curves for each of the sensors used in the data acquisition system**

**The programme**

The programme is based on Labtech Notebook. It is a series of channels each one carrying out a particular function or calculation. A flow chart of the various channels in the programme showing how they relate to each other is given on the next page. Channels 1 to 5 and 8 and 26 are acquisition channels that accept a voltage from their respective sensors every two seconds. These voltages are then converted to their respective parameters according to the calibrations. $T_{ppm}$ (channel 3) is converted from °C to Kelvin (Channel 12) and the density of air at this temperature is then calculated (channel 13). $\Delta p$ (channel 4) measured as a voltage is converted to $\Delta p$ in mm $H_2O$ and then $\Delta p$ in Pascals (channel 16). Channel 18 calculates the flow rate through the generator ($Qm^3h^{-1}$ ) according to the following equation :

$$Q = k\frac{\sqrt{\Delta p}}{\sqrt{\rho_{air}}} \qquad \text{Eq. (1)}$$

where k = a constant,

$\Delta p$ = pressure differential measured at position C

$\rho_{air}$ = density of air at $T_{ppm}$ ($T_{ppm}$ expressed in Kelvin)

Channel 19 normalises the calculated Q value to Q at T= 273K

Channels 6 and 7 are based on the internal clock of the PC and measure the time. Channel 23 measures the response of the FID. Block averages for each parameter are made every 30 seconds. The equations of the calibration curves take the form y = mx + c. Labtech Notebook calculates the same line as y = m (x + c/m). This is why the c values in the flowchart are different from those in the calibration curves.

**Key to Sensors**

$T_{ppm}$ is the sensor measuring the temperature at Point C of Fig 3.1

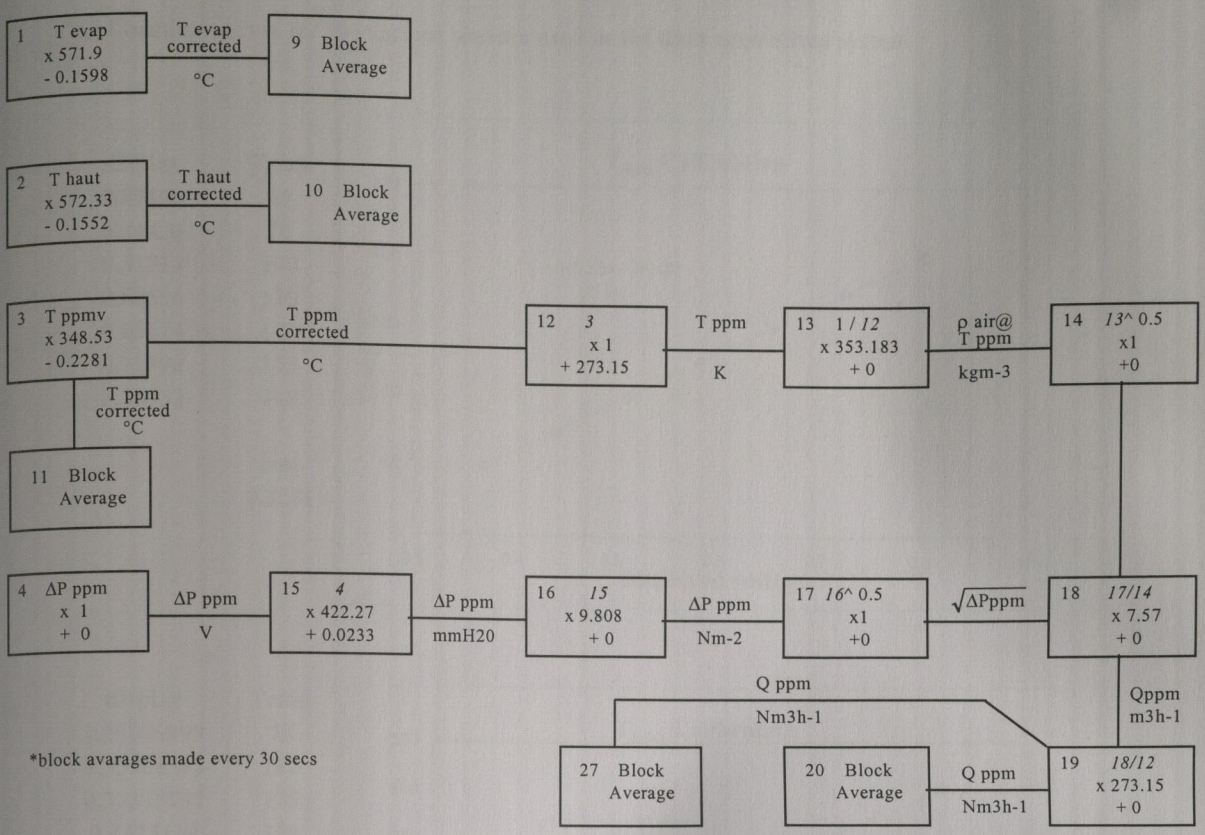
$T_{evap}$ is the sensor measuring the temperature at Point A of Fig 3.1

$T_{haut}$ is the sensor measuring the temperature at Point B of Fig 3.1

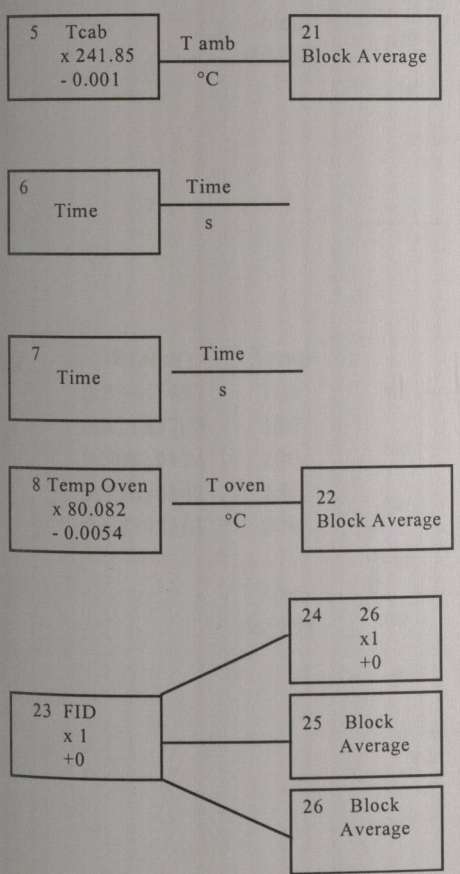
$T_{oven}$ is the sensor measuring the temperature of the adsorbent tube housing

$T_{cab}$ is the sensor measuring the ambient temperature

$\Delta p$ : the pressure differential across the Siemens manometer




*block avarages made every 30 secs



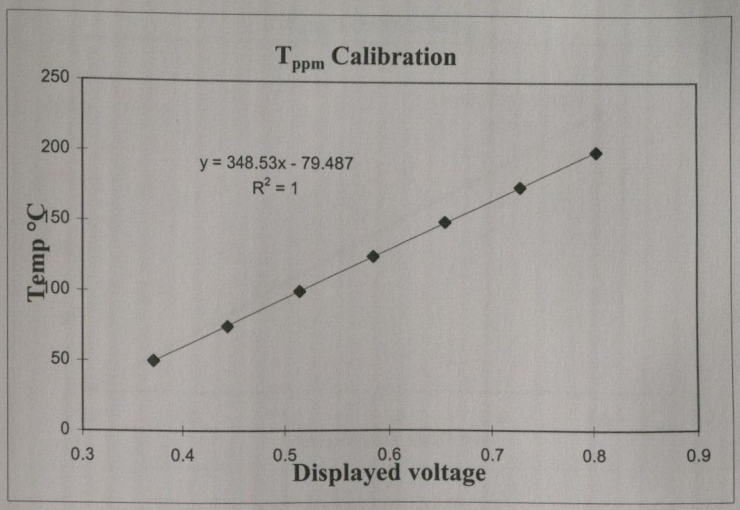

| Output | Parameter | Channel |
|---|---|---|
| LPT1 | FID | 26 |
| | Time | 6 |
| | T Oven | 22 |
| | T Cab | 21 |
| | T Haut | 10 |
| | T Evap | 9 |
| | T PPM | 11 |
| | QPPM | 20 |
| Disk | FID | 25 |
| | Time | 7 |
| | QPPM | 27 |

**Flowchart of the various channels incorporated into the programme.**

**Calibration curves for the various sensors used in the data acquisition system**

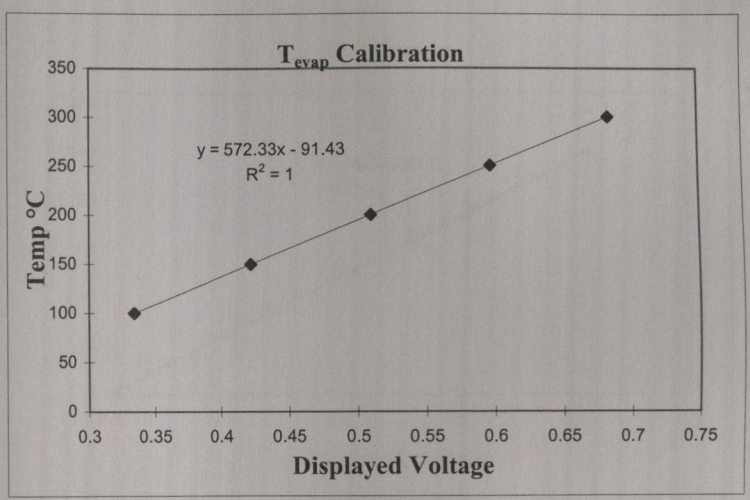
$T_{ppmv}$

| display | Temp |
|---|---|
| 0.37150 | 50 |
| 0.44434 | 75 |
| 0.51514 | 100 |
| 0.58594 | 125 |
| 0.65674 | 150 |
| 0.72998 | 175 |
| 0.80332 | 200 |
| | c/m |
| | 0.2281 |



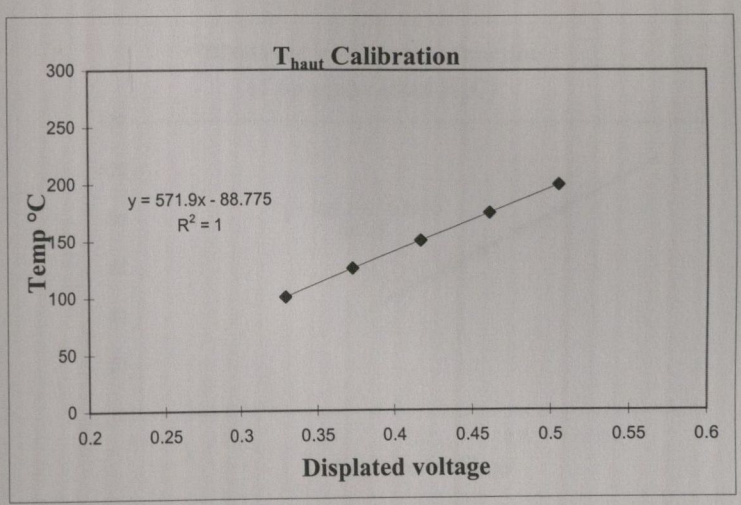

$T_{haut}$

| display | Temp |
|---|---|
| 0.28636999 | 75 |
| 0.33008393 | 100 |
| 0.37379787 | 125 |
| 0.4175118 | 150 |
| 0.46122574 | 175 |
| 0.50493967 | 200 |
| | c/m |
| | 0.1552 |



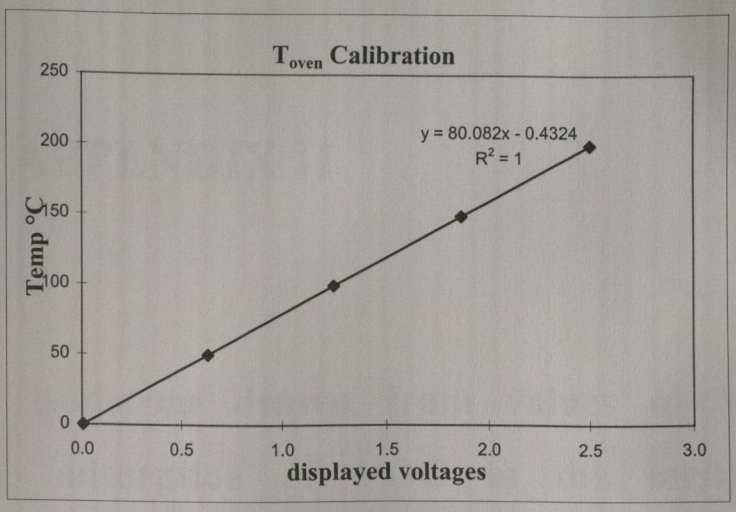

$T_{evap}$

| display | Temp |
|---|---|
| 0.33447487 | 100 |
| 0.42183705 | 150 |
| 0.50919924 | 200 |
| 0.59656142 | 250 |
| 0.68392361 | 300 |
| | c/m |
| | 0.1598 |



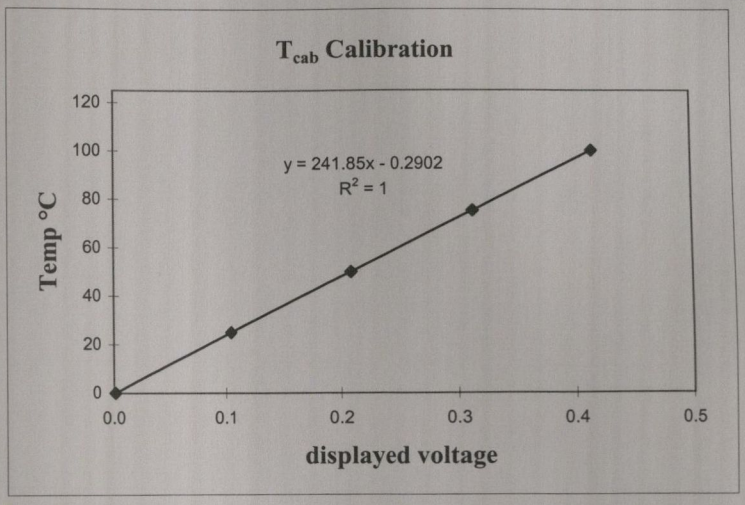
$T_{oven}$

| display | Temp |
|---|---|
| 0.0054 | 0 |
| 0.6298 | 50 |
| 1.2541 | 100 |
| 1.8785 | 150 |
| 2.5028 | 200 |
| | c/m |
| | 0.00540 |



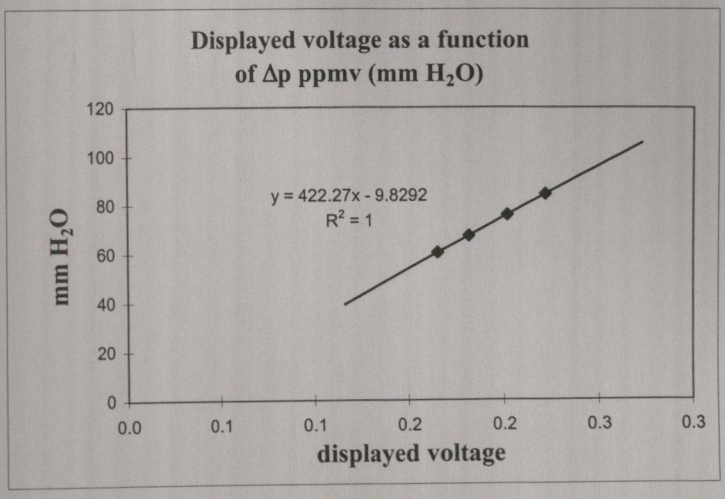

$T_{cab}$

| display | Temp |
|---|---|
| 0.00120 | 0 |
| 0.10457 | 25 |
| 0.20794 | 50 |
| 0.31131 | 75 |
| 0.41468 | 100 |
| | c/m |
| | 0.00120 |



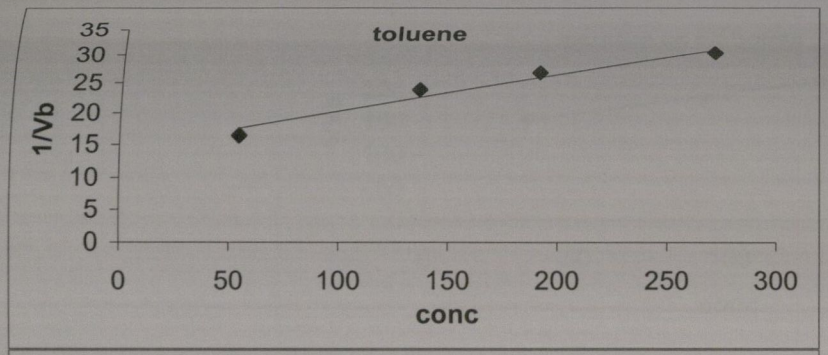

Δp Calibration

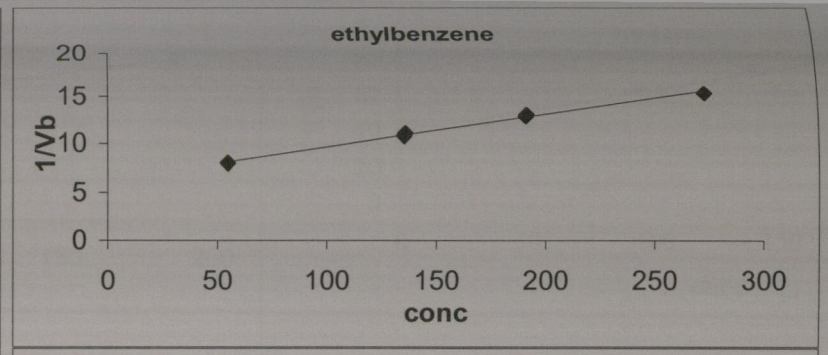
| displayed | mm H2O |
|---|---|
| 0.1661 | 60.3 |
| 0.1824 | 67.2 |
| 0.2028 | 75.8 |
| 0.2229 | 84.3 |
| | c/m |
| | 0.02328 |



# APPENDIX II

**Linear Langmuir isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the $mg/m^3$ concentration range on Carbotrap-B at 298K**


toluene
1/Vb
35
30
25
20
15
10
5
0
0
50
100
150
200
250
300
conc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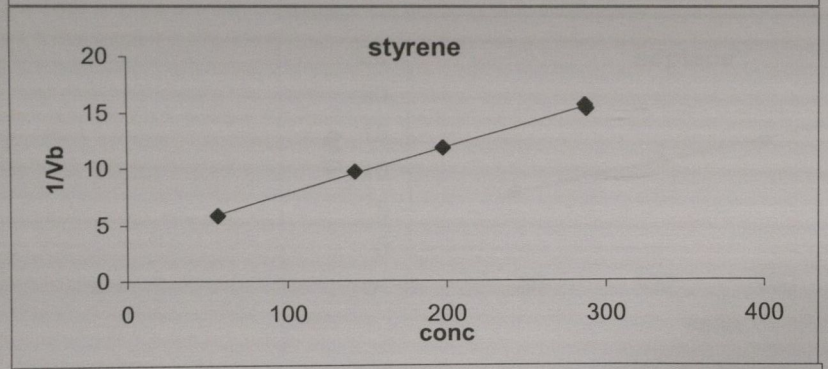
1/Vb
20
15
10
5
0
0
50
100
150
200
250
300
conc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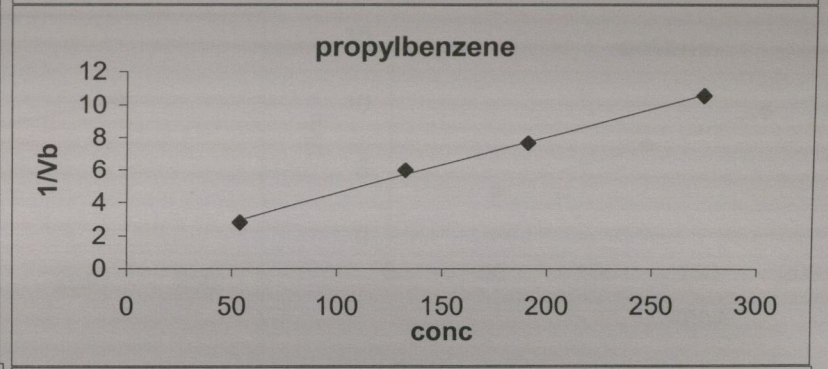
1/Vb
20
15
10
5
0
0
100
200
300
400
conc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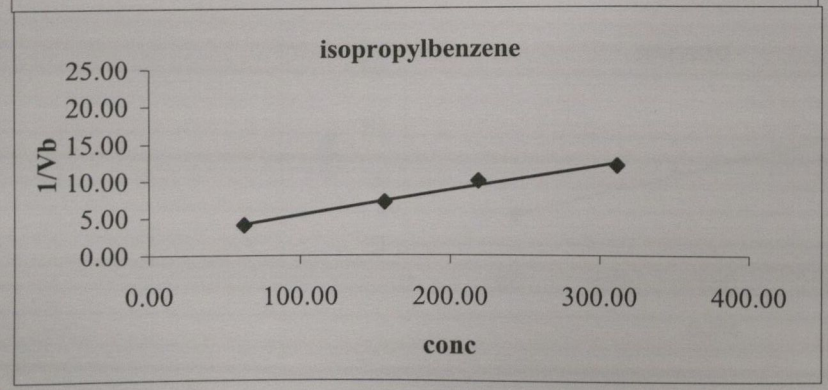
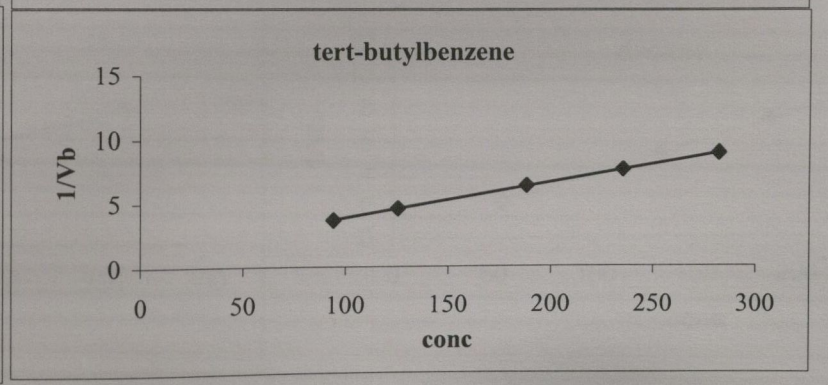
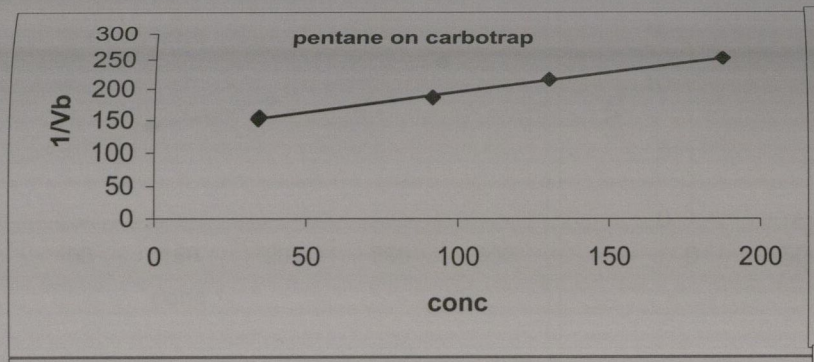
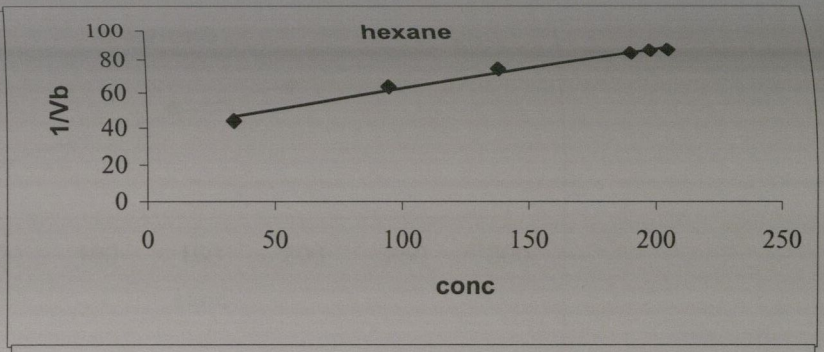
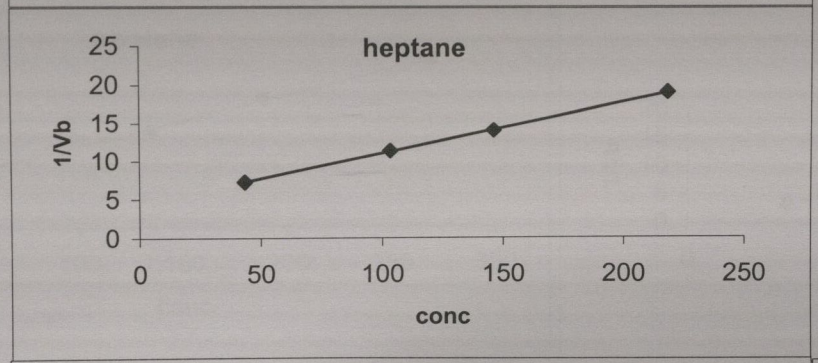
1/Vb
12
10
8
6
4
2
0
0
50
100
150
200
250
300
conc

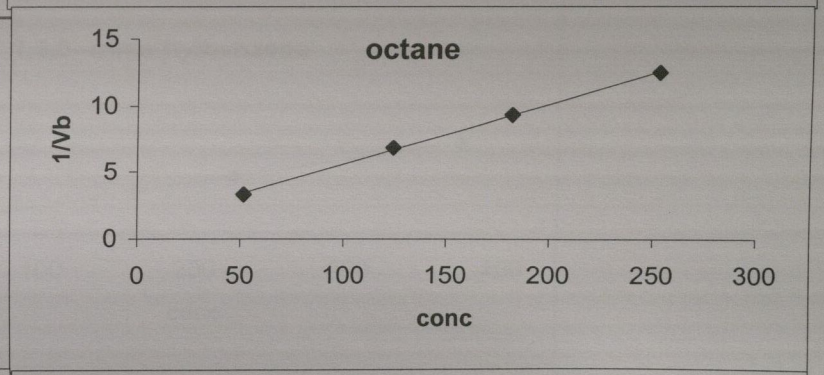

isopropylbenzene
1/Vb
25.00
20.00
15.00
10.00
5.00
0.00
0.00
100.00
200.00
300.00
400.00
conc

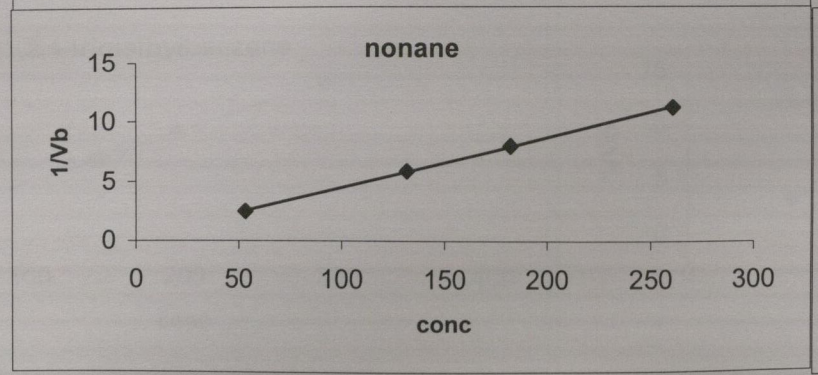

tert-butylbenzene
1/Vb
15
10
5
0
0
50
100
150
200
250
300
conc

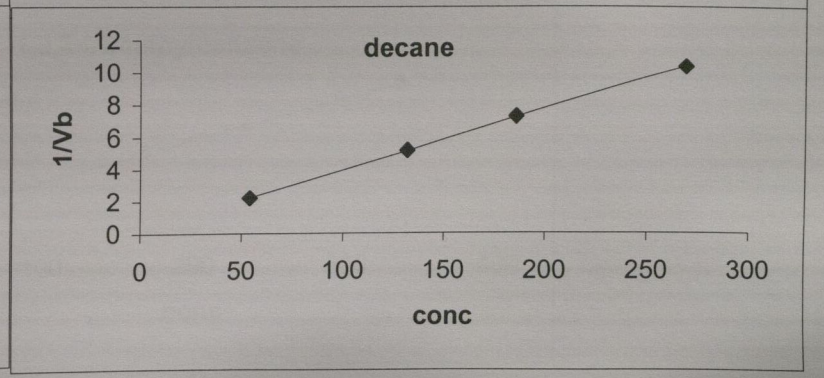

pentane on carbotrap
1/Vb
300
250
200
150
100
50
0
0
50
100
150
200
conc

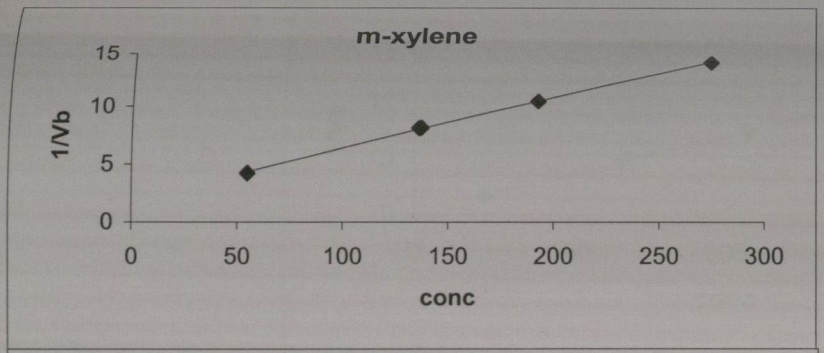

hexane
1/Vb
100
80
60
40
20
0
0
50
100
150
200
250
conc

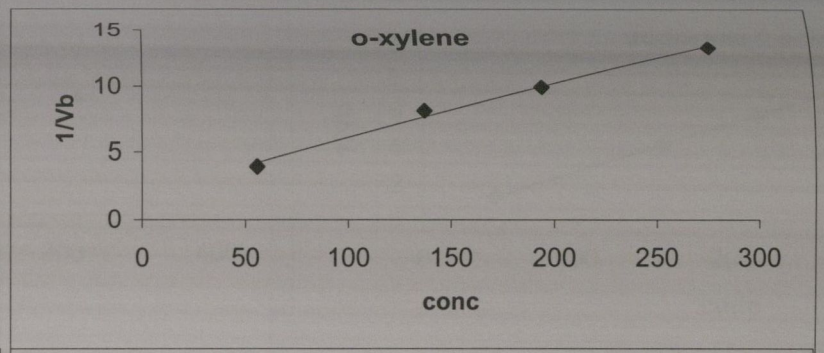

heptane
1/Vb
25
20
15
10
5
0
0
50
100
150
200
250
conc

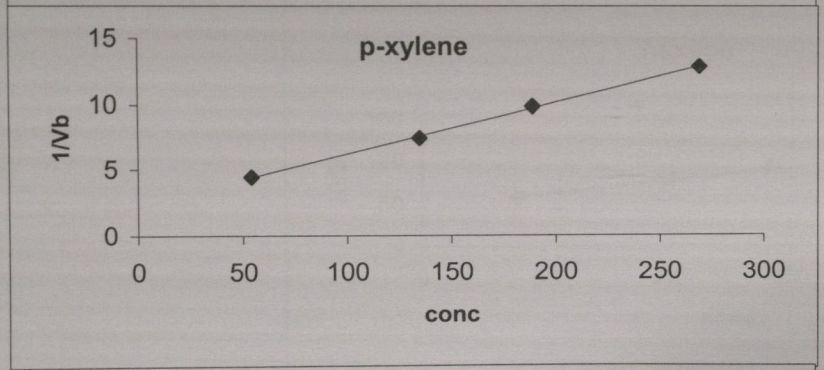

octane
1/Vb
15
10
5
0
0
50
100
150
200
250
300
conc

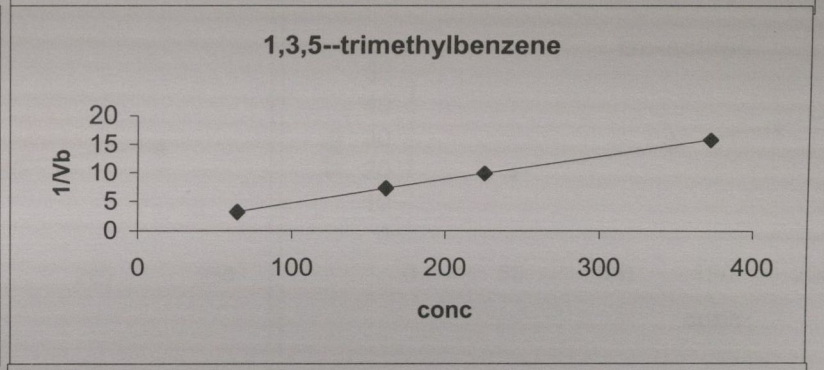

nonane
1/Vb
15
10
5
0
0
50
100
150
200
250
300
conc

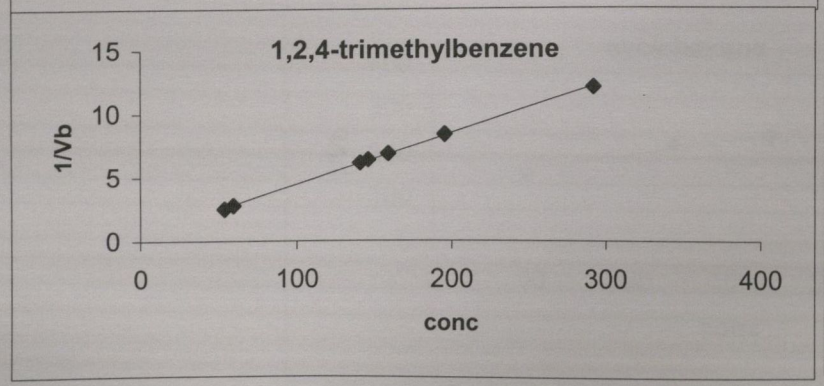

decane
1/Vb
12
10
8
6
4
2
0
0
50
100
150
200
250
300
conc

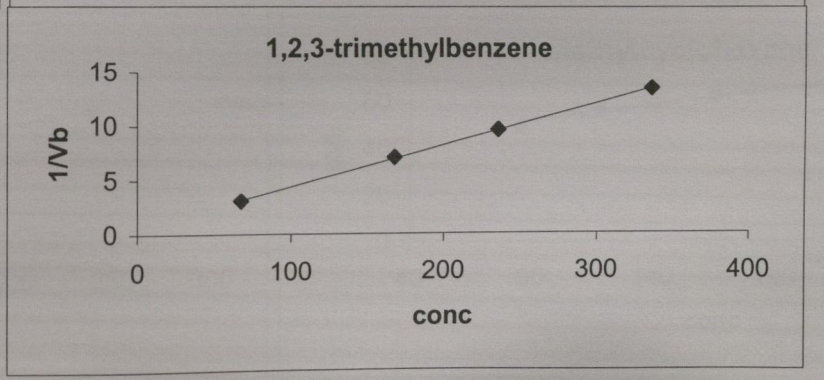

m-xylene
1/Vb
15
10
5
0
0
50
100
150
200
250
300
conc

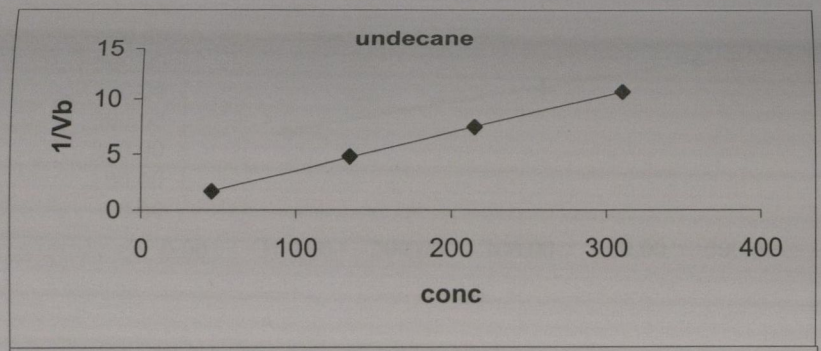

o-xylene
1/Vb
15
10
5
0
0
50
100
150
200
250
300
conc

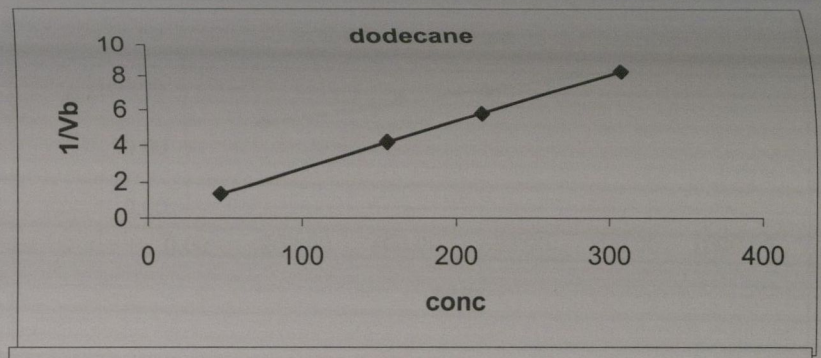

p-xylene
1/Vb
15
10
5
0
0
50
100
150
200
250
300
conc

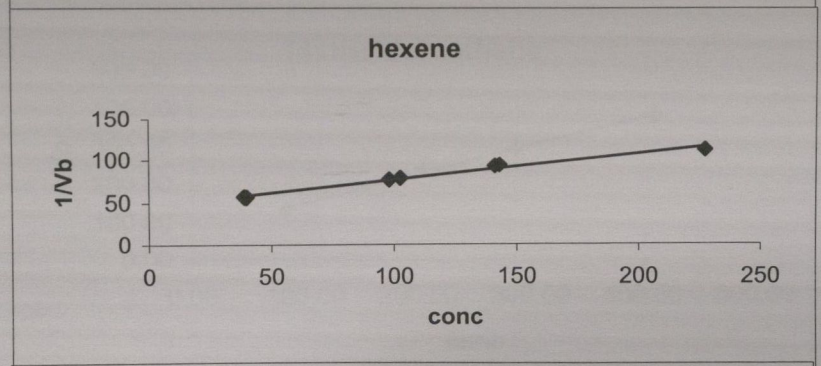

1,3,5--trimethylbenzene
1/Vb
20
15
10
5
0
0
100
200
300
400
conc

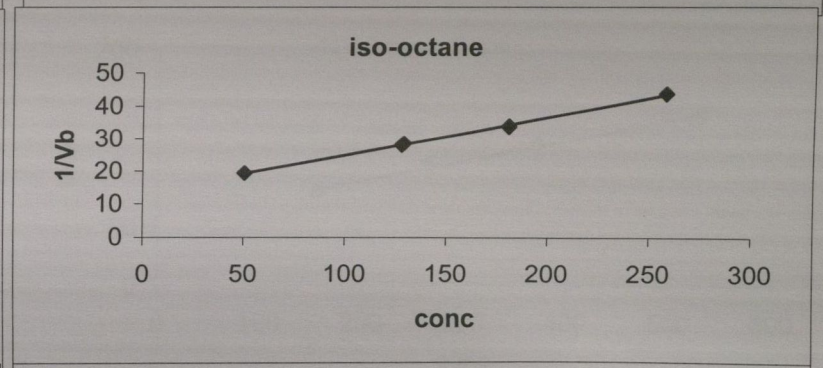

1,2,4-trimethylbenzene
1/Vb
15
10
5
0
0
100
200
300
400
conc

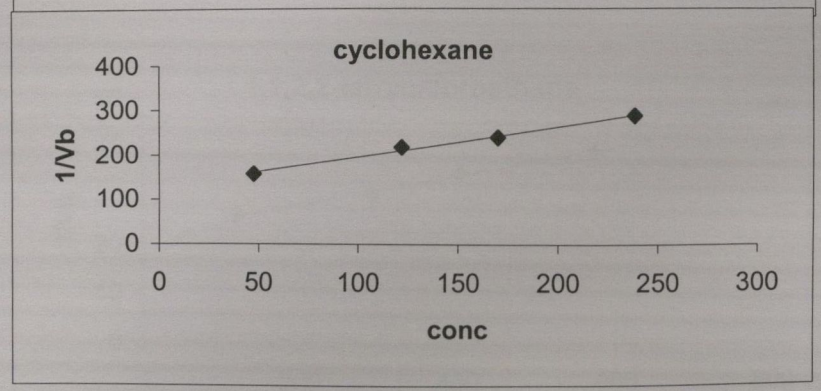

1,2,3-trimethylbenzene
1/Vb
15
10
5
0
0
100
200
300
400
conc

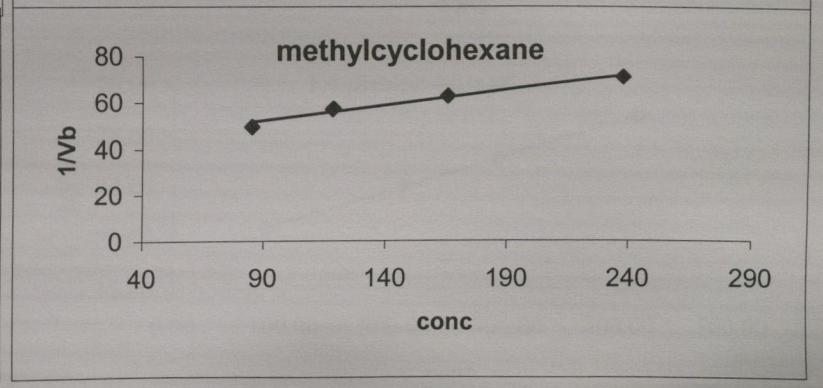

undecane
1/Vb
15
10
5
0
0
100
200
300
400
conc

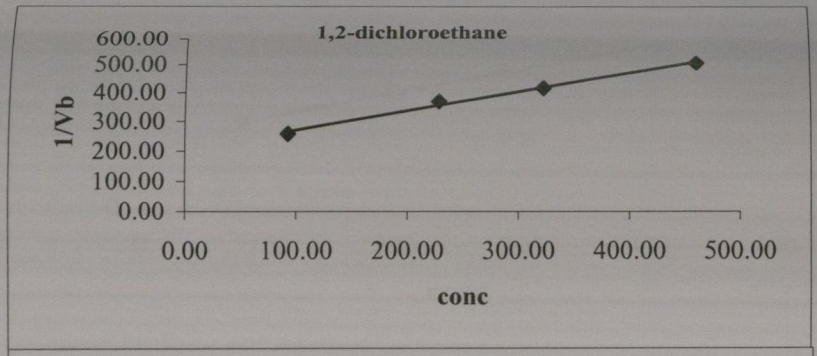

dodecane
1/Vb
10
8
6
4
2
0
0
100
200
300
400
conc

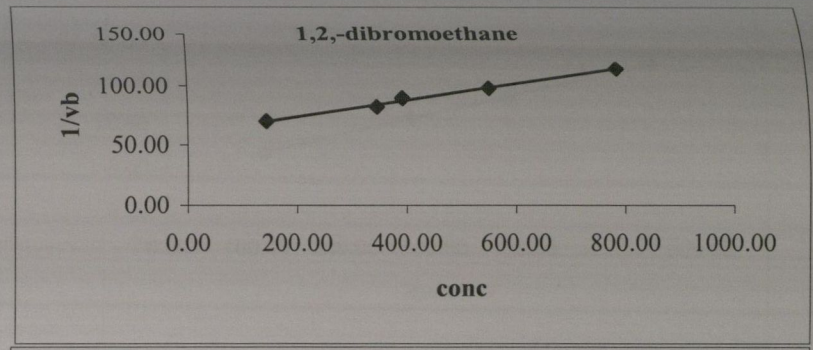

hexene
1/Vb
150
100
50
0
0
50
100
150
200
250
conc

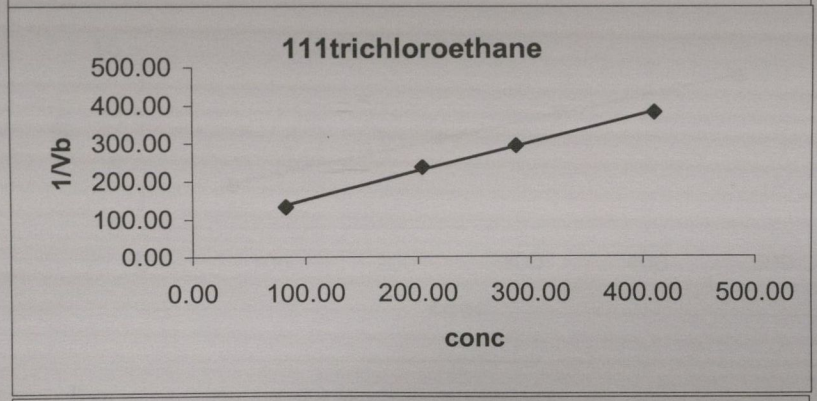

iso-octane
1/Vb
50
40
30
20
10
0
0
50
100
150
200
250
300
conc

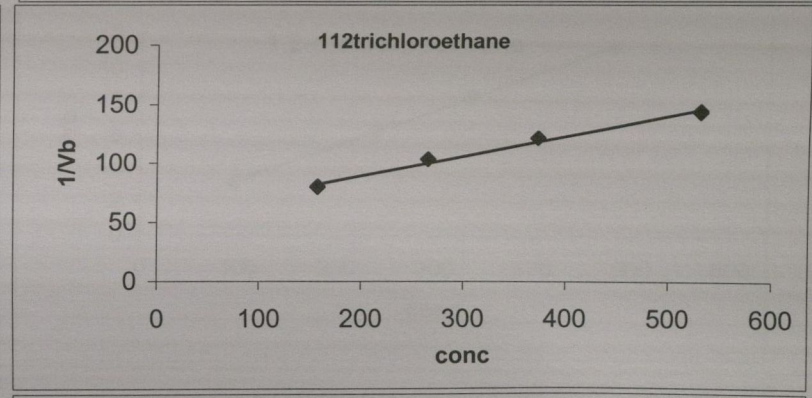

cyclohexane
1/Vb
400
300
200
100
0
0
50
100
150
200
250
300
conc

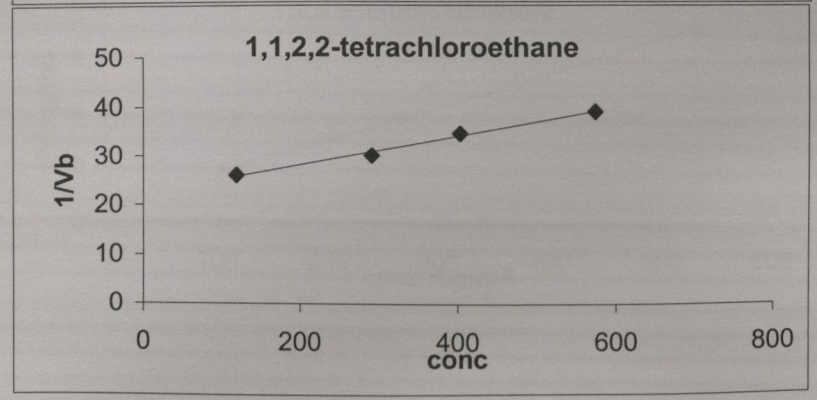

methylcyclohexane
1/Vb
80
60
40
20
0
40
90
140
190
240
290
conc

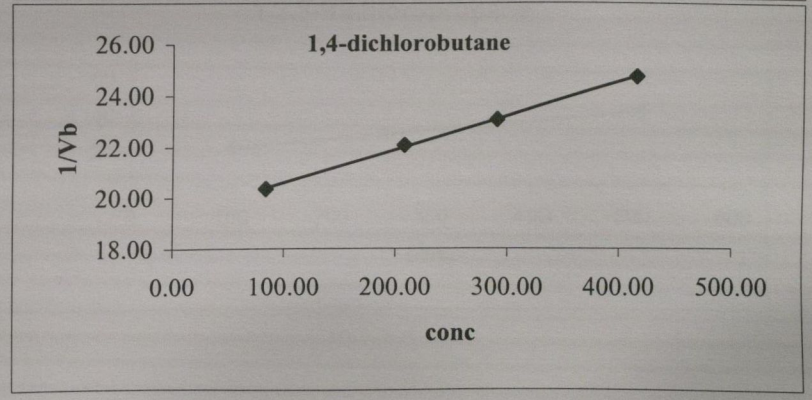

1,2-dichloroethane
1/Vb
600.00
500.00
400.00
300.00
200.00
100.00
0.00
0.00
100.00
200.00
300.00
400.00
500.00
conc

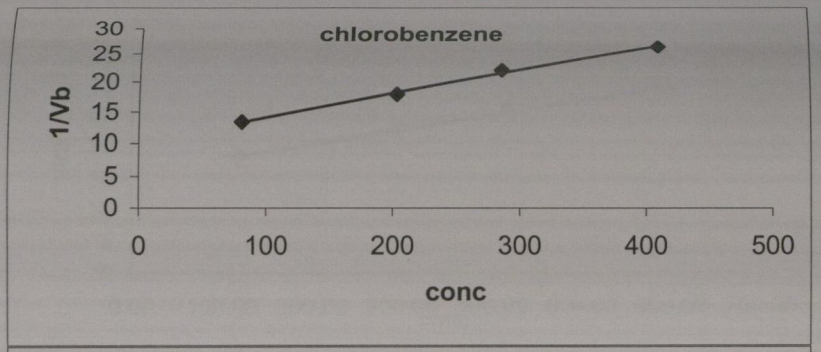

1,2,-dibromoethane
1/vb
150.00
100.00
50.00
0.00
0.00
200.00
400.00
600.00
800.00
1000.00
conc

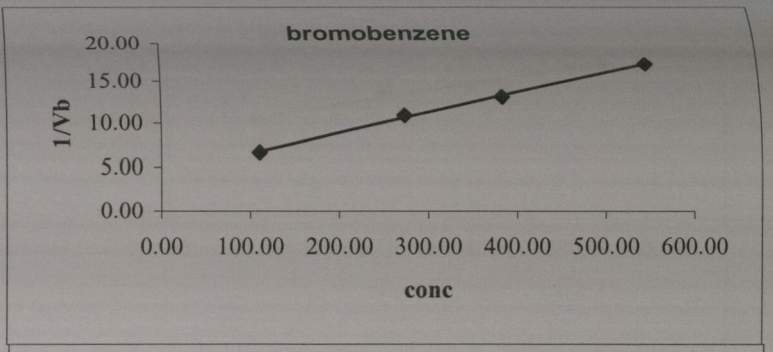

111trichloroethane
1/Vb
500.00
400.00
300.00
200.00
100.00
0.00
0.00
100.00
200.00
300.00
400.00
500.00
conc

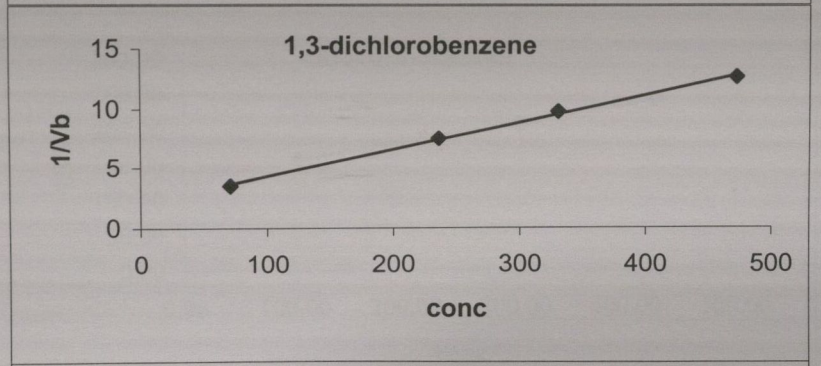

112trichloroethane
1/Vb
200
150
100
50
0
0
100
200
300
400
500
600
conc

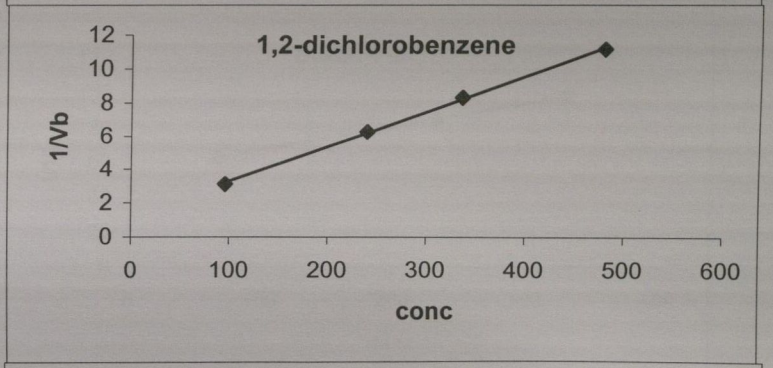

1,1,2,2-tetrachloroethane
1/Vb
50
40
30
20
10
0
0
200
400
600
800
conc

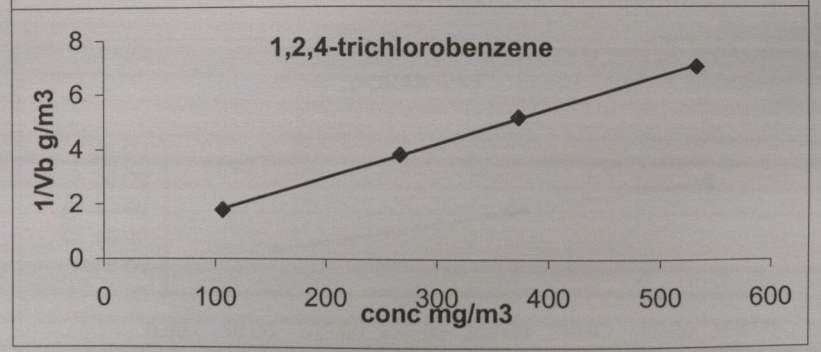

1,4-dichlorobutane
1/Vb
26.00
24.00
22.00
20.00
18.00
0.00
100.00
200.00
300.00
400.00
500.00
conc

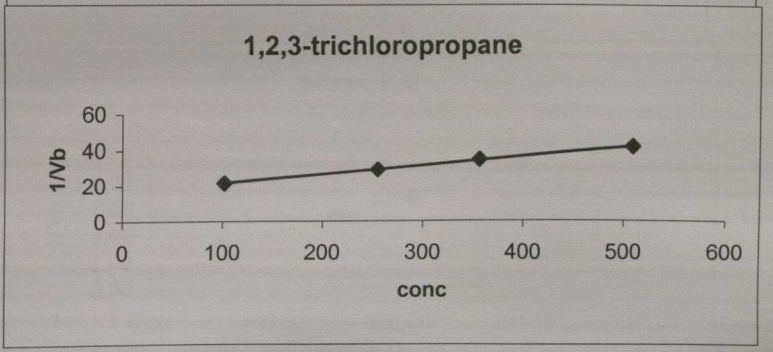

chlorobenzene
1/Vb
30
25
20
15
10
5
0
0
100
200
300
400
500
conc

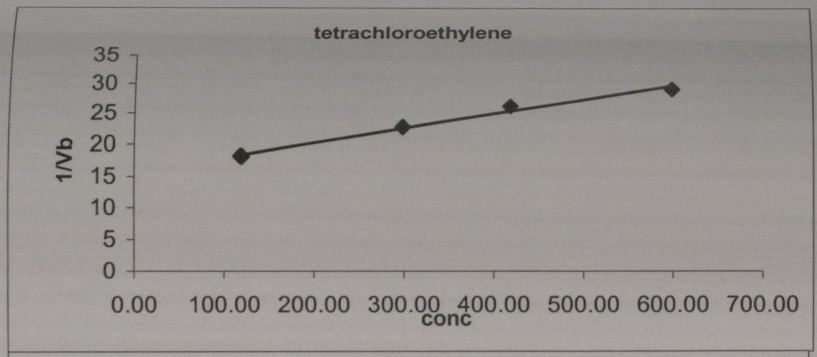

bromobenzene
1/Vb
20.00
15.00
10.00
5.00
0.00
0.00
100.00
200.00
300.00
400.00
500.00
600.00
conc

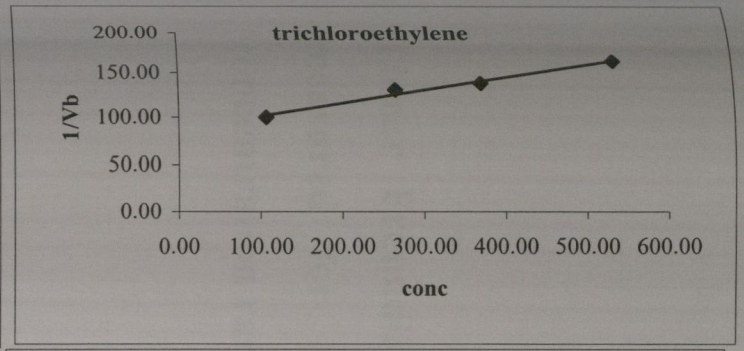

1,3-dichlorobenzene
1/Vb
15
10
5
0
0
100
200
300
400
500
conc

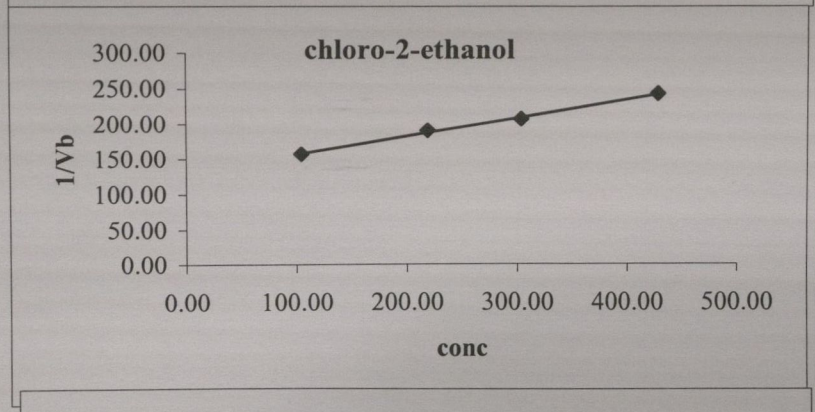

1,2-dichlorobenzene
1/Vb
12
10
8
6
4
2
0
0
100
200
300
400
500
600
conc

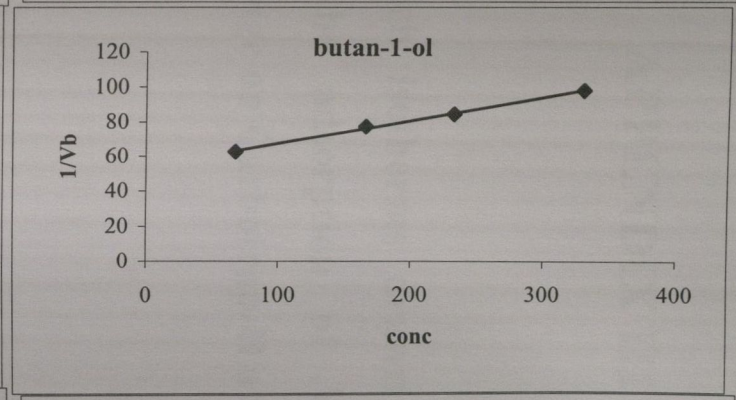

1,2,4-trichlorobenzene
1/Vb g/m3
8
6
4
2
0
0
100
200
300
400
500
600
conc mg/m3

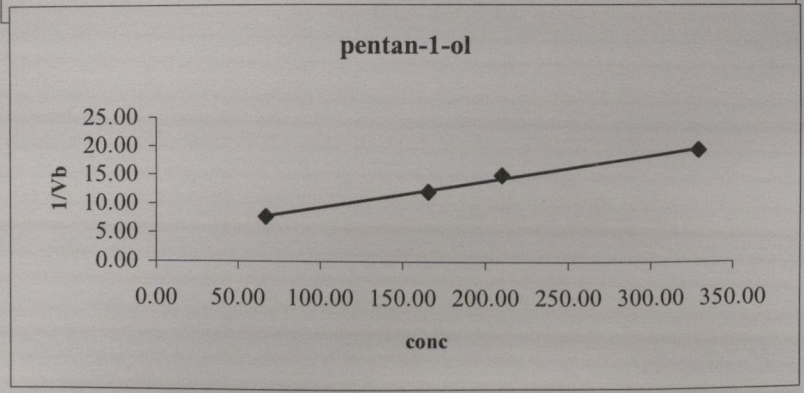

1,2,3-trichloropropane
1/Vb
60
40
20
0
0
100
200
300
400
500
600
conc

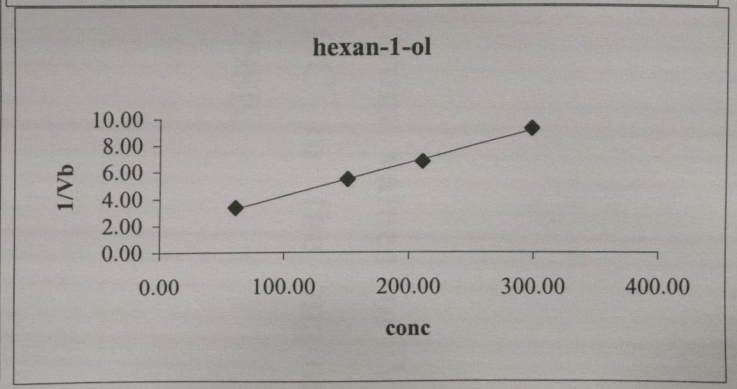

tetrachloroethylene
1/Vb
35
30
25
20
15
10
5
0
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
conc


trichloroethylene
1/Vb
200.00
150.00
100.00
50.00
0.00
0.00
100.00
200.00
300.00
400.00
500.00
600.00
conc


chloro-2-ethanol
1/Vb
300.00
250.00
200.00
150.00
100.00
50.00
0.00
0.00
100.00
200.00
300.00
400.00
500.00
conc

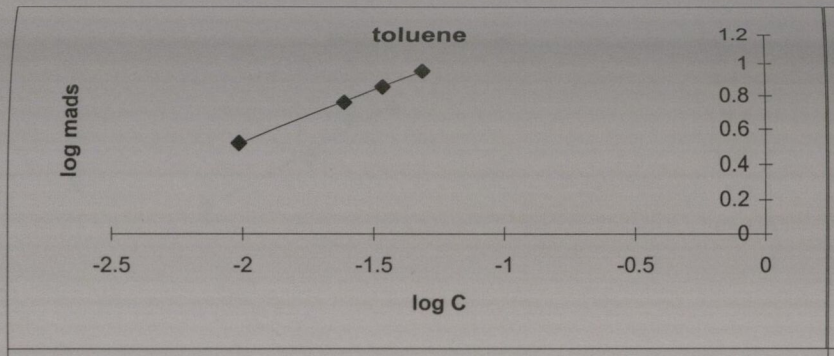

butan-1-ol
1/Vb
120
100
80
60
40
20
0
0
100
200
300
400
conc

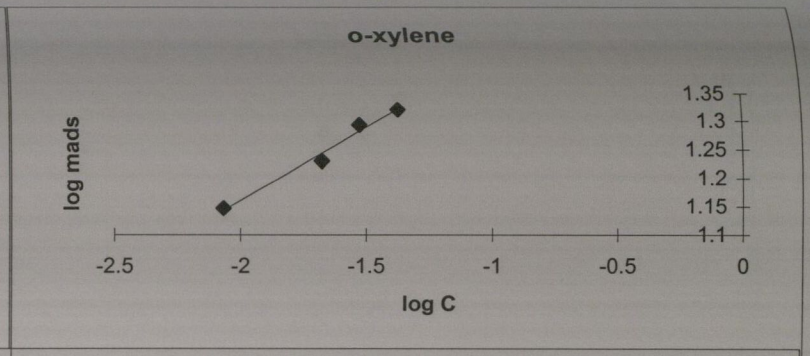

pentan-1-ol
1/Vb
25.00
20.00
15.00
10.00
5.00
0.00
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
conc

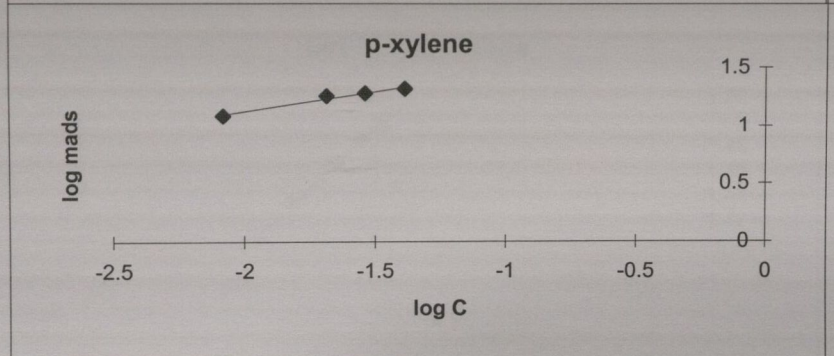

hexan-1-ol
1/Vb
10.00
8.00
6.00
4.00
2.00
0.00
0.00
100.00
200.00
300.00
400.00
conc

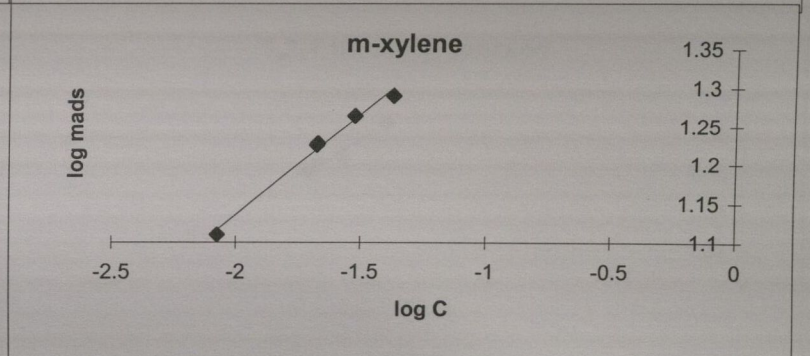
# APPENDIX III

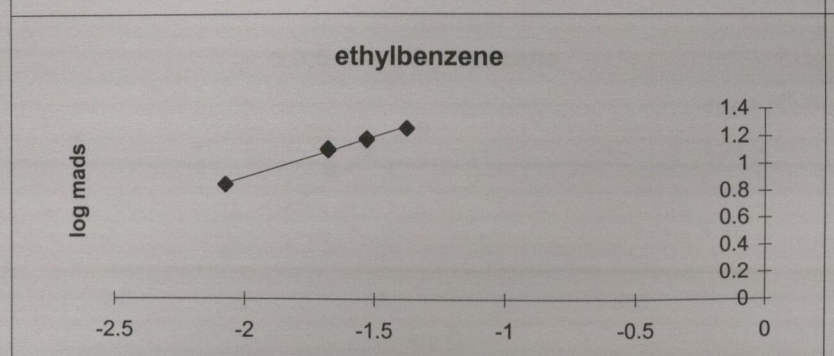
**Linear Freundlich isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the $mg/m^3$ concentration range on Carbotrap-B at 298K**

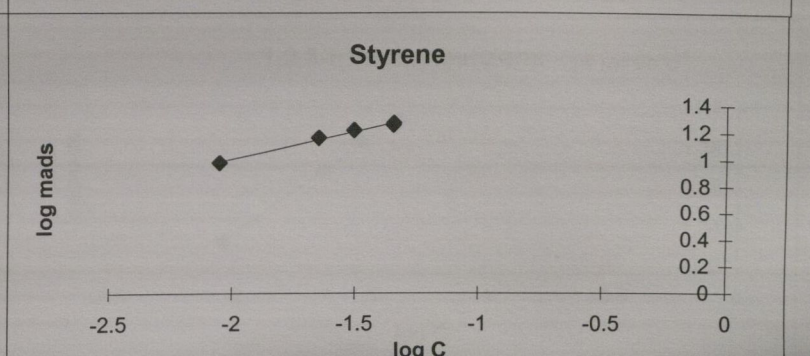

toluene
log mads
log C
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

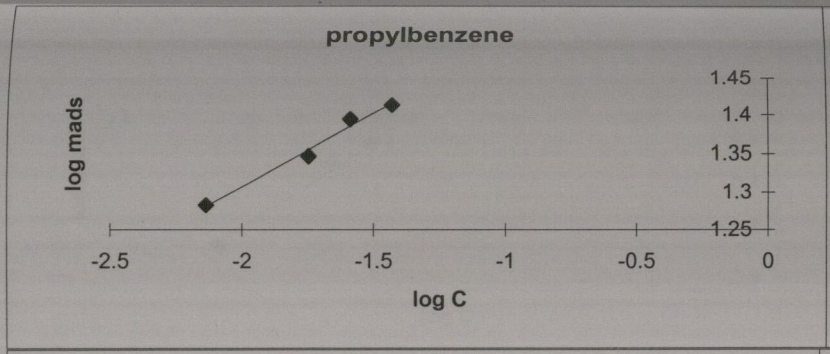

o-xylene
log mads
log C
1.35
1.3
1.25
1.2
1.15
1.1
-2.5
-2
-1.5
-1
-0.5
0

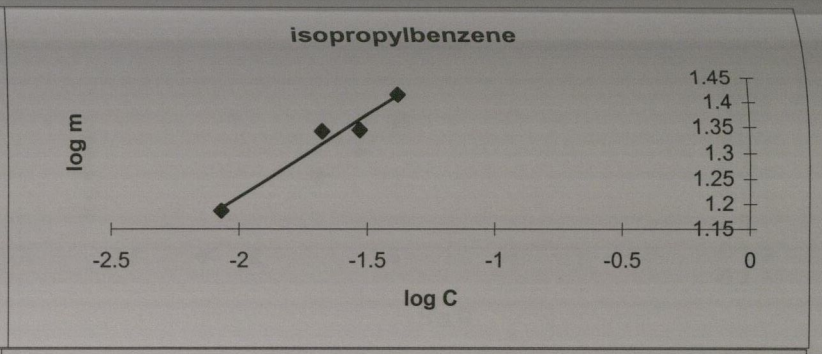

p-xylene
log mads
log C
1.5
1
0.5
0
-2.5
-2
-1.5
-1
-0.5
0

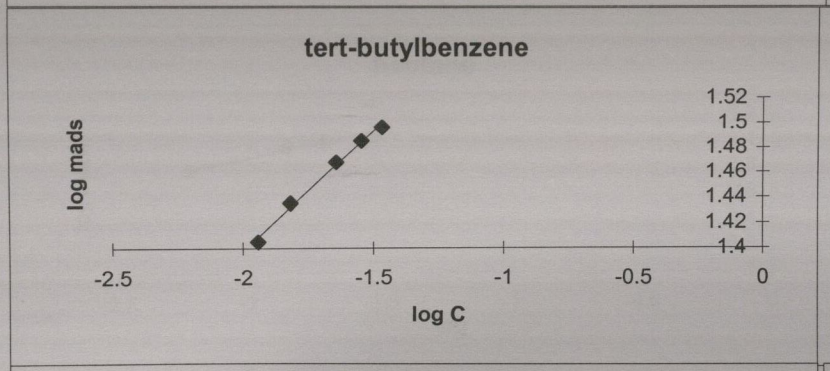

m-xylene
log mads
log C
1.35
1.3
1.25
1.2
1.15
1.1
-2.5
-2
-1.5
-1
-0.5
0

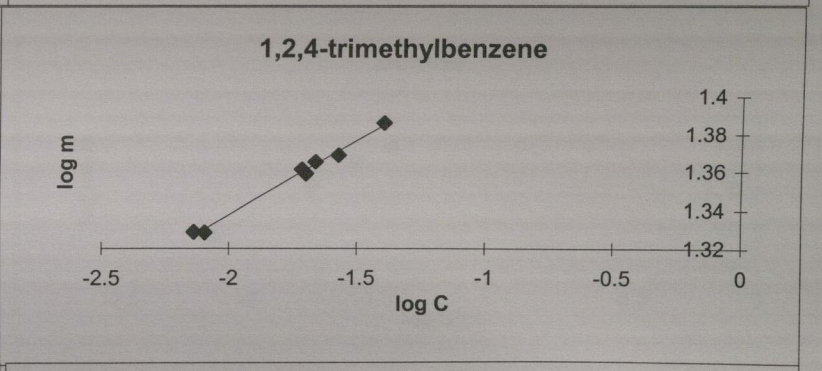

ethylbenzene
log mads
log C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

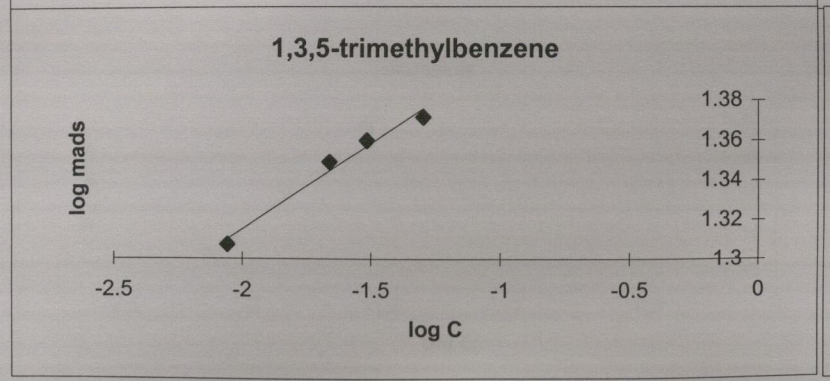

Styrene
log mads
log C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

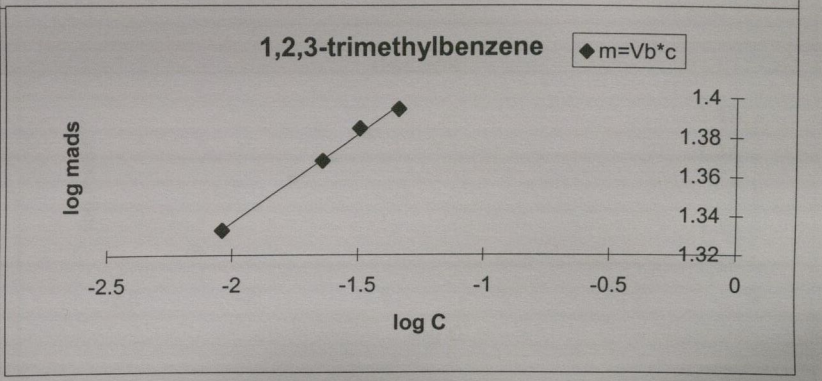

propylbenzene
log mads
1.45
1.4
1.35
1.3
1.25
-2.5
-2
-1.5
-1
-0.5
0
log C

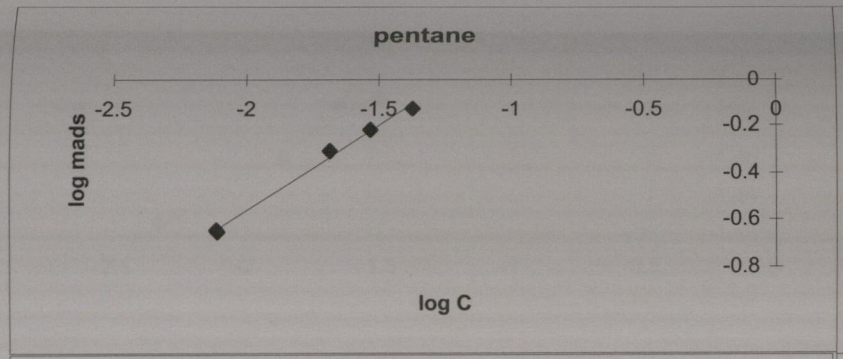

isopropylbenzene
log m
1.45
1.4
1.35
1.3
1.25
1.2
1.15
-2.5
-2
-1.5
-1
-0.5
0
log C

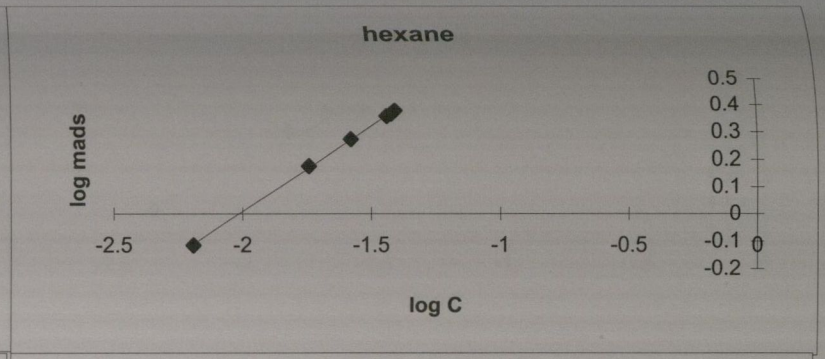

tert-butylbenzene
log mads
1.52
1.5
1.48
1.46
1.44
1.42
1.4
-2.5
-2
-1.5
-1
-0.5
0
log C

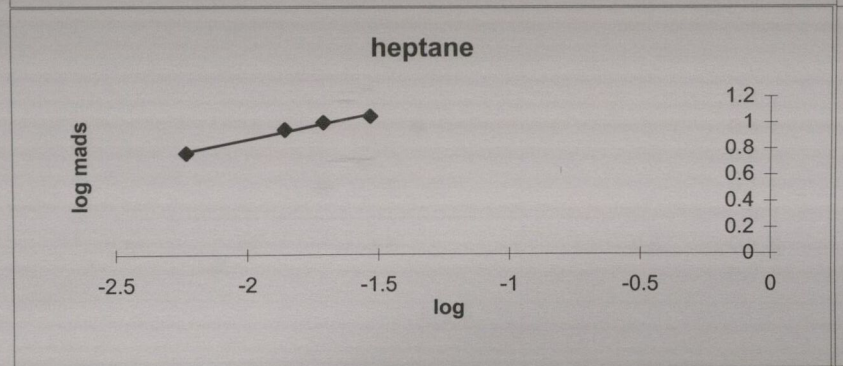

1,2,4-trimethylbenzene
log m
1.4
1.38
1.36
1.34
1.32
-2.5
-2
-1.5
-1
-0.5
0
log C

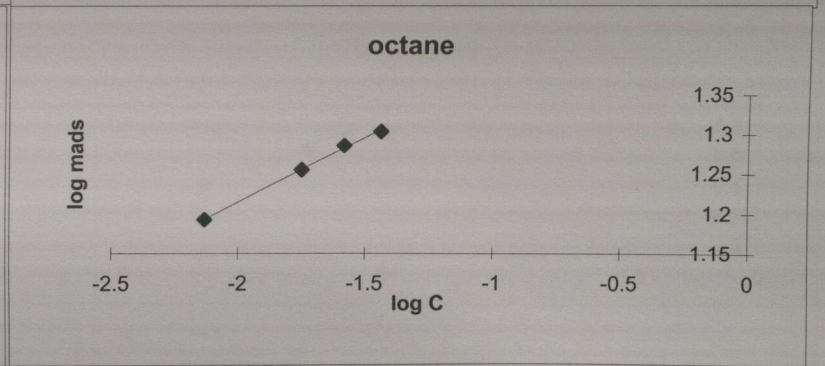

1,3,5-trimethylbenzene
log mads
1.38
1.36
1.34
1.32
1.3
-2.5
-2
-1.5
-1
-0.5
0
log C

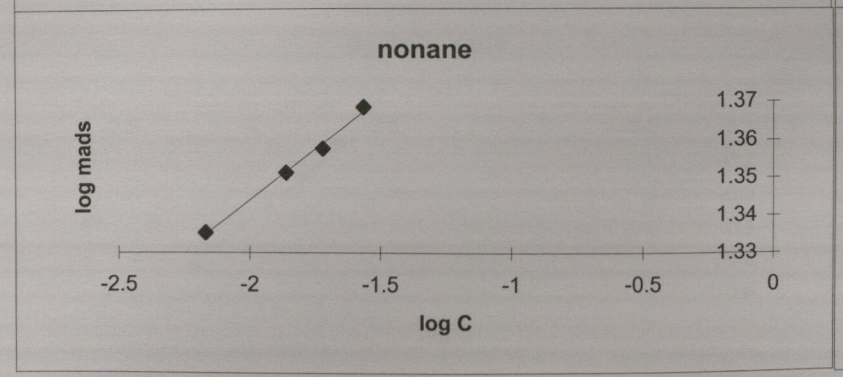

1,2,3-trimethylbenzene
m=Vb*c
log mads
1.4
1.38
1.36
1.34
1.32
-2.5
-2
-1.5
-1
-0.5
0
log C

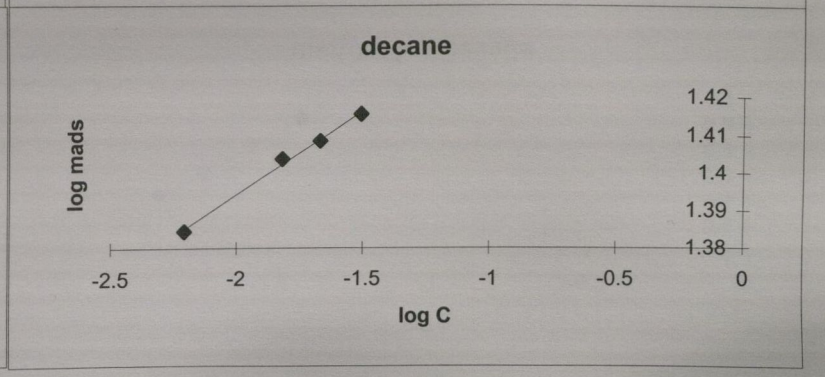

pentane
log mads
log C
-2.5
-2
-1.5
-1
-0.5
0
-0.2
-0.4
-0.6
-0.8

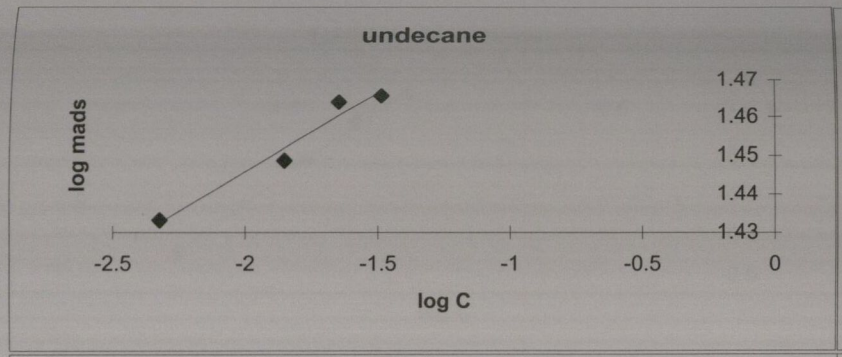

hexane
log mads
log C
-2.5
-2
-1.5
-1
-0.5
0
0.5
0.4
0.3
0.2
0.1
-0.1
-0.2

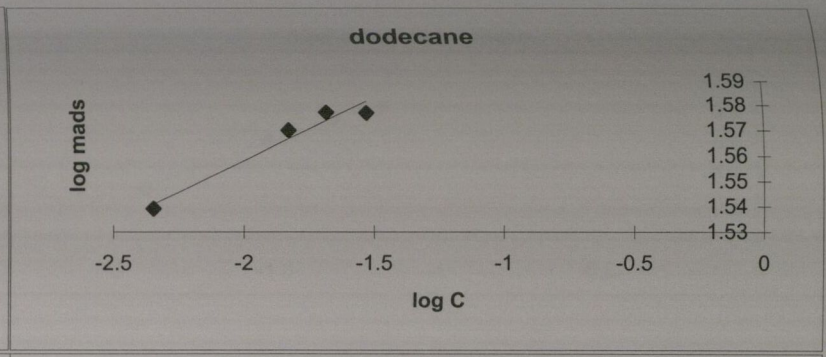

heptane
log mads
log
-2.5
-2
-1.5
-1
-0.5
0
1.2
1
0.8
0.6
0.4
0.2

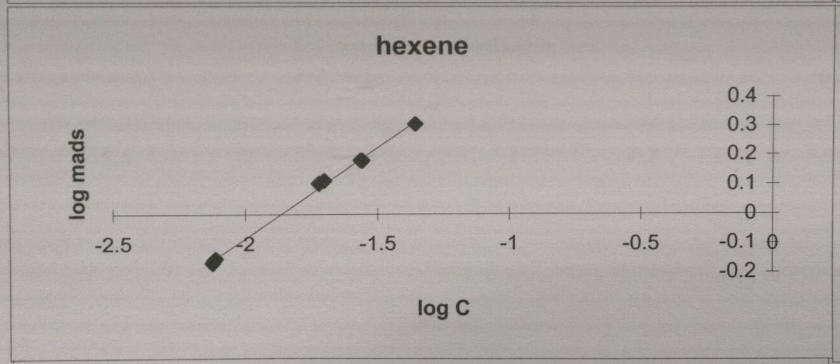

octane
log mads
log C
-2.5
-2
-1.5
-1
-0.5
0
1.35
1.3
1.25
1.2
1.15

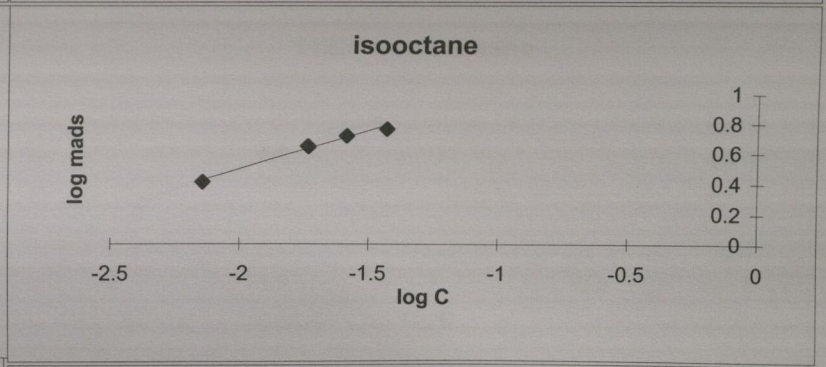

nonane
log mads
log C
-2.5
-2
-1.5
-1
-0.5
0
1.37
1.36
1.35
1.34
1.33

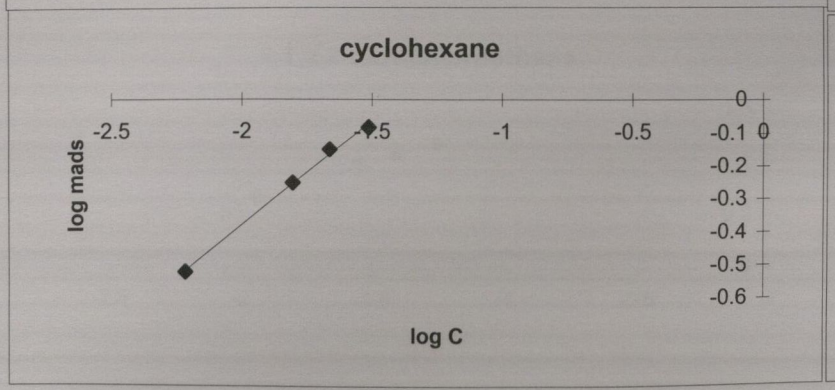

decane
log mads
log C
-2.5
-2
-1.5
-1
-0.5
0
1.42
1.41
1.4
1.39
1.38

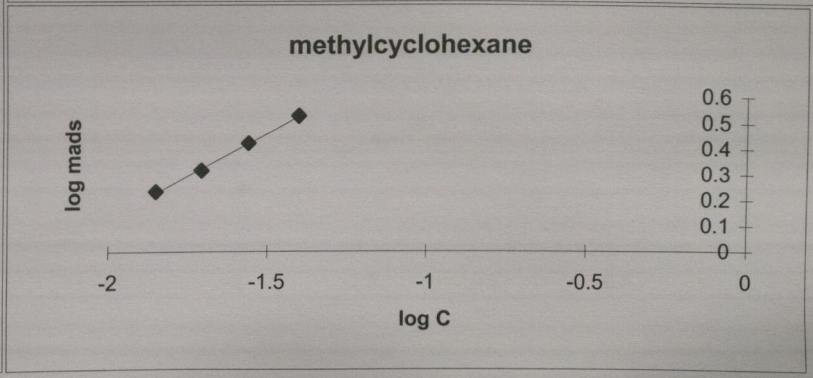

undecane
log mads
1.47
1.46
1.45
1.44
1.43
-2.5
-2
-1.5
-1
-0.5
0
log C

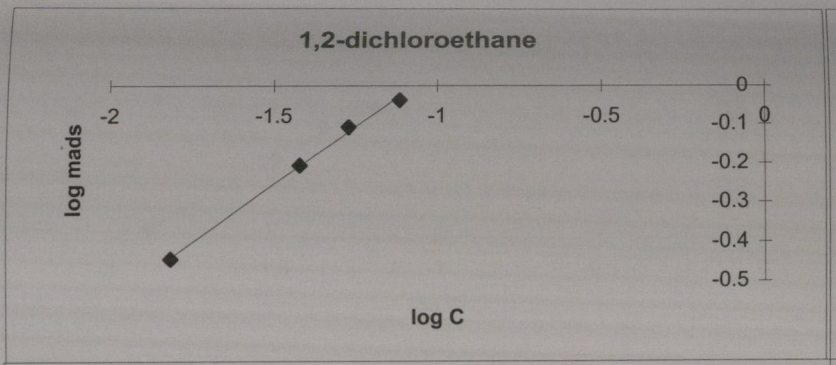

dodecane
log mads
1.59
1.58
1.57
1.56
1.55
1.54
1.53
-2.5
-2
-1.5
-1
-0.5
0
log C

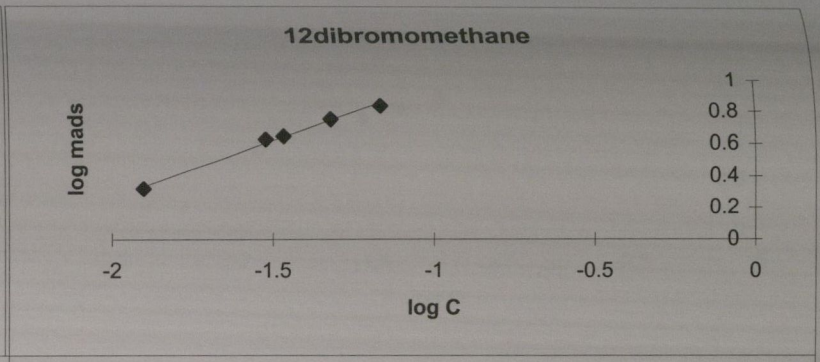

hexene
log mads
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-2.5
-2
-1.5
-1
-0.5
0
log C

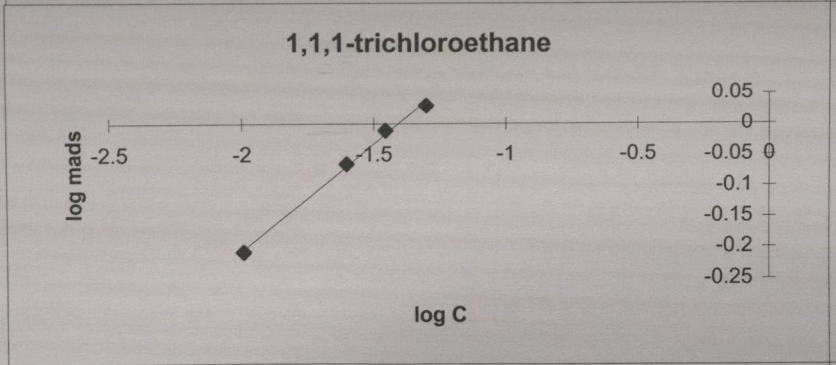

isooctane
log mads
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0
log C

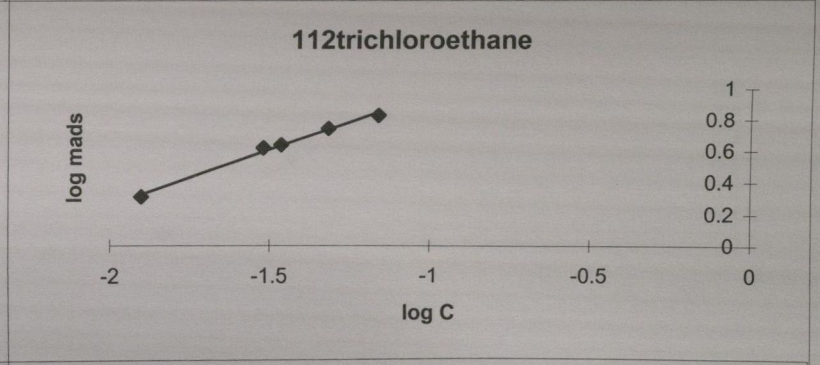

cyclohexane
log mads
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-2.5
-2
-1.5
-1
-0.5
0
log C

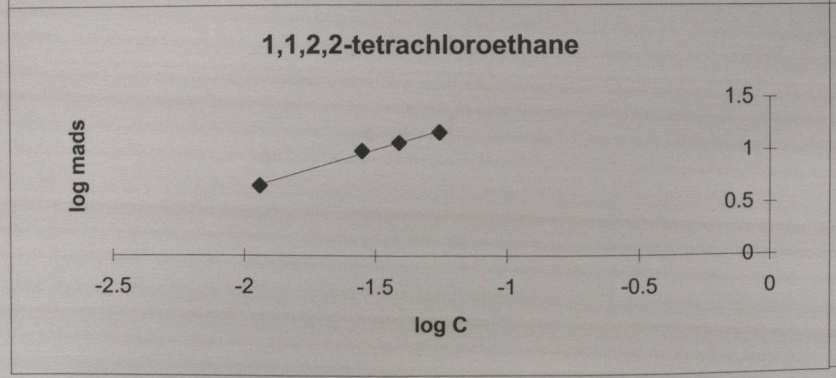

methylcyclohexane
log mads
0.6
0.5
0.4
0.3
0.2
0.1
0
-2
-1.5
-1
-0.5
0
log C

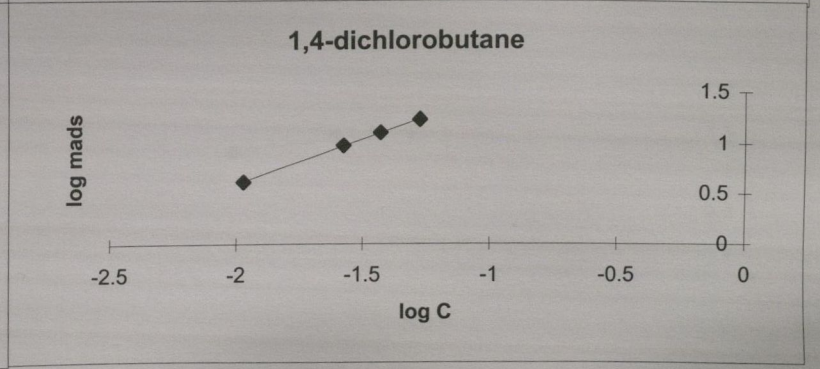

1,2-dichloroethane
log mads
log C
-2
-1.5
-1
-0.5
0
-0.1
-0.2
-0.3
-0.4
-0.5

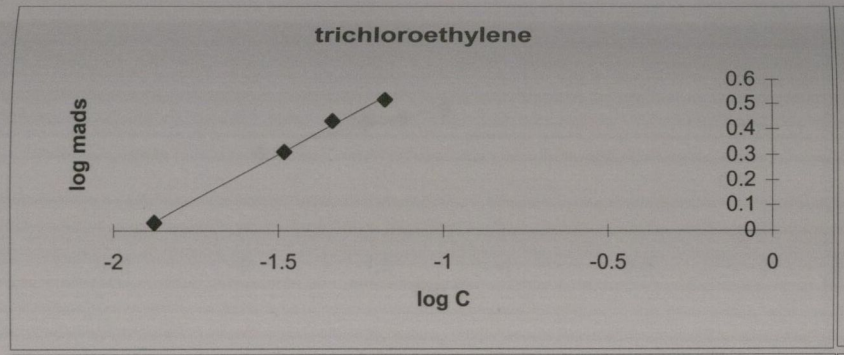

12dibromomethane
log mads
log C
-2
-1.5
-1
-0.5
0
0.2
0.4
0.6
0.8
1

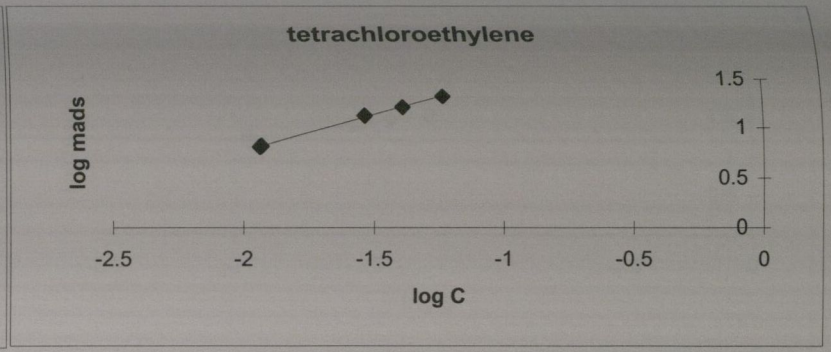

1,1,1-trichloroethane
log mads
log C
-2.5
-2
-1.5
-1
-0.5
0
0.05
-0.05
-0.1
-0.15
-0.2
-0.25

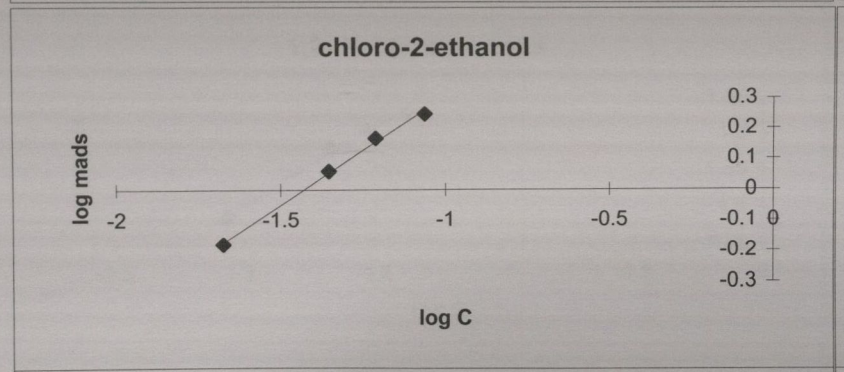

112trichloroethane
log mads
log C
-2
-1.5
-1
-0.5
0
0.2
0.4
0.6
0.8
1

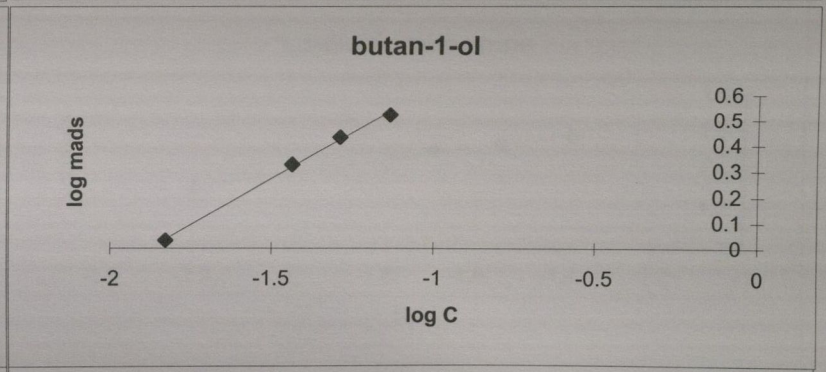

1,1,2,2-tetrachloroethane
log mads
log C
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5

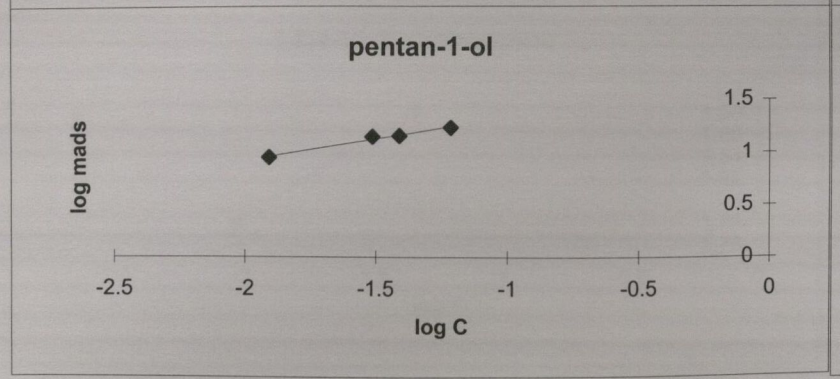

1,4-dichlorobutane
log mads
log C
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5

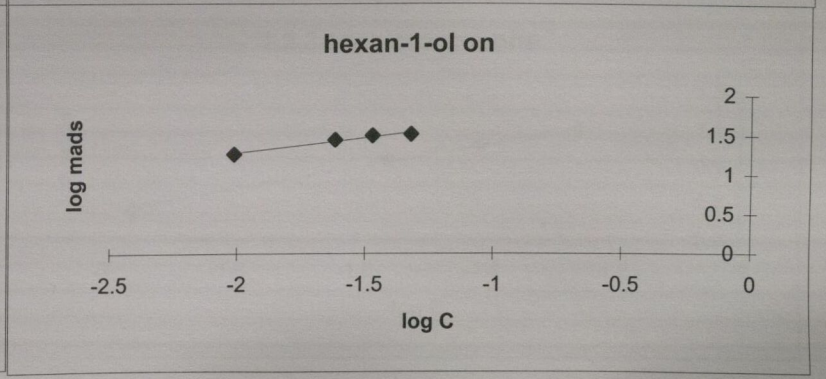

trichloroethylene
log mads
0.6
0.5
0.4
0.3
0.2
0.1
0
-2
-1.5
-1
-0.5
0
log C

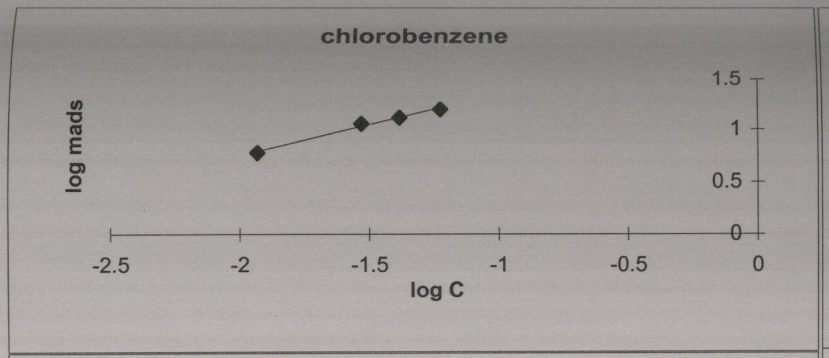

tetrachloroethylene
log mads
1.5
1
0.5
0
-2.5
-2
-1.5
-1
-0.5
0
log C

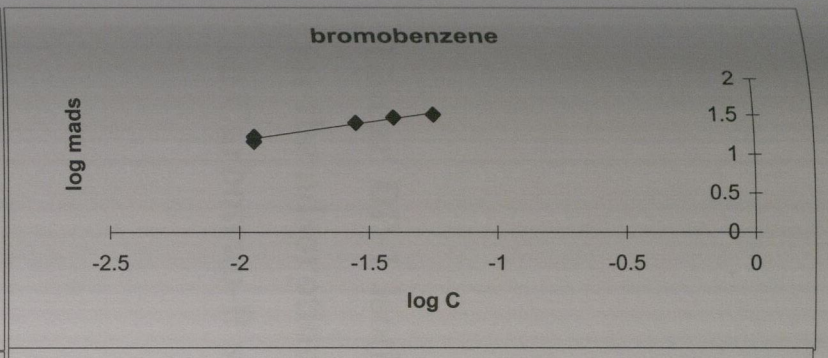

chloro-2-ethanol
log mads
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-2
-1.5
-1
-0.5
0
log C

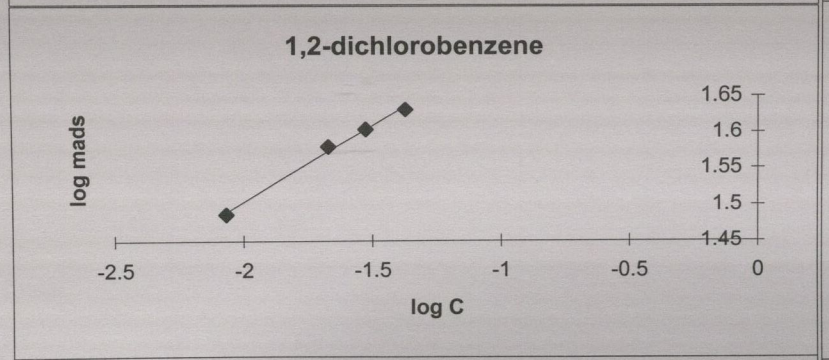

butan-1-ol
log mads
0.6
0.5
0.4
0.3
0.2
0.1
0
-2
-1.5
-1
-0.5
0
log C

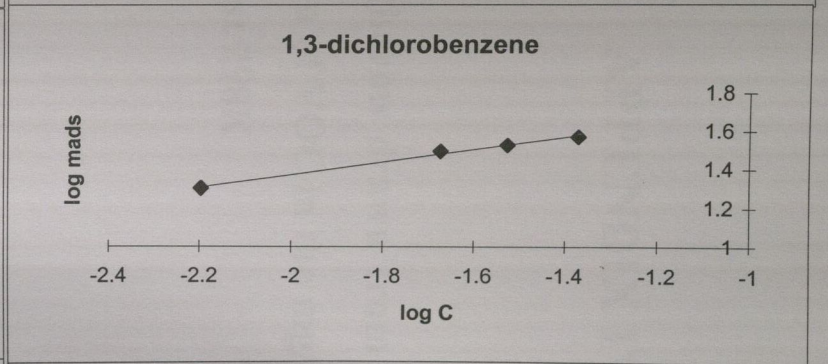

pentan-1-ol
log mads
1.5
1
0.5
0
-2.5
-2
-1.5
-1
-0.5
0
log C

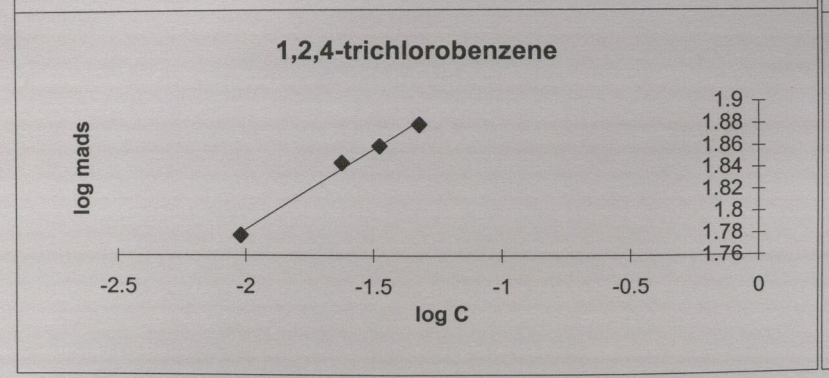

hexan-1-ol on
log mads
2
1.5
1
0.5
0
-2.5
-2
-1.5
-1
-0.5
0
log C

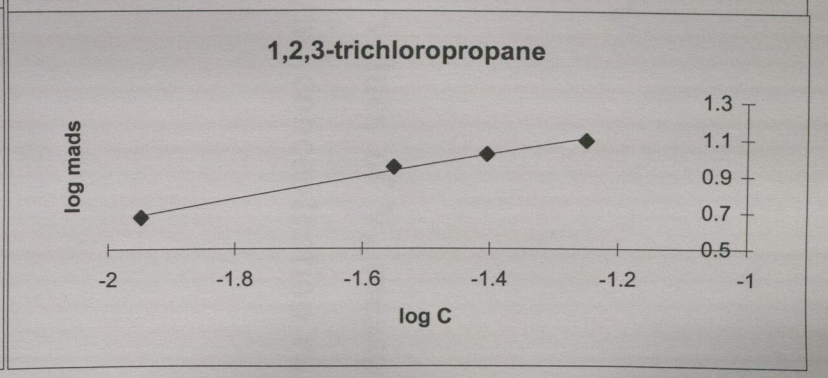

chlorobenzene
log mads
1.5
1
0.5
0
-2.5
-2
-1.5
-1
-0.5
0
log C


bromobenzene
log mads
2
1.5
1
0.5
0
-2.5
-2
-1.5
-1
-0.5
0
log C


1,2-dichlorobenzene
log mads
1.65
1.6
1.55
1.5
1.45
-2.5
-2
-1.5
-1
-0.5
0
log C

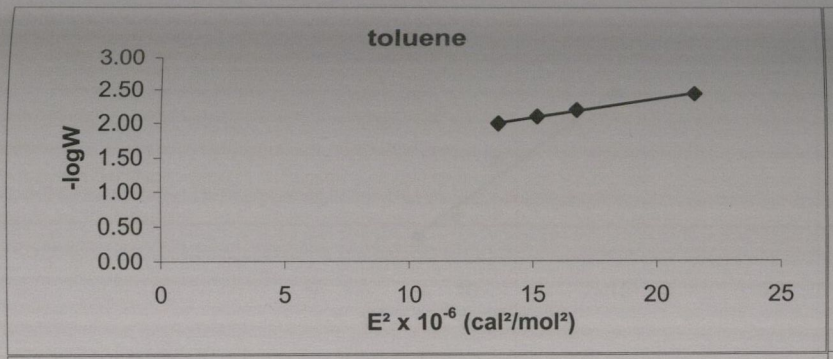

1,3-dichlorobenzene
log mads
1.8
1.6
1.4
1.2
1
-2.4
-2.2
-2
-1.8
-1.6
-1.4
-1.2
-1
log C

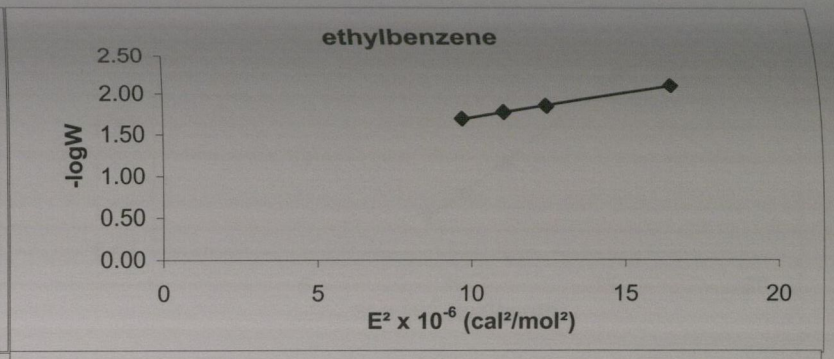

1,2,4-trichlorobenzene
log mads
1.9
1.88
1.86
1.84
1.82
1.8
1.78
1.76
-2.5
-2
-1.5
-1
-0.5
0
log C

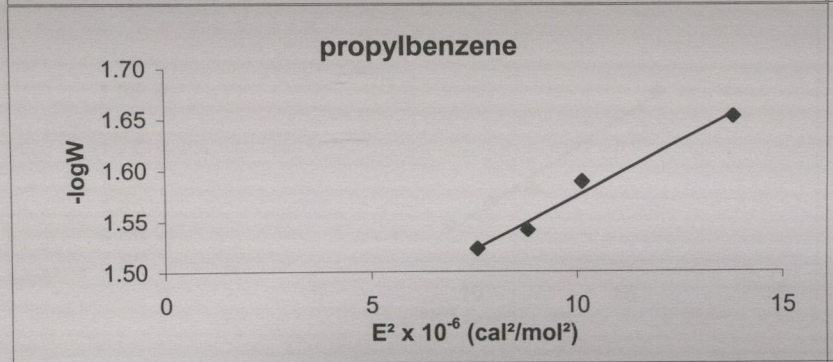

1,2,3-trichloropropane
log mads
1.3
1.1
0.9
0.7
0.5
-2
-1.8
-1.6
-1.4
-1.2
-1
log C

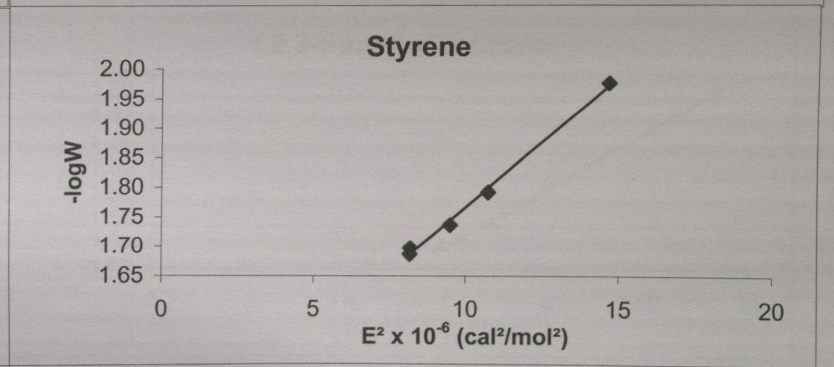
# APPENDIX IV

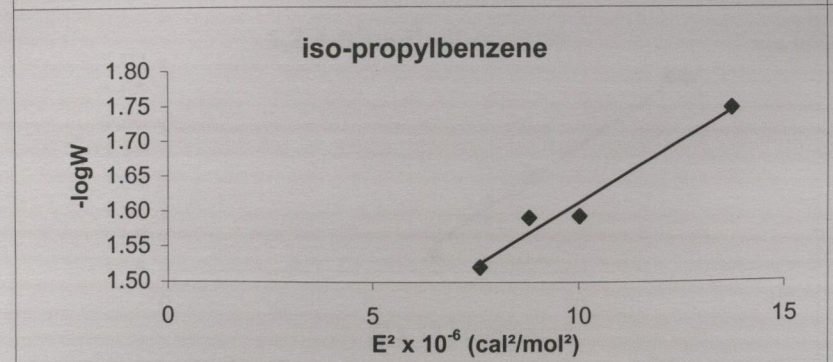
**Linear DP-1 isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the mg/m$^3$ concentration range on Carbotrap-B at 298K**

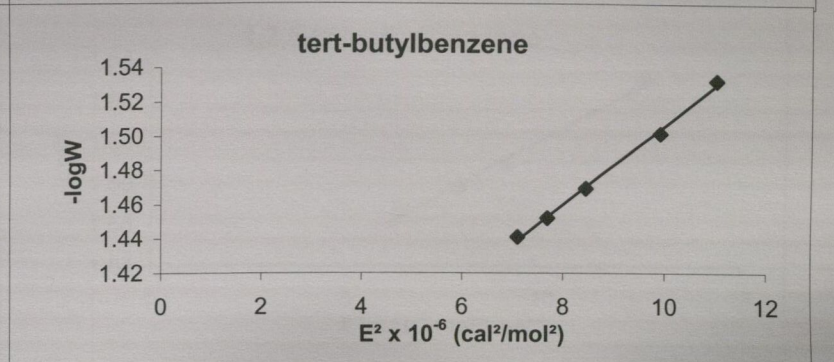

toluene
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
20
25
E² x 10⁻⁶ (cal²/mol²)

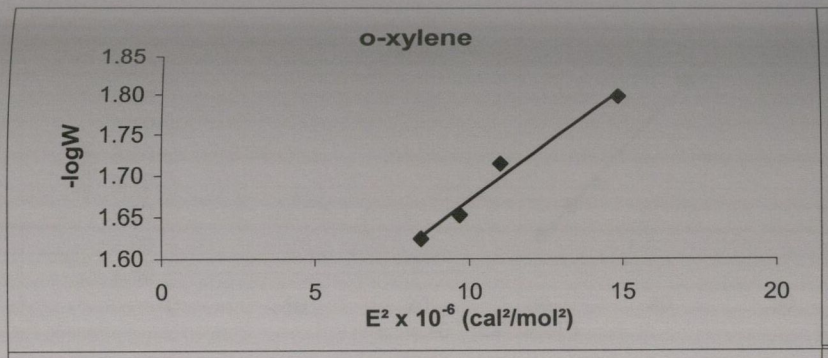

ethylbenzene
-logW
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

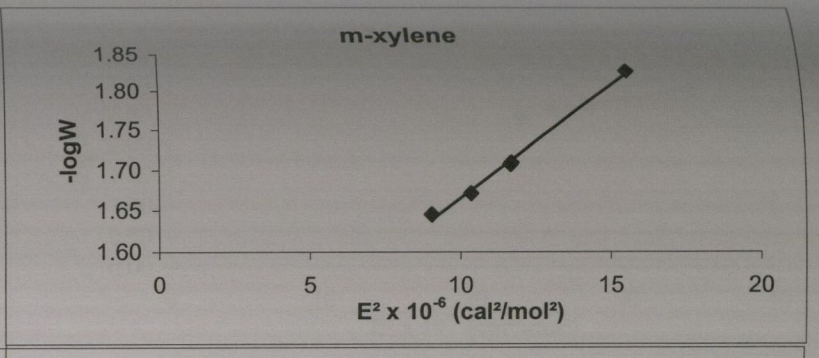

propylbenzene
-logW
1.70
1.65
1.60
1.55
1.50
0
5
10
15
E² x 10⁻⁶ (cal²/mol²)

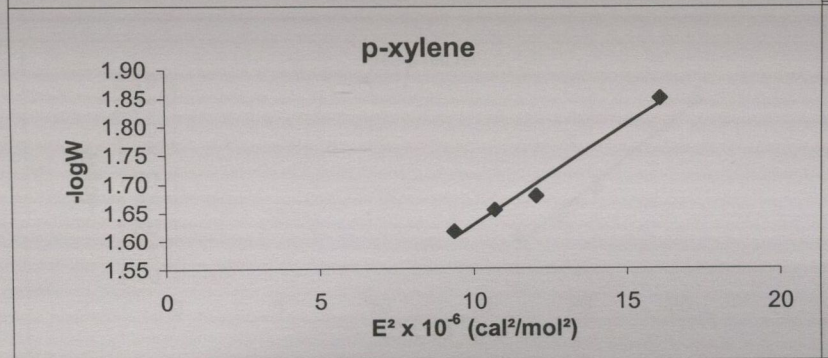

Styrene
-logW
2.00
1.95
1.90
1.85
1.80
1.75
1.70
1.65
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

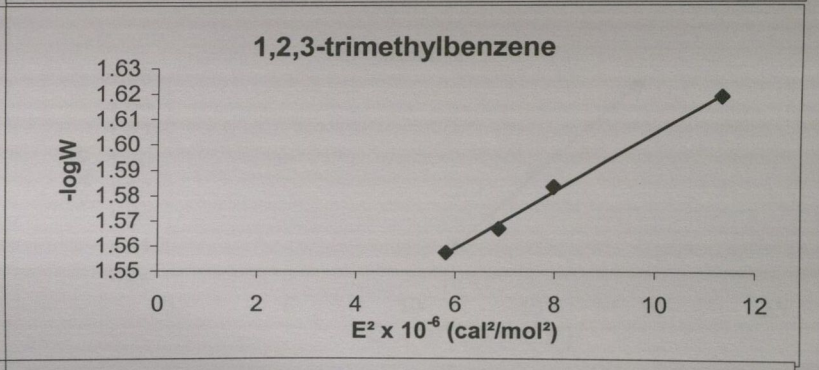

iso-propylbenzene
-logW
1.80
1.75
1.70
1.65
1.60
1.55
1.50
0
5
10
15
E² x 10⁻⁶ (cal²/mol²)

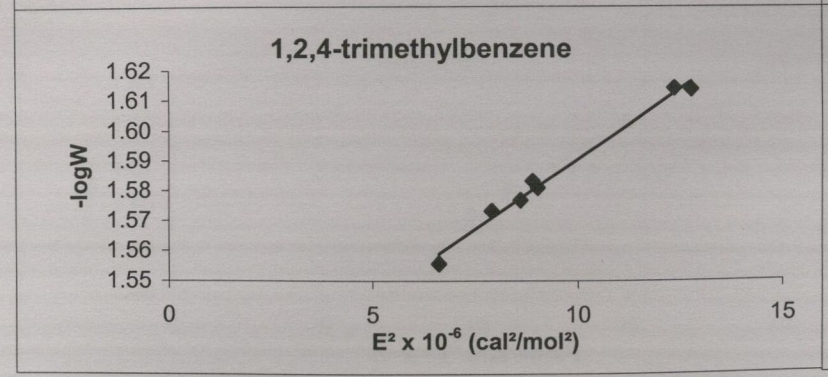

tert-butylbenzene
-logW
1.54
1.52
1.50
1.48
1.46
1.44
1.42
0
2
4
6
8
10
12
E² x 10⁻⁶ (cal²/mol²)

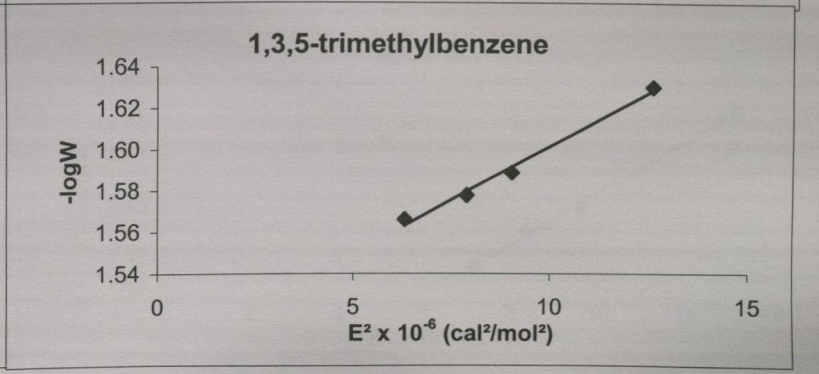

o-xylene
-logW
1.85
1.80
1.75
1.70
1.65
1.60
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

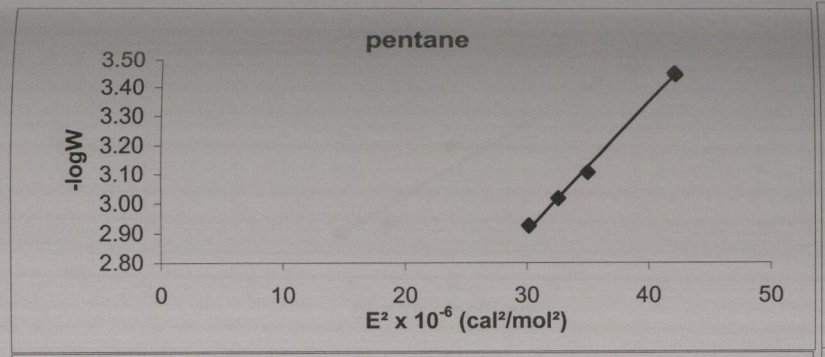

m-xylene
-logW
1.85
1.80
1.75
1.70
1.65
1.60
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

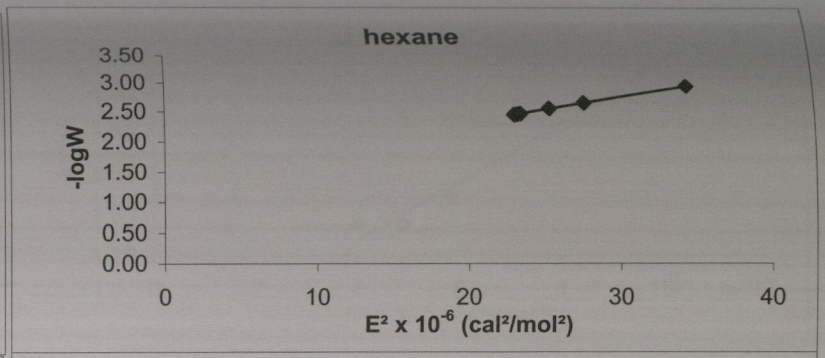

p-xylene
-logW
1.90
1.85
1.80
1.75
1.70
1.65
1.60
1.55
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

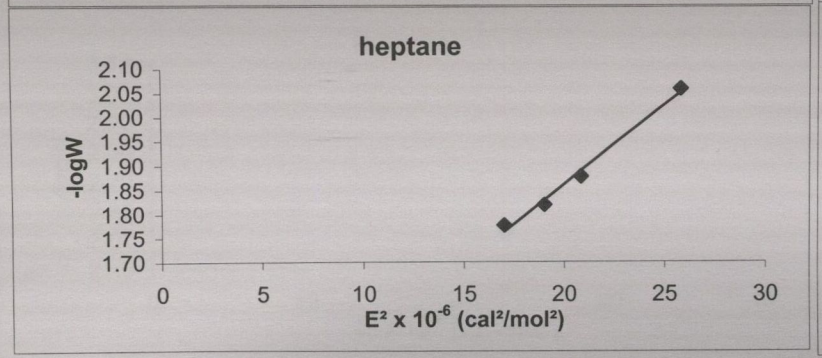

1,2,3-trimethylbenzene
-logW
1.63
1.62
1.61
1.60
1.59
1.58
1.57
1.56
1.55
0
2
4
6
8
10
12
E² x 10⁻⁶ (cal²/mol²)

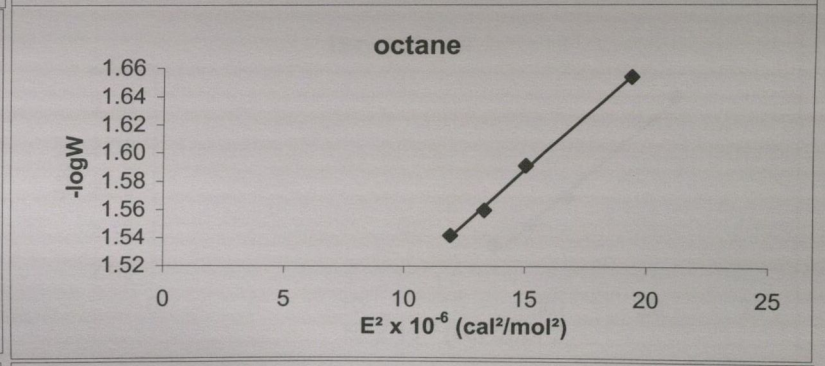

1,2,4-trimethylbenzene
-logW
1.62
1.61
1.60
1.59
1.58
1.57
1.56
1.55
0
5
10
15
E² x 10⁻⁶ (cal²/mol²)

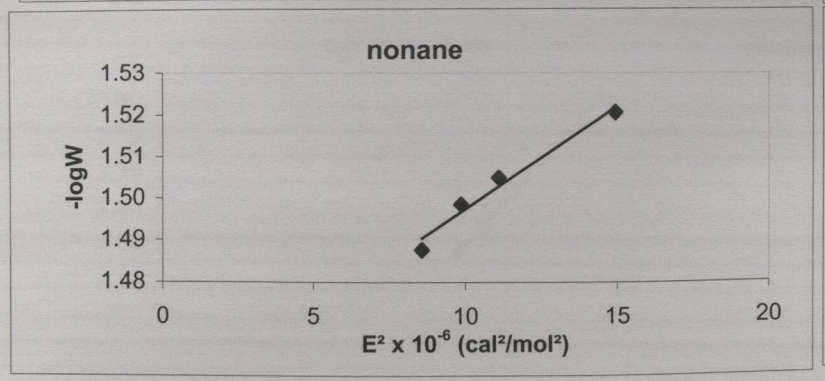

1,3,5-trimethylbenzene
-logW
1.64
1.62
1.60
1.58
1.56
1.54
0
5
10
15
E² x 10⁻⁶ (cal²/mol²)

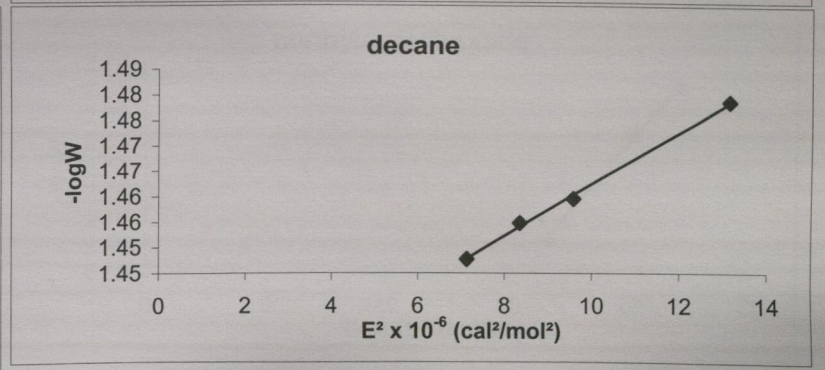

pentane
-logW
3.50
3.40
3.30
3.20
3.10
3.00
2.90
2.80
0
10
20
30
40
50
E² x 10⁻⁶ (cal²/mol²)

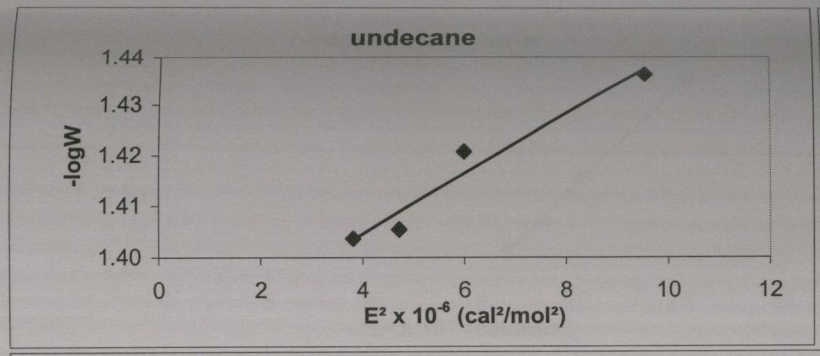

hexane
-logW
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
10
20
30
40
E² x 10⁻⁶ (cal²/mol²)

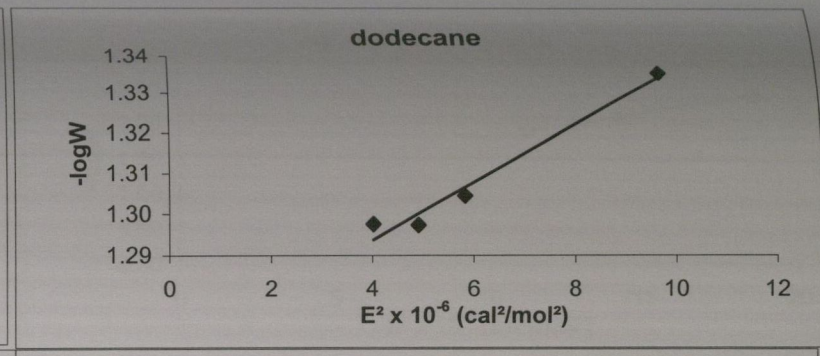

heptane
-logW
2.10
2.05
2.00
1.95
1.90
1.85
1.80
1.75
1.70
0
5
10
15
20
25
30
E² x 10⁻⁶ (cal²/mol²)

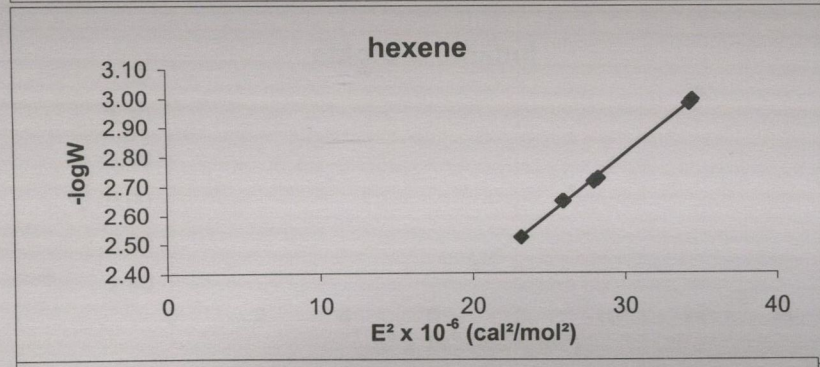

octane
-logW
1.66
1.64
1.62
1.60
1.58
1.56
1.54
1.52
0
5
10
15
20
25
E² x 10⁻⁶ (cal²/mol²)

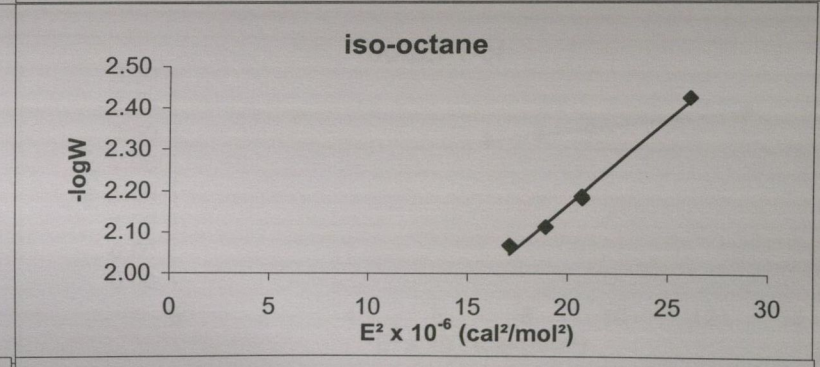

nonane
-logW
1.53
1.52
1.51
1.50
1.49
1.48
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

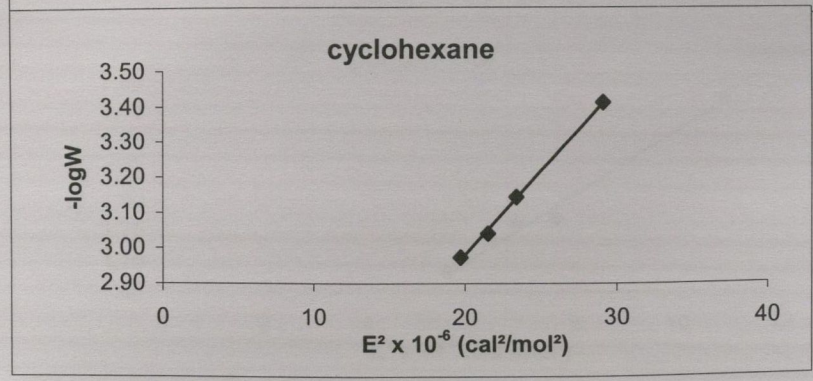

decane
-logW
1.49
1.48
1.48
1.47
1.47
1.46
1.46
1.45
1.45
0
2
4
6
8
10
12
14
E² x 10⁻⁶ (cal²/mol²)

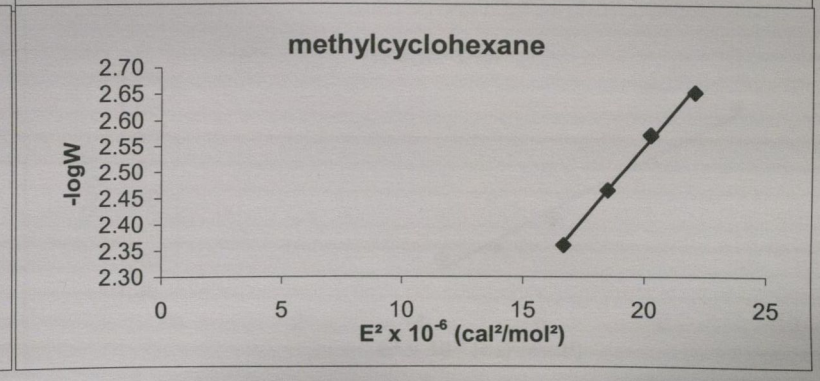

undecane
-logW
1.44
1.43
1.42
1.41
1.40
0
2
4
6
8
10
12
E² x 10⁻⁶ (cal²/mol²)

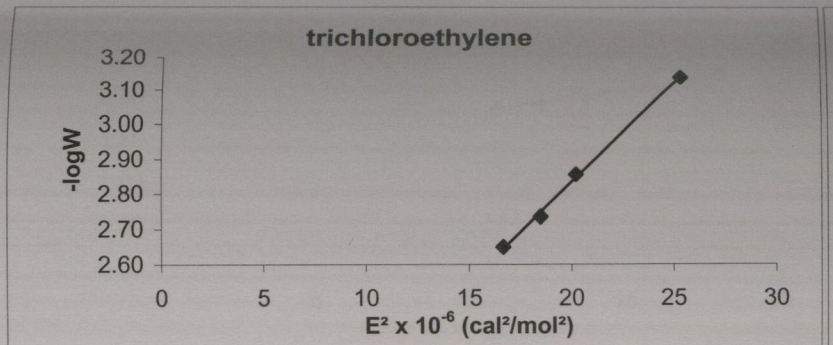

dodecane
-logW
1.34
1.33
1.32
1.31
1.30
1.29
0
2
4
6
8
10
12
E² x 10⁻⁶ (cal²/mol²)

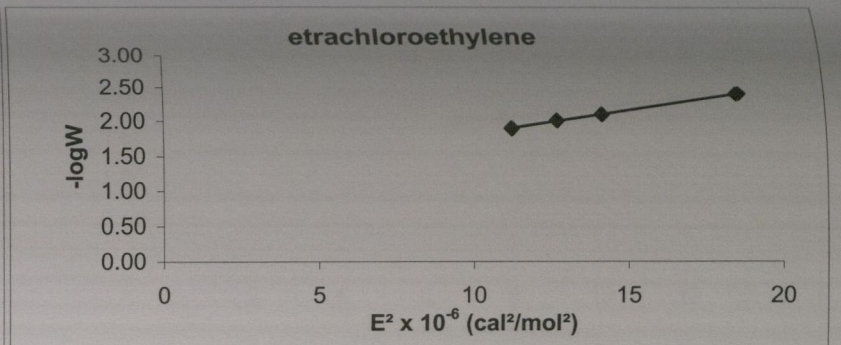

hexene
-logW
3.10
3.00
2.90
2.80
2.70
2.60
2.50
2.40
0
10
20
30
40
E² x 10⁻⁶ (cal²/mol²)

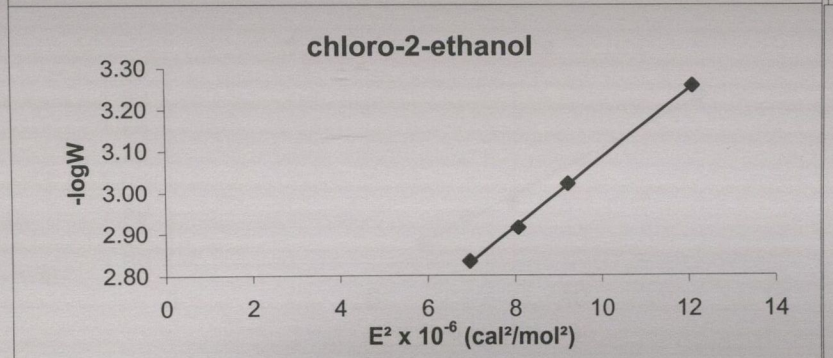

iso-octane
-logW
2.50
2.40
2.30
2.20
2.10
2.00
0
5
10
15
20
25
30
E² x 10⁻⁶ (cal²/mol²)

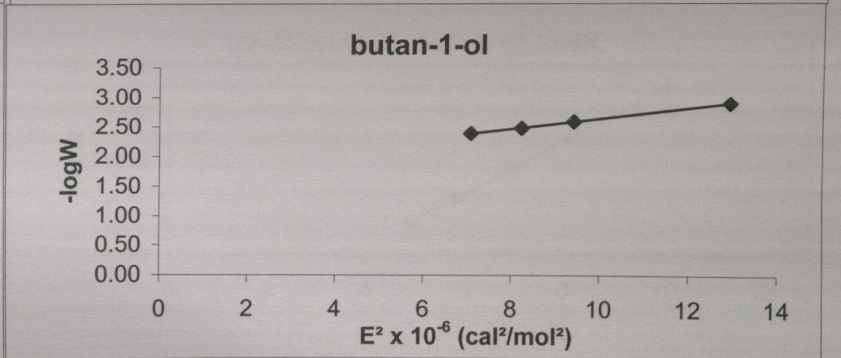

cyclohexane
-logW
3.50
3.40
3.30
3.20
3.10
3.00
2.90
0
10
20
30
40
E² x 10⁻⁶ (cal²/mol²)

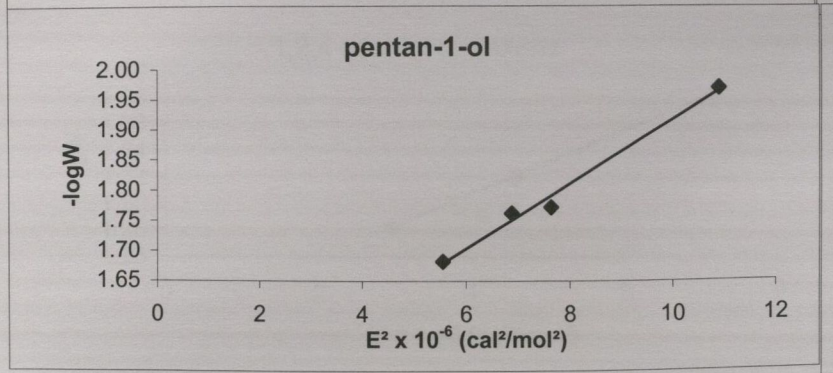

methylcyclohexane
-logW
2.70
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
0
5
10
15
20
25
E² x 10⁻⁶ (cal²/mol²)

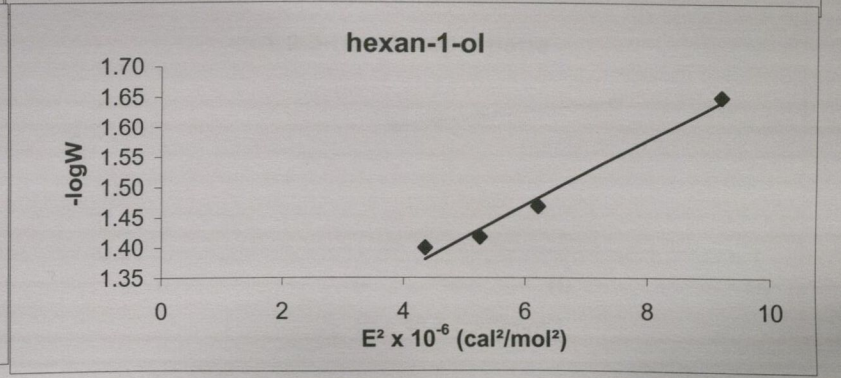

trichloroethylene
-logW
3.20
3.10
3.00
2.90
2.80
2.70
2.60
0
5
10
15
20
25
30
E² x 10⁻⁶ (cal²/mol²)

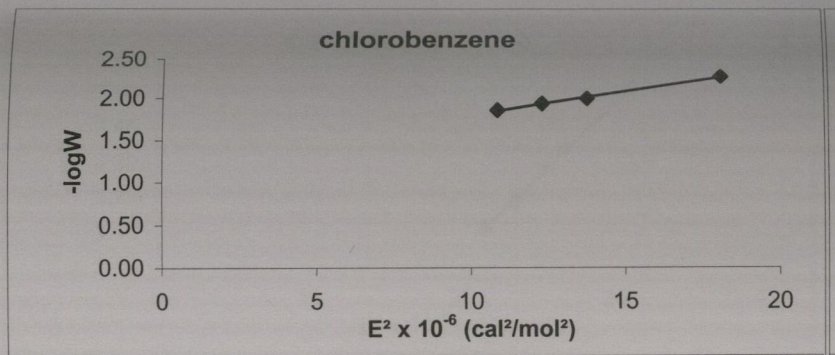

etrachloroethylene
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

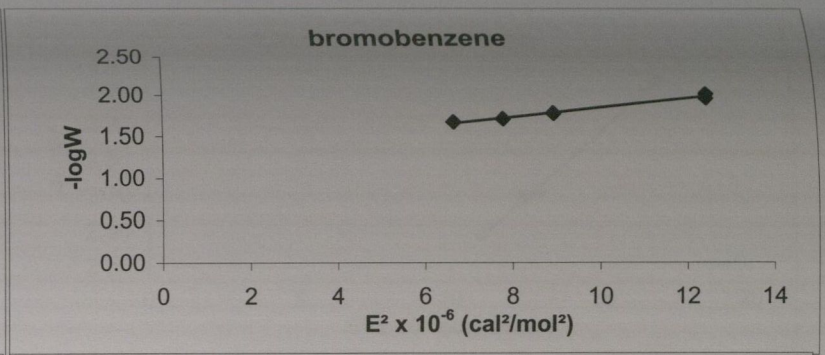

chloro-2-ethanol
-logW
3.30
3.20
3.10
3.00
2.90
2.80
0
2
4
6
8
10
12
14
E² x 10⁻⁶ (cal²/mol²)

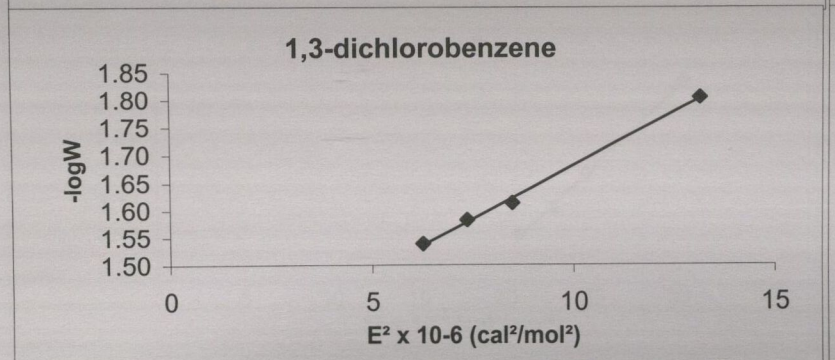

butan-1-ol
-logW
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
2
4
6
8
10
12
14
E² x 10⁻⁶ (cal²/mol²)

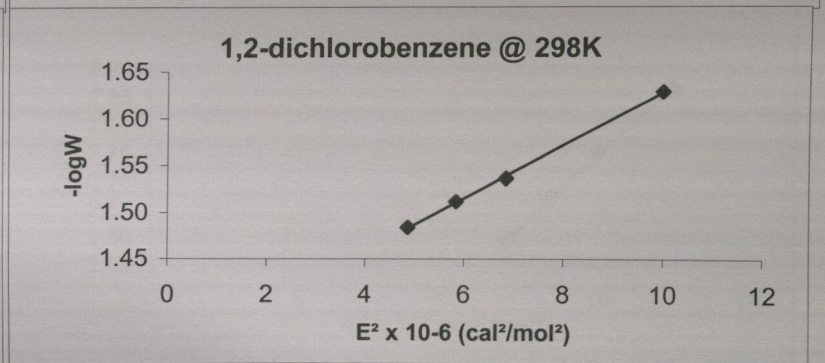

pentan-1-ol
-logW
2.00
1.95
1.90
1.85
1.80
1.75
1.70
1.65
0
2
4
6
8
10
12
E² x 10⁻⁶ (cal²/mol²)

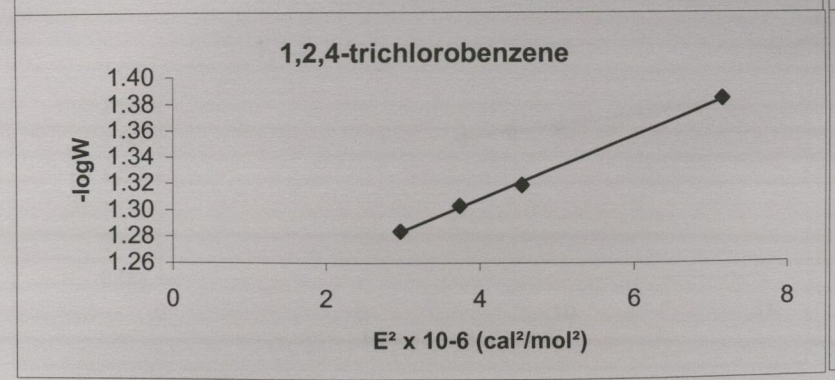

hexan-1-ol
-logW
1.70
1.65
1.60
1.55
1.50
1.45
1.40
1.35
0
2
4
6
8
10
E² x 10⁻⁶ (cal²/mol²)

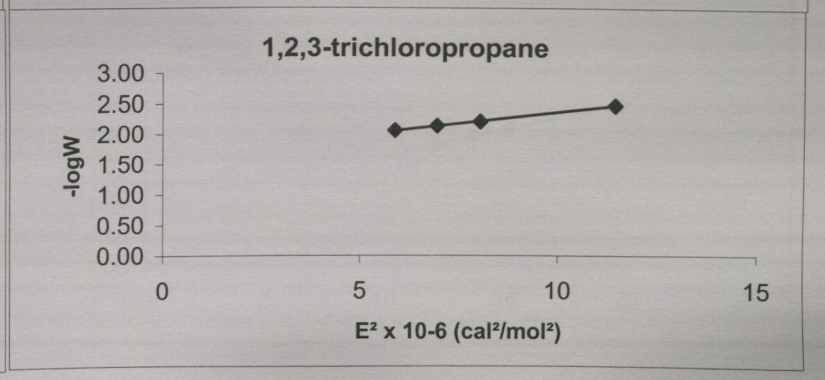

chlorobenzene
-logW
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

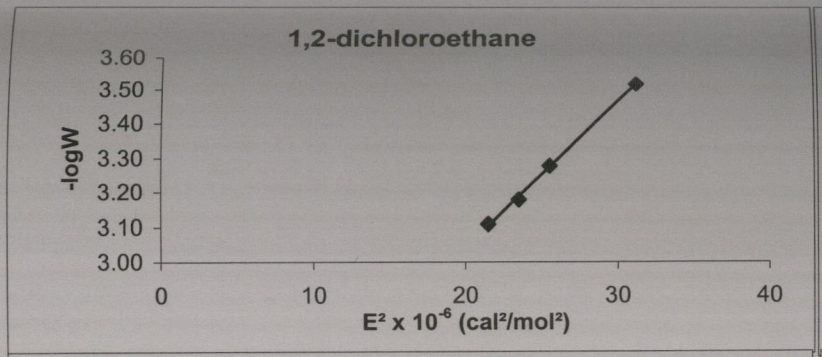

bromobenzene
-logW
2.50
2.00
1.50
1.00
0.50
0.00
0
2
4
6
8
10
12
14
E² x 10⁻⁶ (cal²/mol²)

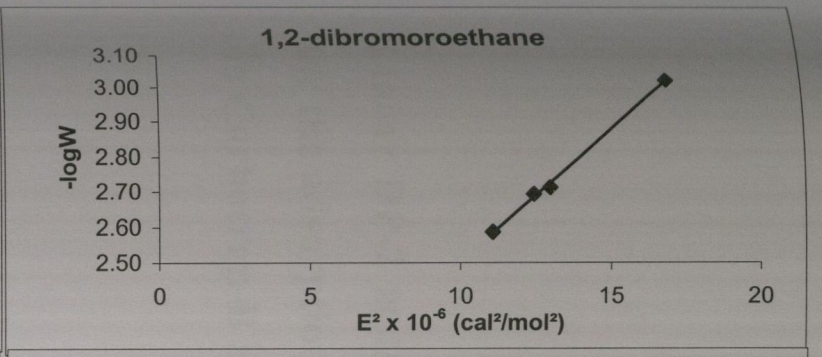

1,3-dichlorobenzene
-logW
1.85
1.80
1.75
1.70
1.65
1.60
1.55
1.50
0
5
10
15
E² x 10-6 (cal²/mol²)

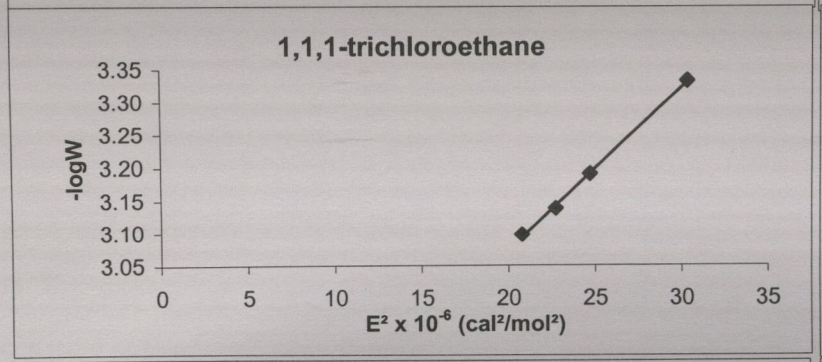

1,2-dichlorobenzene @ 298K
-logW
1.65
1.60
1.55
1.50
1.45
0
2
4
6
8
10
12
E² x 10-6 (cal²/mol²)

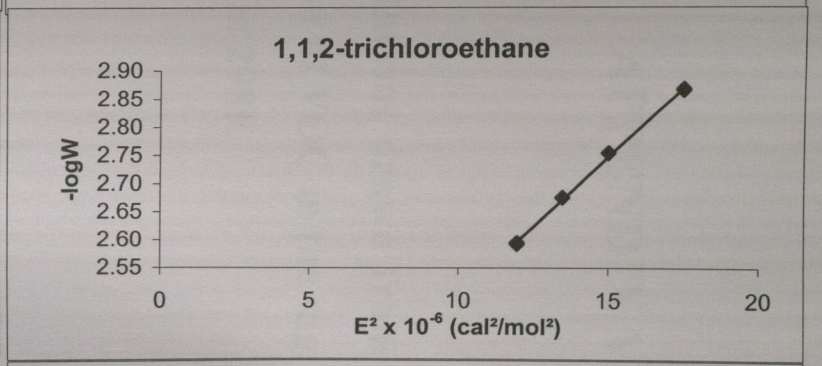

1,2,4-trichlorobenzene
-logW
1.40
1.38
1.36
1.34
1.32
1.30
1.28
1.26
0
2
4
6
8
E² x 10-6 (cal²/mol²)

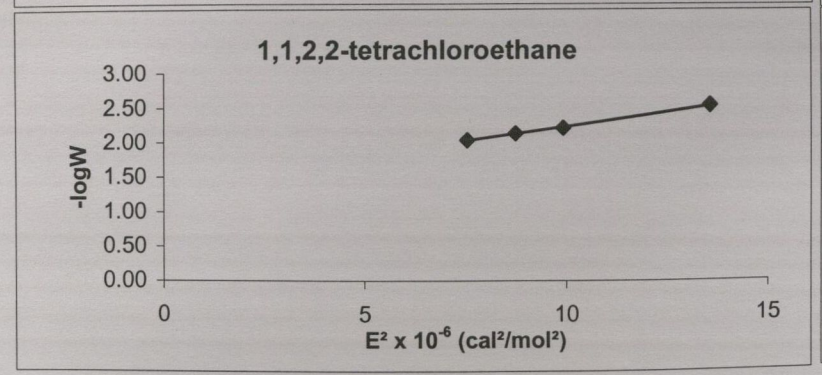

1,2,3-trichloropropane
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
E² x 10-6 (cal²/mol²)

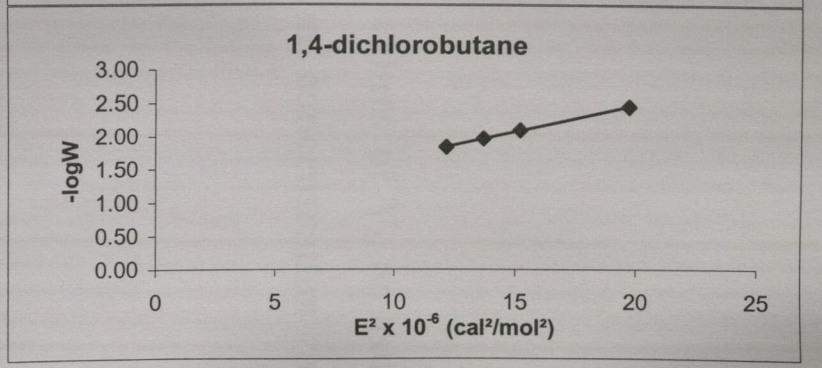

1,2-dichloroethane
-logW
3.60
3.50
3.40
3.30
3.20
3.10
3.00
0
10
20
30
40
E² x 10⁻⁶ (cal²/mol²)


1,2-dibromoroethane
-logW
3.10
3.00
2.90
2.80
2.70
2.60
2.50
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)


1,1,1-trichloroethane
-logW
3.35
3.30
3.25
3.20
3.15
3.10
3.05
0
5
10
15
20
25
30
35
E² x 10⁻⁶ (cal²/mol²)

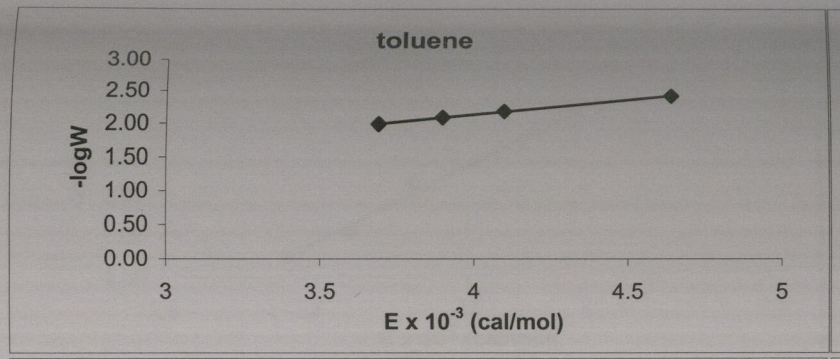

1,1,2-trichloroethane
-logW
2.90
2.85
2.80
2.75
2.70
2.65
2.60
2.55
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

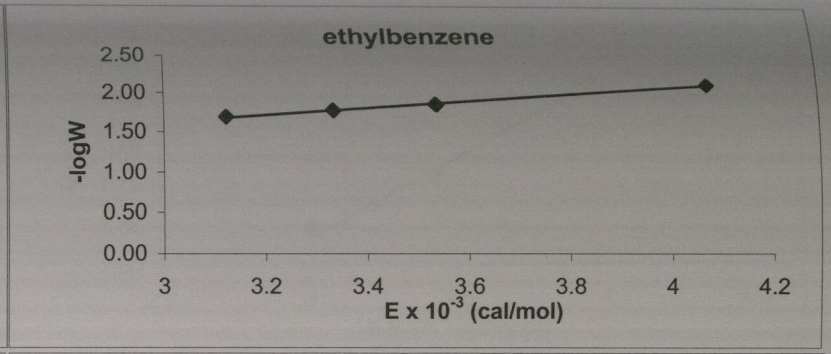

1,1,2,2-tetrachloroethane
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
E² x 10⁻⁶ (cal²/mol²)

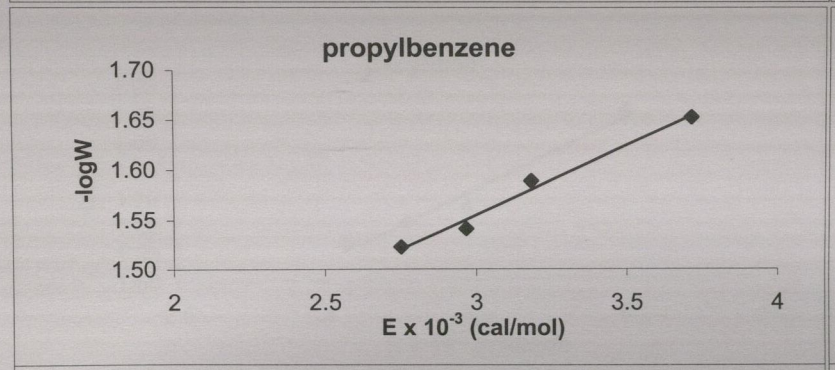

1,4-dichlorobutane
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
20
25
E² x 10⁻⁶ (cal²/mol²)

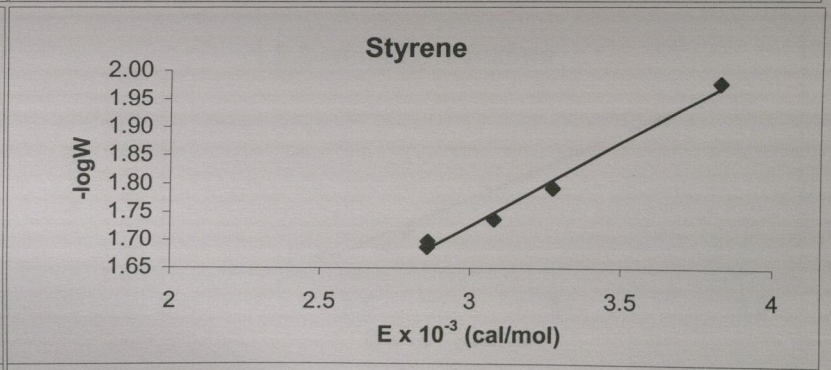
# APPENDIX V

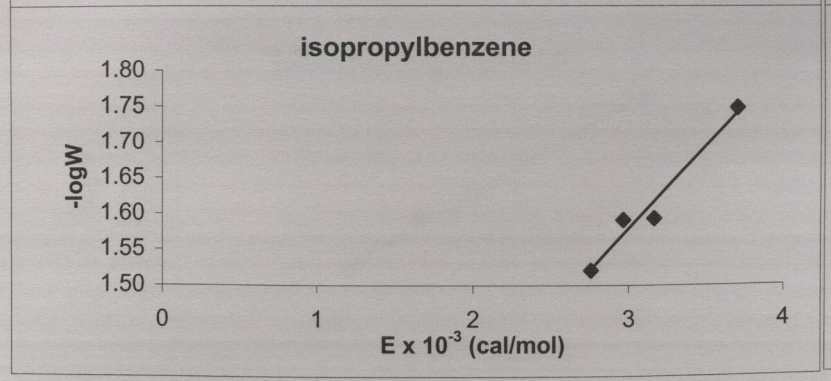
**Linear DP-2 isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the mg/m$^3$ concentration range on Carbotrap-B at 298K**

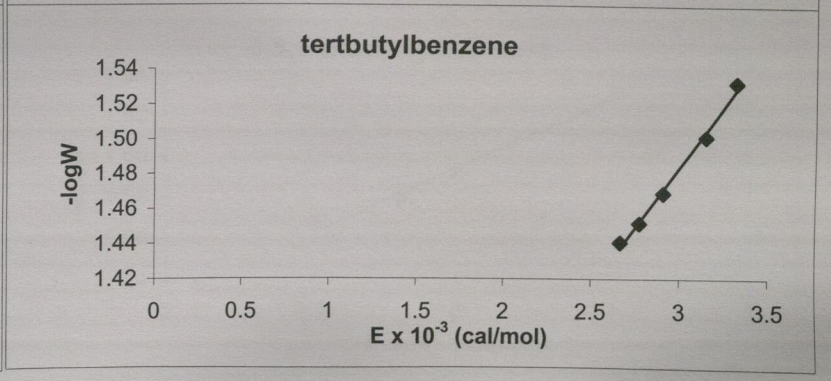

toluene
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
3
3.5
4
4.5
5
E x 10-3 (cal/mol)

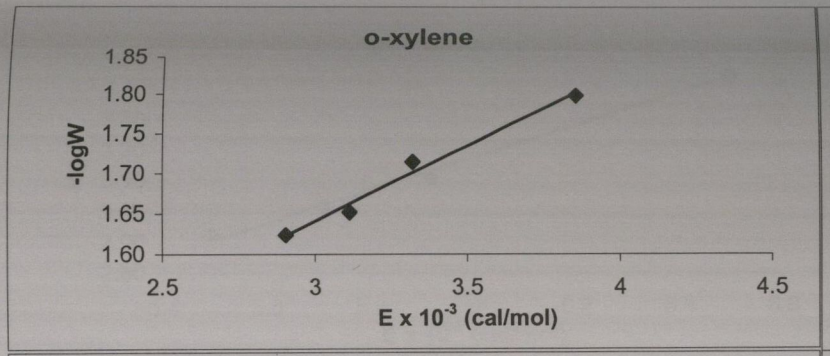

ethylbenzene
-logW
2.50
2.00
1.50
1.00
0.50
0.00
3
3.2
3.4
3.6
3.8
4
4.2
E x 10-3 (cal/mol)

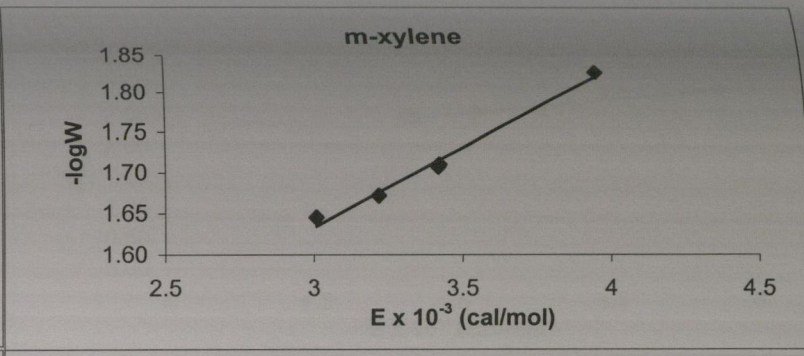

propylbenzene
-logW
1.70
1.65
1.60
1.55
1.50
2
2.5
3
3.5
4
E x 10-3 (cal/mol)

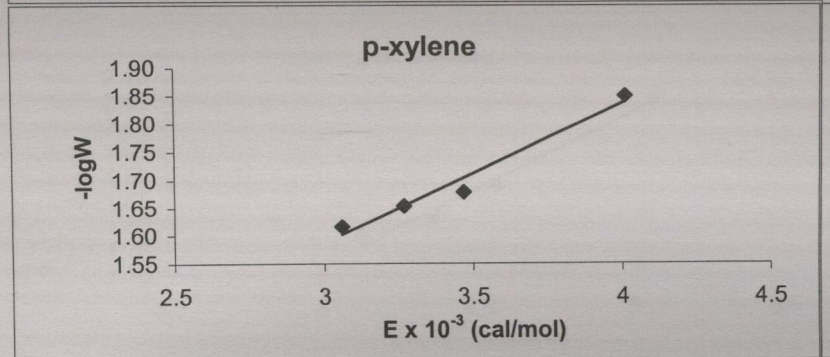

Styrene
-logW
2.00
1.95
1.90
1.85
1.80
1.75
1.70
1.65
2
2.5
3
3.5
4
E x 10-3 (cal/mol)

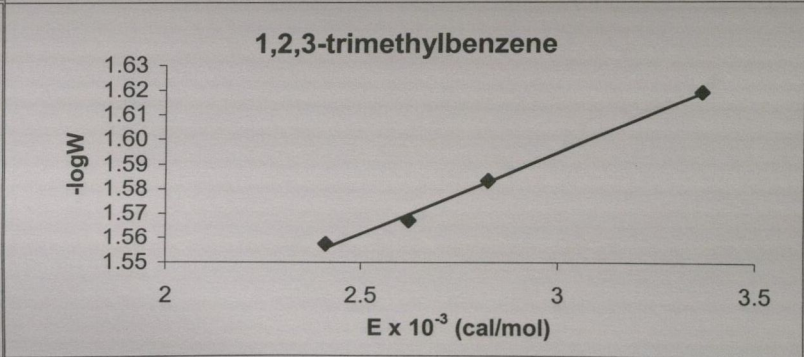

isopropylbenzene
-logW
1.80
1.75
1.70
1.65
1.60
1.55
1.50
0
1
2
3
4
E x 10-3 (cal/mol)

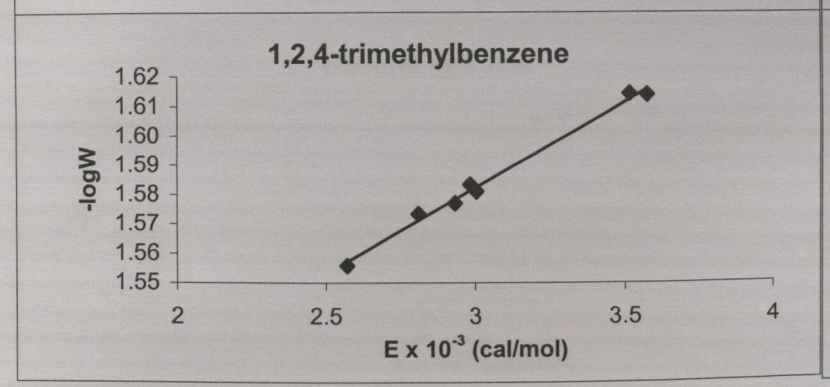

tertbutylbenzene
-logW
1.54
1.52
1.50
1.48
1.46
1.44
1.42
0
0.5
1
1.5
2
2.5
3
3.5
E x 10-3 (cal/mol)

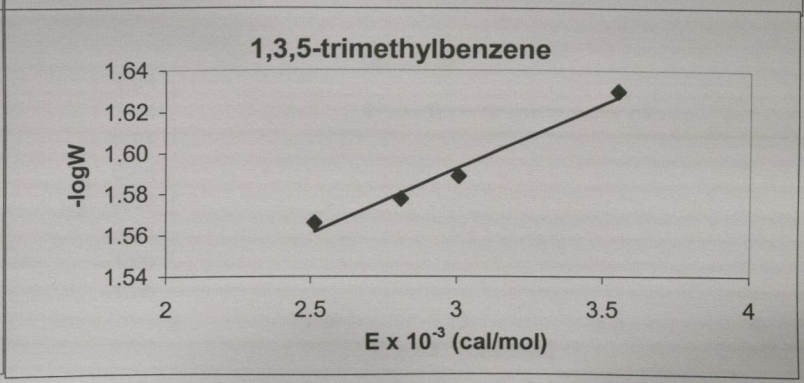

o-xylene
-logW
1.85
1.80
1.75
1.70
1.65
1.60
2.5
3
3.5
4
4.5
E x 10-3 (cal/mol)

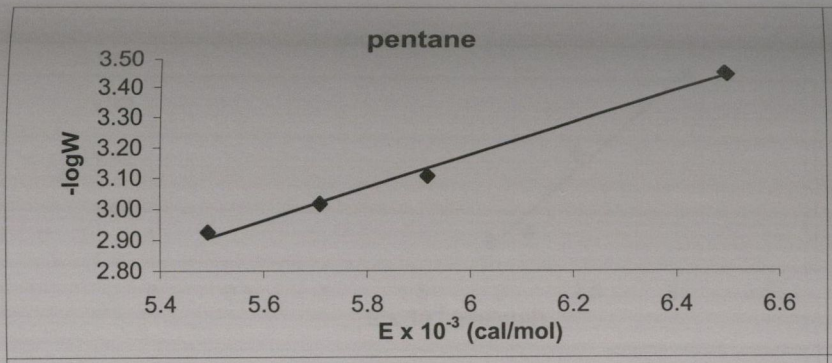

m-xylene
-logW
1.85
1.80
1.75
1.70
1.65
1.60
2.5
3
3.5
4
4.5
E x 10-3 (cal/mol)

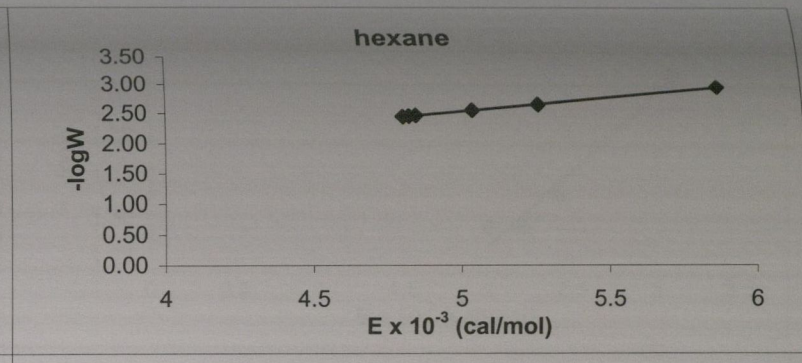

p-xylene
-logW
1.90
1.85
1.80
1.75
1.70
1.65
1.60
1.55
2.5
3
3.5
4
4.5
E x 10-3 (cal/mol)

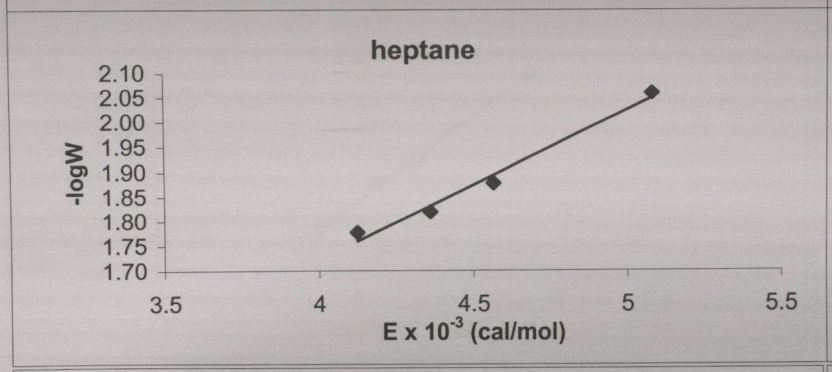

1,2,3-trimethylbenzene
-logW
1.63
1.62
1.61
1.60
1.59
1.58
1.57
1.56
1.55
2
2.5
3
3.5
E x 10-3 (cal/mol)

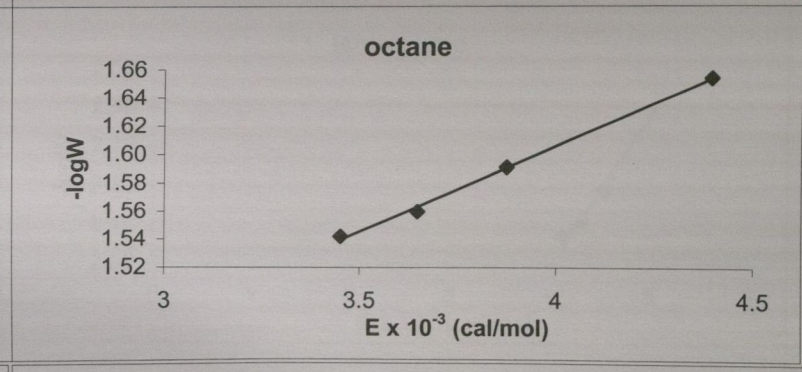

1,2,4-trimethylbenzene
-logW
1.62
1.61
1.60
1.59
1.58
1.57
1.56
1.55
2
2.5
3
3.5
4
E x 10-3 (cal/mol)

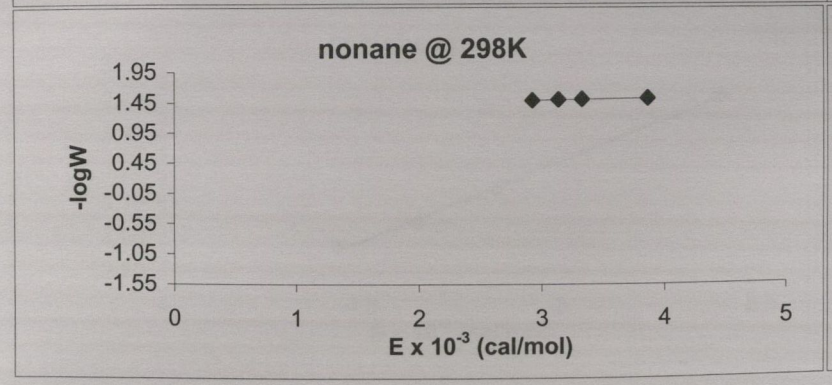

1,3,5-trimethylbenzene
-logW
1.64
1.62
1.60
1.58
1.56
1.54
2
2.5
3
3.5
4
E x 10-3 (cal/mol)

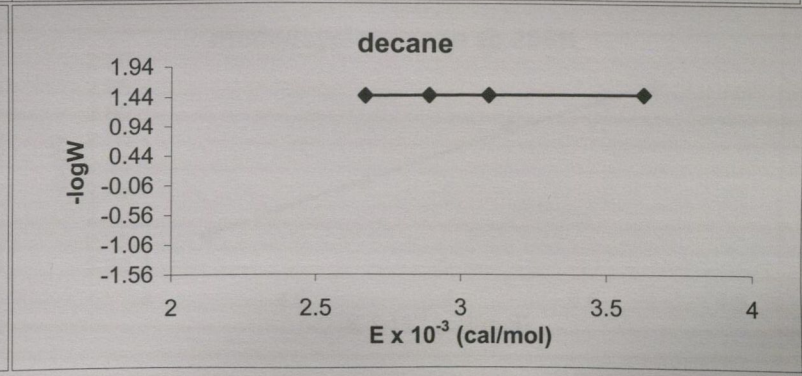

pentane
-logW
3.50
3.40
3.30
3.20
3.10
3.00
2.90
2.80
5.4
5.6
5.8
6
6.2
6.4
6.6
E x 10-3 (cal/mol)

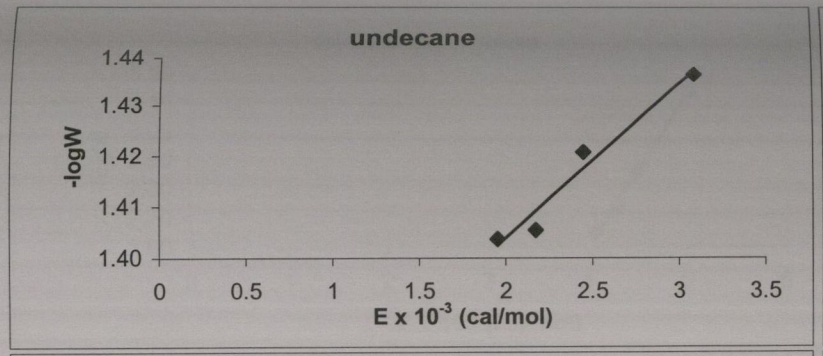

hexane
-logW
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
4
4.5
5
5.5
6
E x 10-3 (cal/mol)

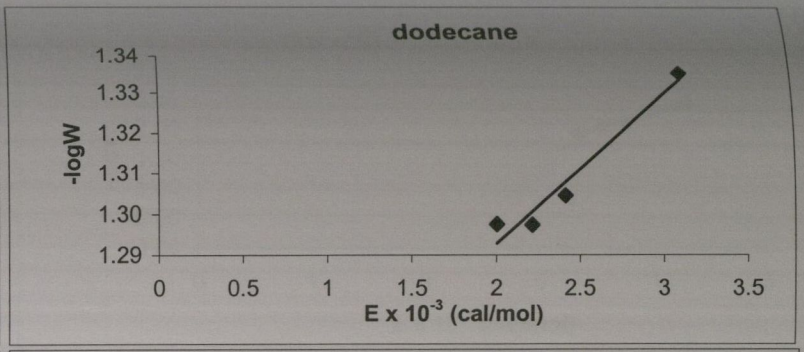

heptane
-logW
2.10
2.05
2.00
1.95
1.90
1.85
1.80
1.75
1.70
3.5
4
4.5
5
5.5
E x 10-3 (cal/mol)

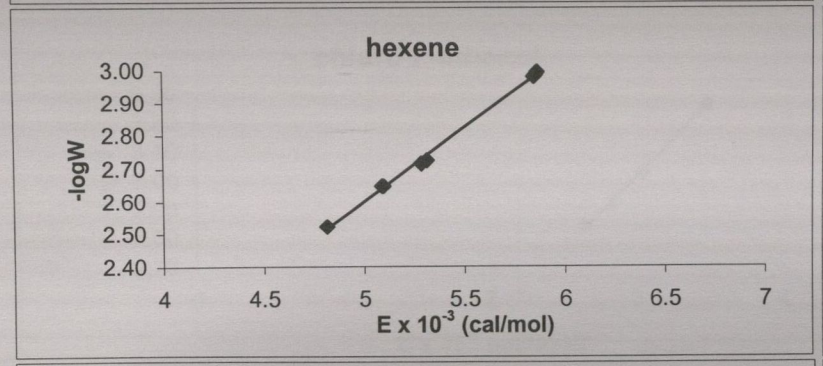

octane
-logW
1.66
1.64
1.62
1.60
1.58
1.56
1.54
1.52
3
3.5
4
4.5
E x 10-3 (cal/mol)

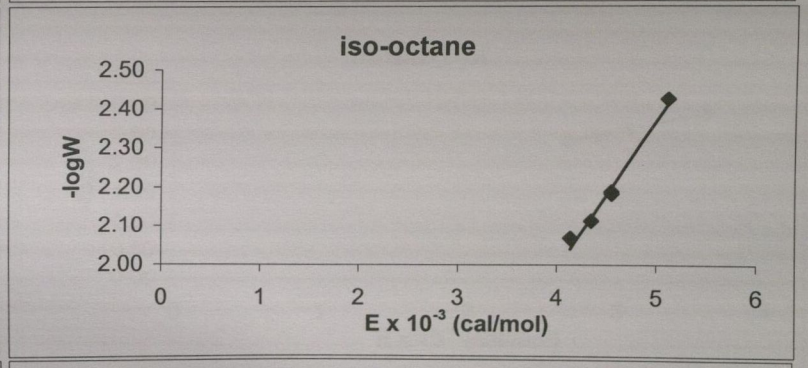

nonane @ 298K
-logW
1.95
1.45
0.95
0.45
-0.05
-0.55
-1.05
-1.55
0
1
2
3
4
5
E x 10-3 (cal/mol)

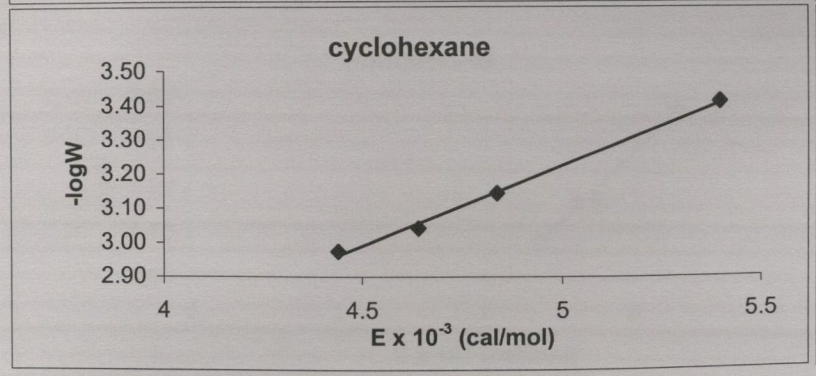

decane
-logW
1.94
1.44
0.94
0.44
-0.06
-0.56
-1.06
-1.56
2
2.5
3
3.5
4
E x 10-3 (cal/mol)

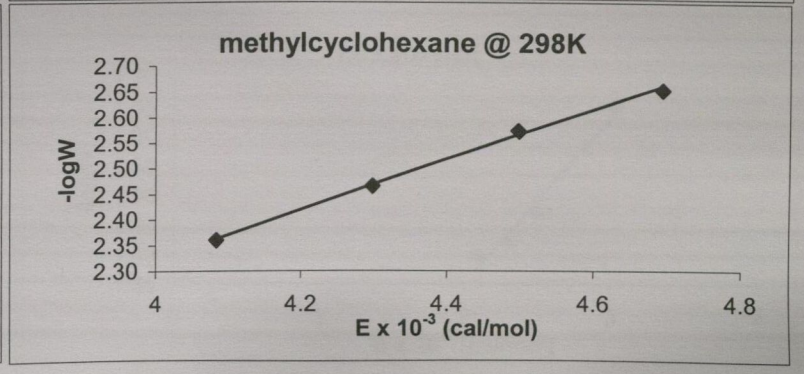

undecane
-logW
1.44
1.43
1.42
1.41
1.40
0
0.5
1
1.5
2
2.5
3
3.5
E x 10-3 (cal/mol)

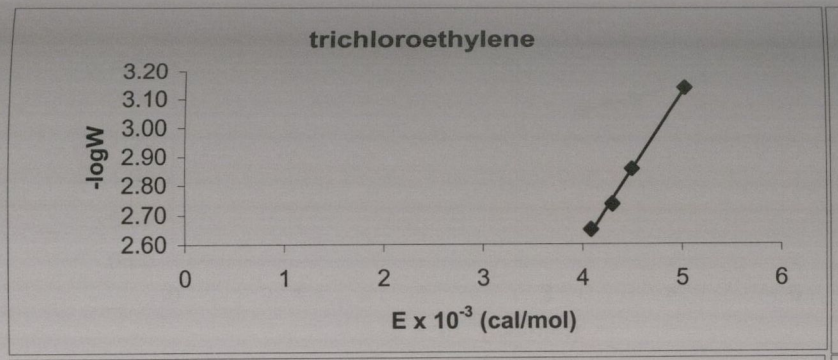

dodecane
-logW
1.34
1.33
1.32
1.31
1.30
1.29
0
0.5
1
1.5
2
2.5
3
3.5
E x 10-3 (cal/mol)

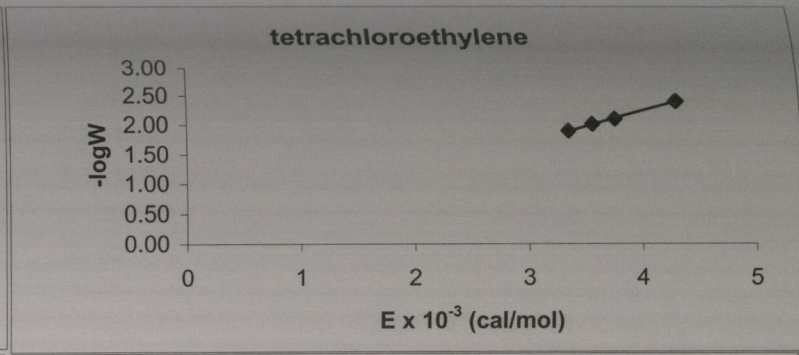

hexene
-logW
3.00
2.90
2.80
2.70
2.60
2.50
2.40
4
4.5
5
5.5
6
6.5
7
E x 10-3 (cal/mol)

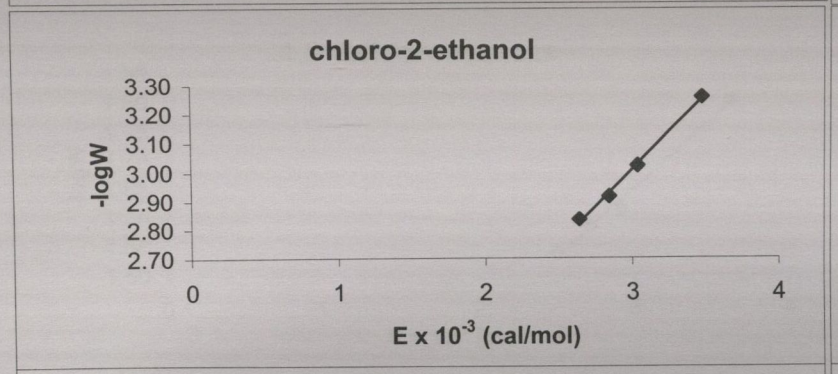

iso-octane
-logW
2.50
2.40
2.30
2.20
2.10
2.00
0
1
2
3
4
5
6
E x 10-3 (cal/mol)

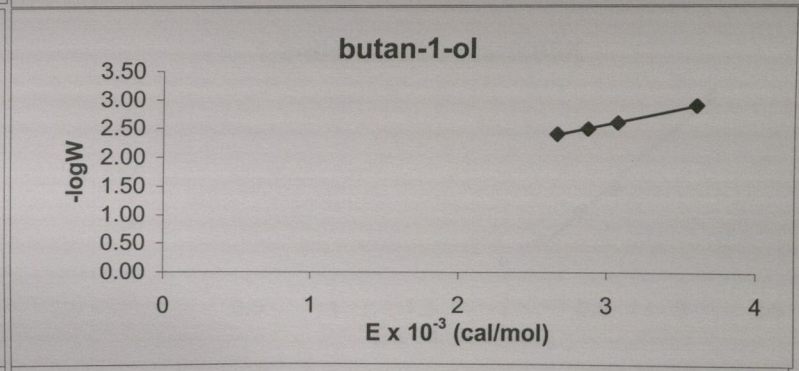

cyclohexane
-logW
3.50
3.40
3.30
3.20
3.10
3.00
2.90
4
4.5
5
5.5
E x 10-3 (cal/mol)

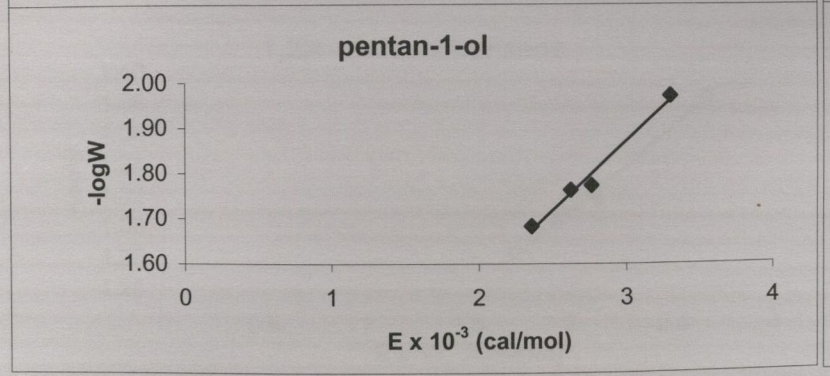

methylcyclohexane @ 298K
-logW
2.70
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
4
4.2
4.4
4.6
4.8
E x 10-3 (cal/mol)

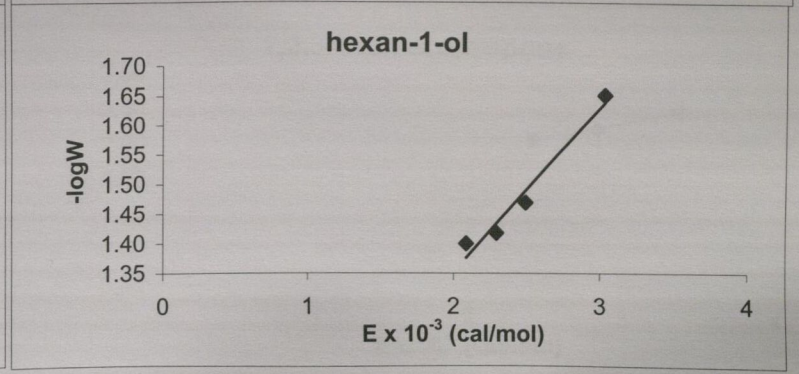

trichloroethylene
-logW
3.20
3.10
3.00
2.90
2.80
2.70
2.60
0
1
2
3
4
5
6
E x 10-3 (cal/mol)

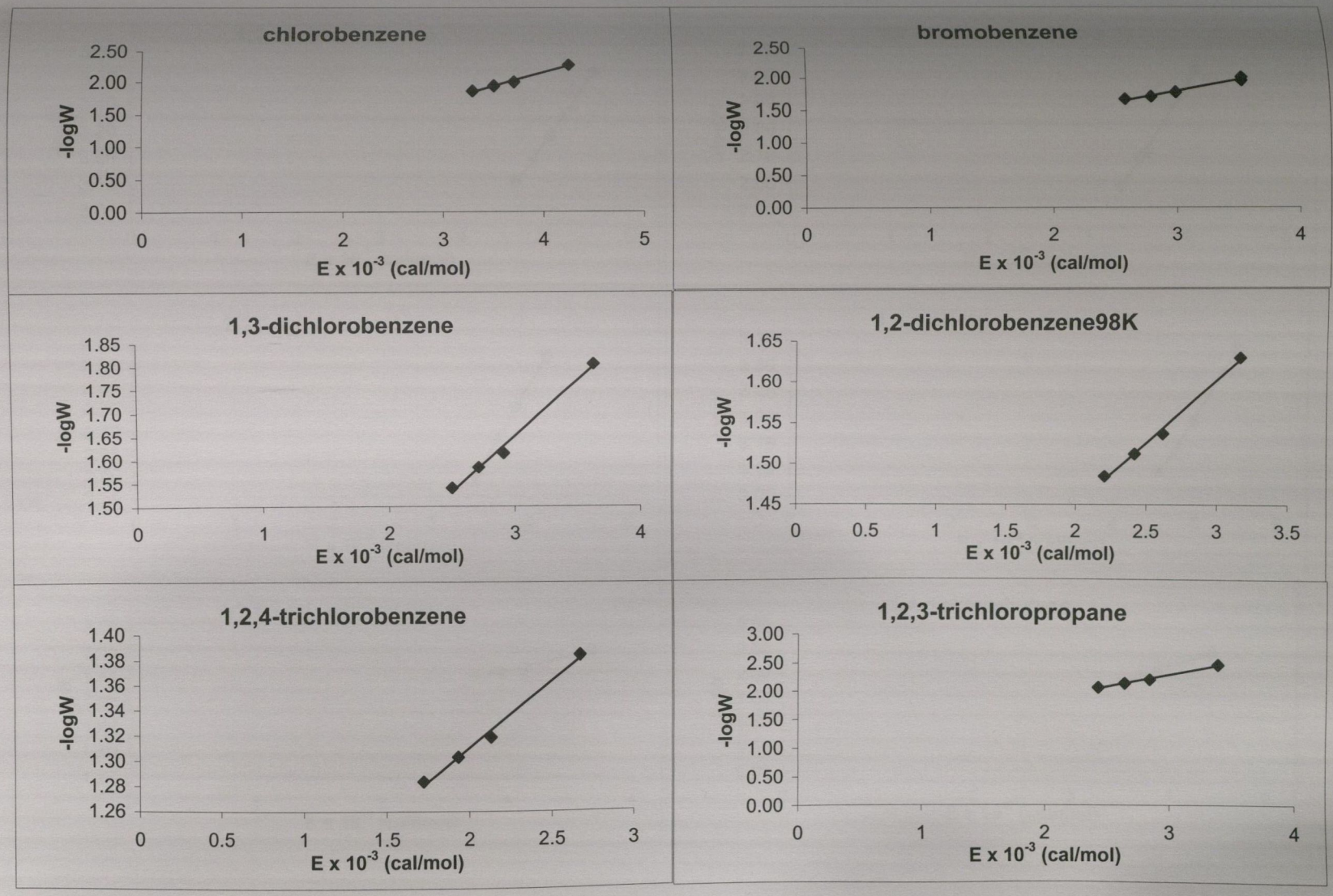

tetrachloroethylene
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
5
E x 10-3 (cal/mol)

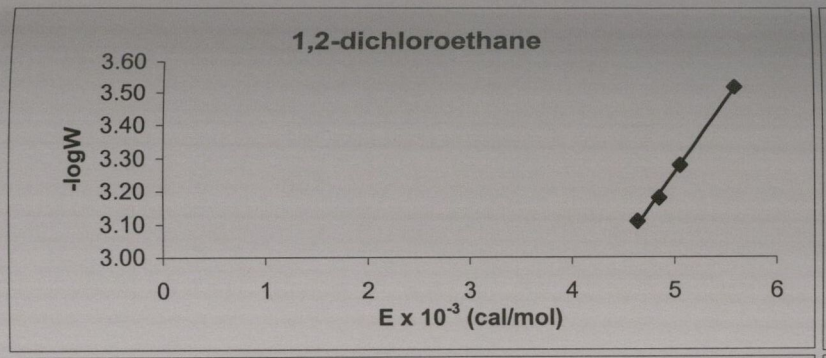

chloro-2-ethanol
-logW
3.30
3.20
3.10
3.00
2.90
2.80
2.70
0
1
2
3
4
E x 10-3 (cal/mol)

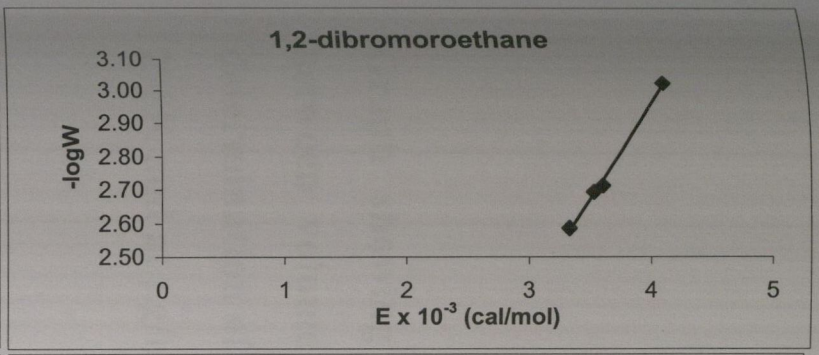

butan-1-ol
-logW
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
E x 10-3 (cal/mol)

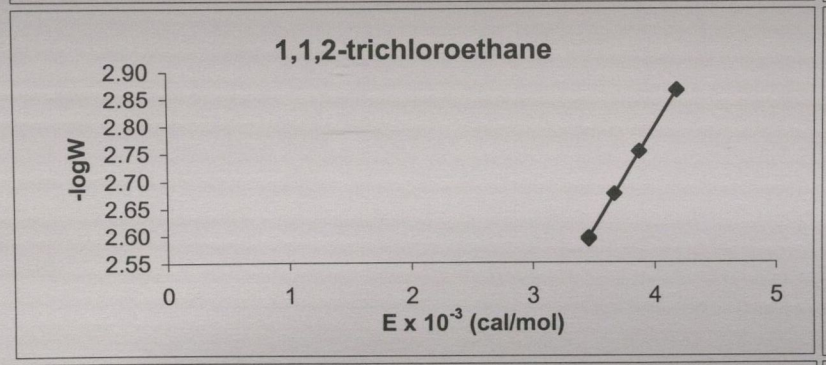

pentan-1-ol
-logW
2.00
1.90
1.80
1.70
1.60
0
1
2
3
4
E x 10-3 (cal/mol)

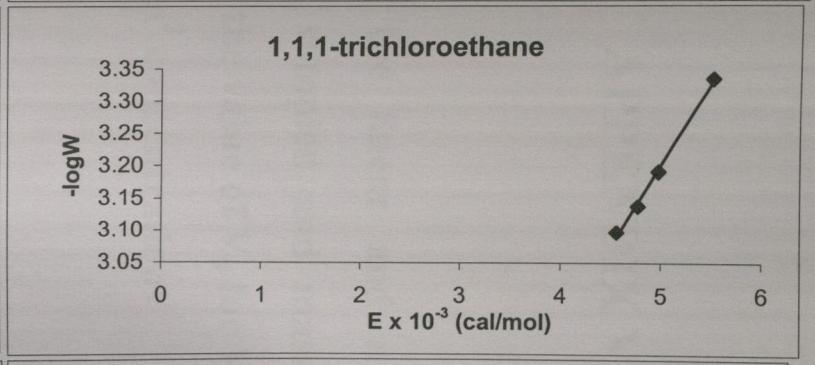

hexan-1-ol
-logW
1.70
1.65
1.60
1.55
1.50
1.45
1.40
1.35
0
1
2
3
4
E x 10-3 (cal/mol)

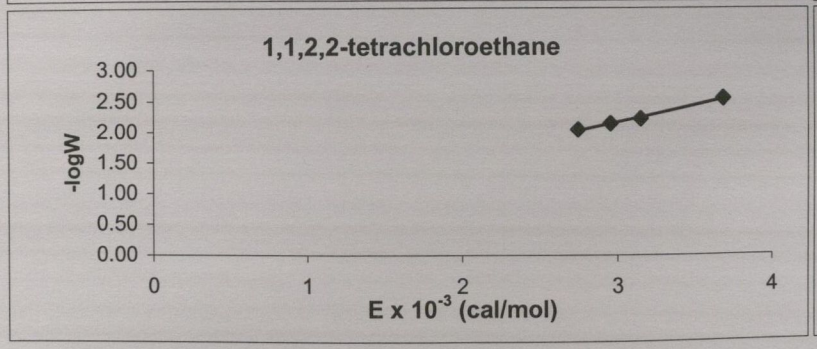

chlorobenzene
-logW
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
5
E x 10-3 (cal/mol)
bromobenzene
-logW
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
E x 10-3 (cal/mol)
1,3-dichlorobenzene
-logW
1.85
1.80
1.75
1.70
1.65
1.60
1.55
1.50
0
1
2
3
4
E x 10-3 (cal/mol)
1,2-dichlorobenzene98K
-logW
1.65
1.60
1.55
1.50
1.45
0
0.5
1
1.5
2
2.5
3
3.5
E x 10-3 (cal/mol)
1,2,4-trichlorobenzene
-logW
1.40
1.38
1.36
1.34
1.32
1.30
1.28
1.26
0
0.5
1
1.5
2
2.5
3
E x 10-3 (cal/mol)
1,2,3-trichloropropane
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
E x 10-3 (cal/mol)

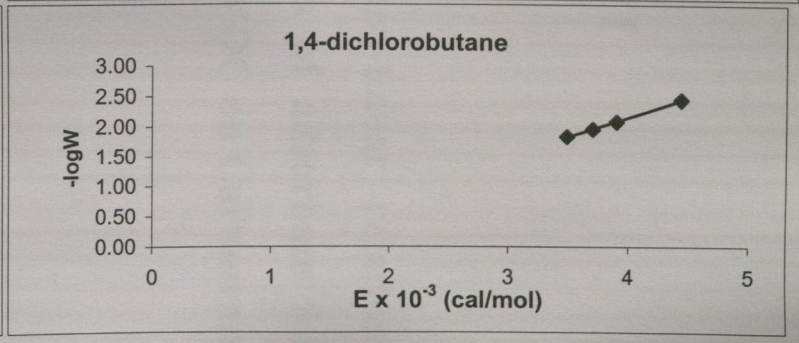

1,2-dichloroethane
-logW
3.60
3.50
3.40
3.30
3.20
3.10
3.00
0
1
2
3
4
5
6
E x 10-3 (cal/mol)


1,2-dibromoroethane
-logW
3.10
3.00
2.90
2.80
2.70
2.60
2.50
0
1
2
3
4
5
E x 10-3 (cal/mol)


1,1,2-trichloroethane
-logW
2.90
2.85
2.80
2.75
2.70
2.65
2.60
2.55
0
1
2
3
4
5
E x 10-3 (cal/mol)

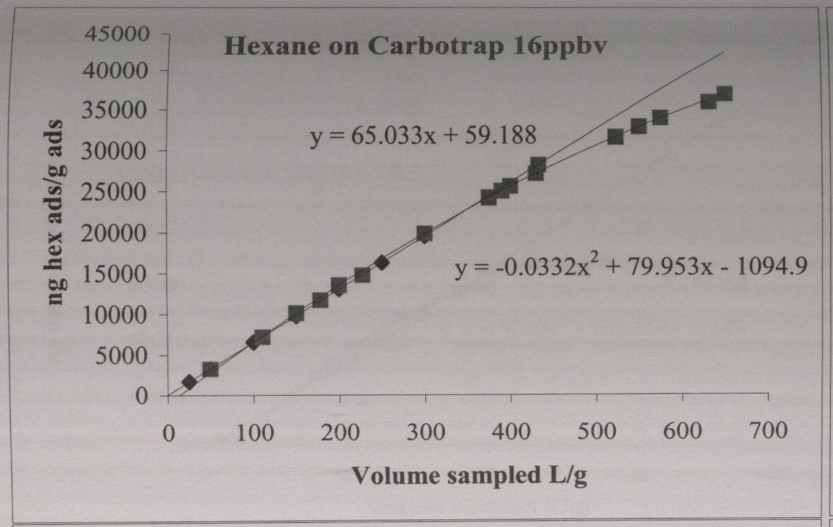

1,1,1-trichloroethane
-logW
3.35
3.30
3.25
3.20
3.15
3.10
3.05
0
1
2
3
4
5
6
E x 10-3 (cal/mol)

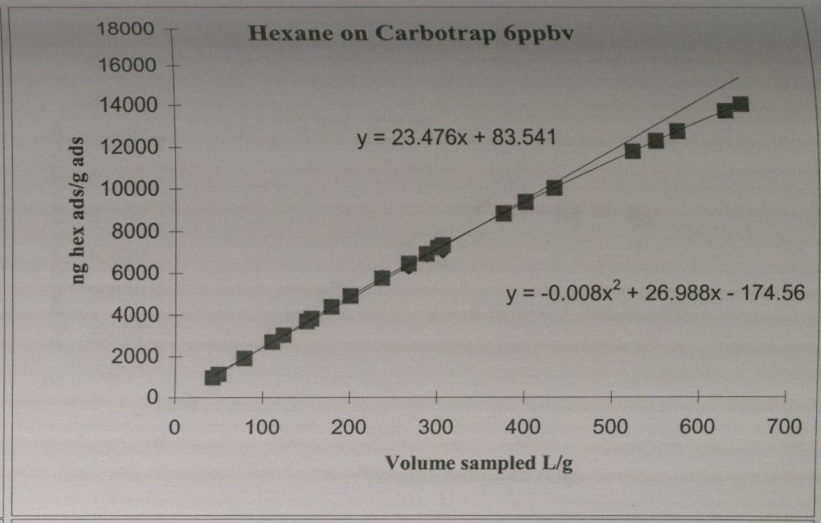

1,1,2,2-tetrachloroethane
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
E x 10-3 (cal/mol)

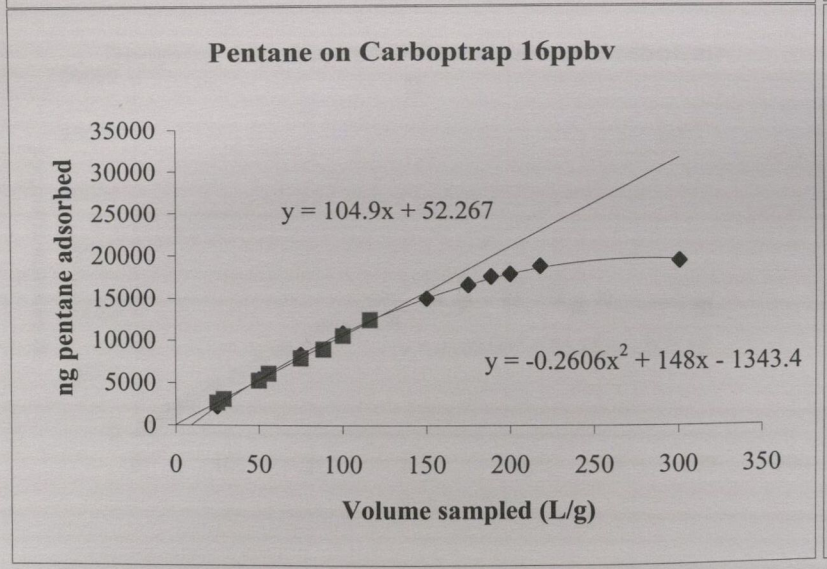

1,4-dichlorobutane
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
5
E x 10-3 (cal/mol)

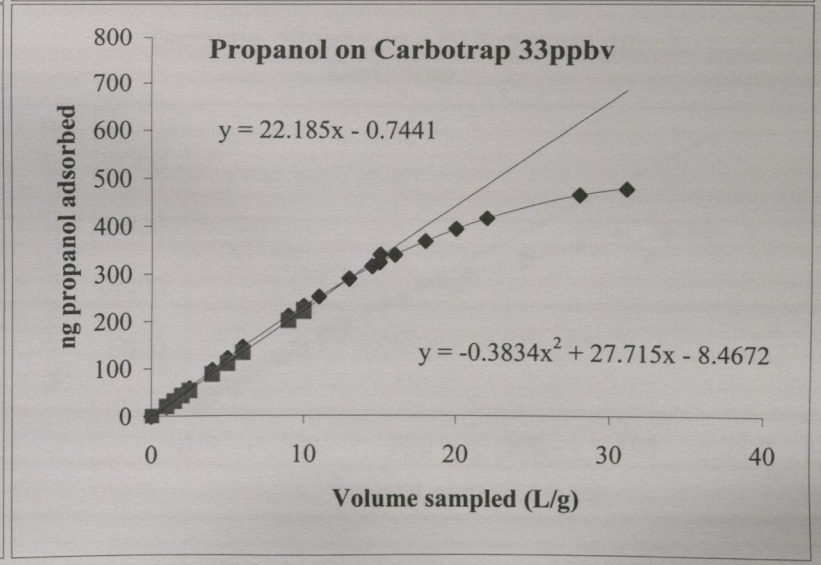
# APPENDIX VI

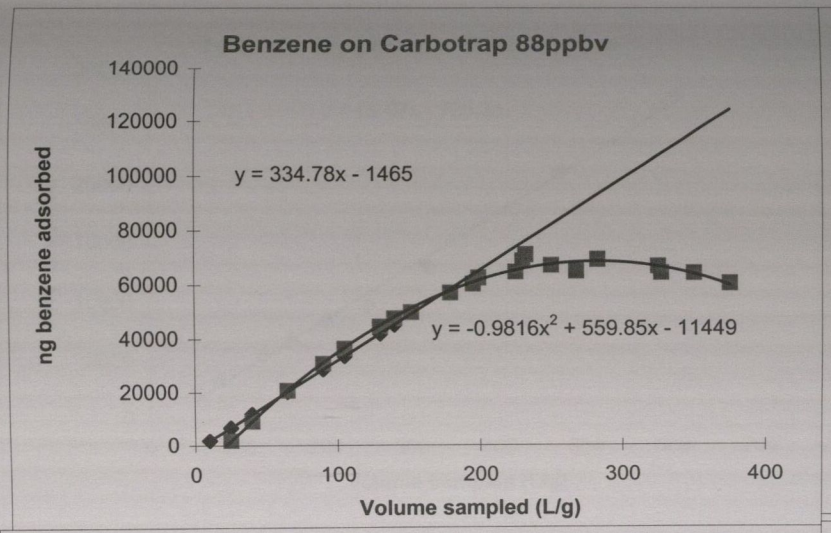
**Graph showing the linear and non-linear relationships between volume sampled and mass of adsorbate for the determination of the value of $V_b$ for VOC on Carbotrap-B at 298K and at $\mu g/m^3$ concentrations**

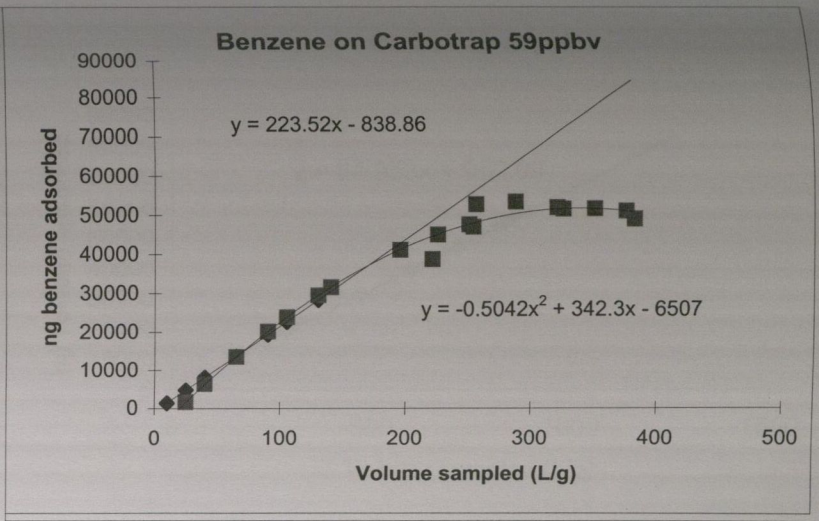

Hexane on Carbotrap 16ppbv
ng hex ads/g ads
y = 65.033x + 59.188
y = -0.0332x² + 79.953x - 1094.9
Volume sampled L/g
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
0
100
200
300
400
500
600
700

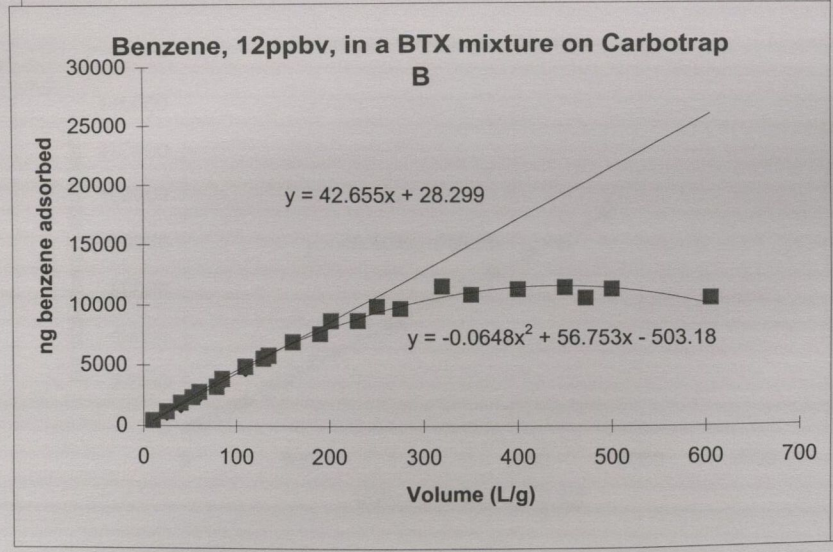

Hexane on Carbotrap 6ppbv
ng hex ads/g ads
y = 23.476x + 83.541
y = -0.008x² + 26.988x - 174.56
Volume sampled L/g
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
0
100
200
300
400
500
600
700

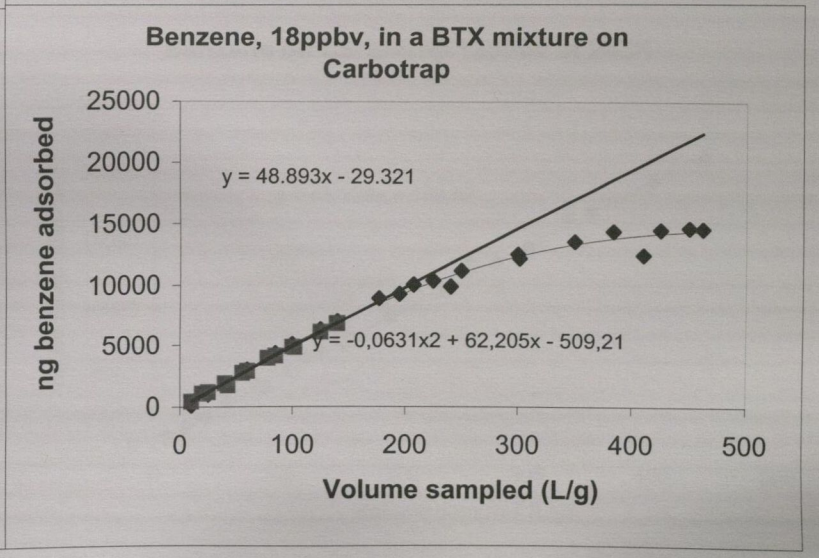

Pentane on Carboptrap 16ppbv
ng pentane adsorbed
y = 104.9x + 52.267
y = -0.2606x² + 148x - 1343.4
Volume sampled (L/g)
0
5000
10000
15000
20000
25000
30000
35000
0
50
100
150
200
250
300
350

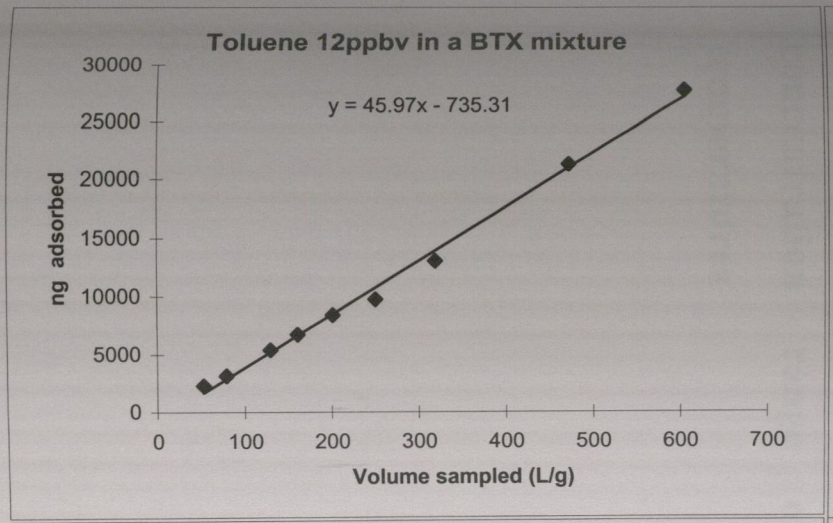

Propanol on Carbotrap 33ppbv
ng propanol adsorbed
y = 22.185x - 0.7441
y = -0.3834x² + 27.715x - 8.4672
Volume sampled (L/g)
0
100
200
300
400
500
600
700
800
0
10
20
30
40

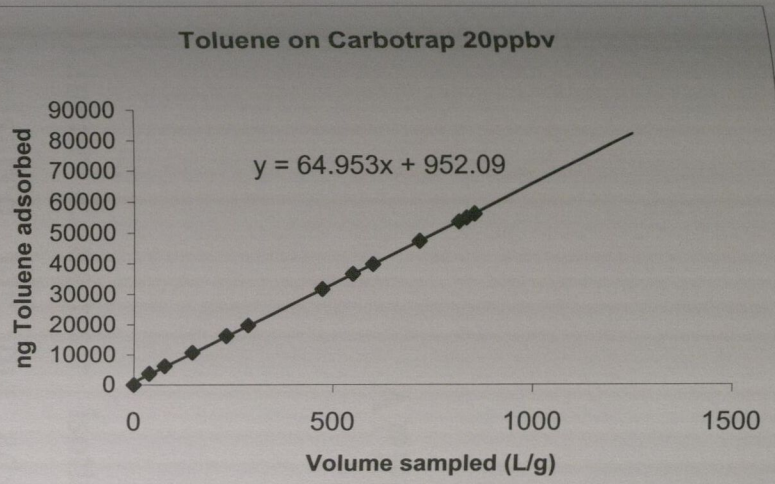

Benzene on Carbotrap 88ppbv
ng benzene adsorbed
140000
120000
100000
80000
60000
40000
20000
0
y = 334.78x - 1465
y = -0.9816x2 + 559.85x - 11449
0
100
200
300
400
Volume sampled (L/g)

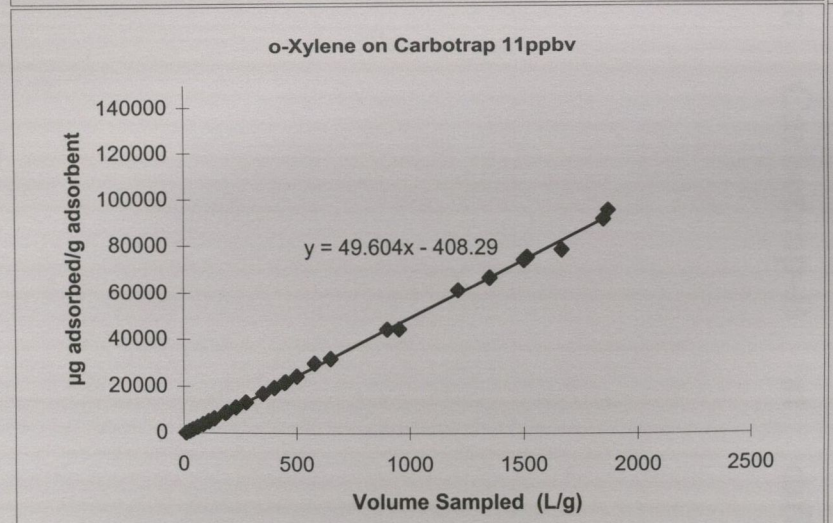

Benzene on Carbotrap 59ppbv
ng benzene adsorbed
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
y = 223.52x - 838.86
y = -0.5042x2 + 342.3x - 6507
0
100
200
300
400
500
Volume sampled (L/g)

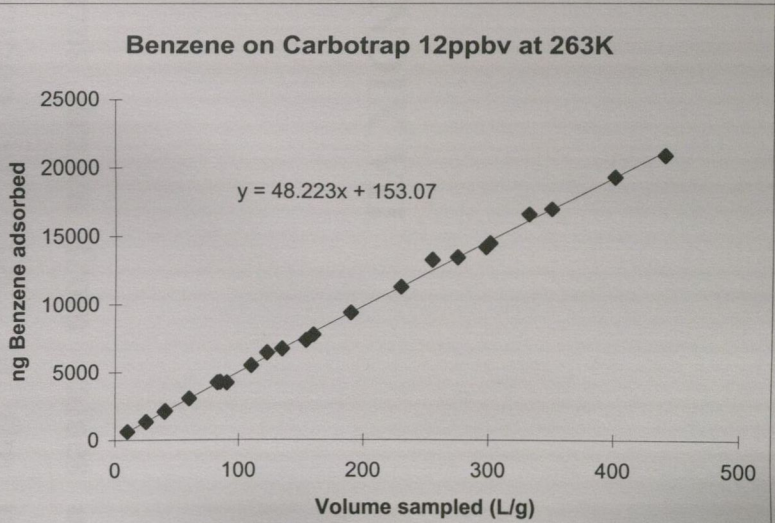

Benzene, 12ppbv, in a BTX mixture on Carbotrap B
ng benzene adsorbed
30000
25000
20000
15000
10000
5000
0
y = 42.655x + 28.299
y = -0.0648x2 + 56.753x - 503.18
0
100
200
300
400
500
600
700
Volume (L/g)


Benzene, 18ppbv, in a BTX mixture on Carbotrap
ng benzene adsorbed
25000
20000
15000
10000
5000
0
y = 48.893x - 29.321
y = -0,0631x2 + 62,205x - 509,21
0
100
200
300
400
500
Volume sampled (L/g)


Toluene 12ppbv in a BTX mixture
y = 45.97x - 735.31
ng adsorbed
Volume sampled (L/g)
0
5000
10000
15000
20000
25000
30000
0
100
200
300
400
500
600
700

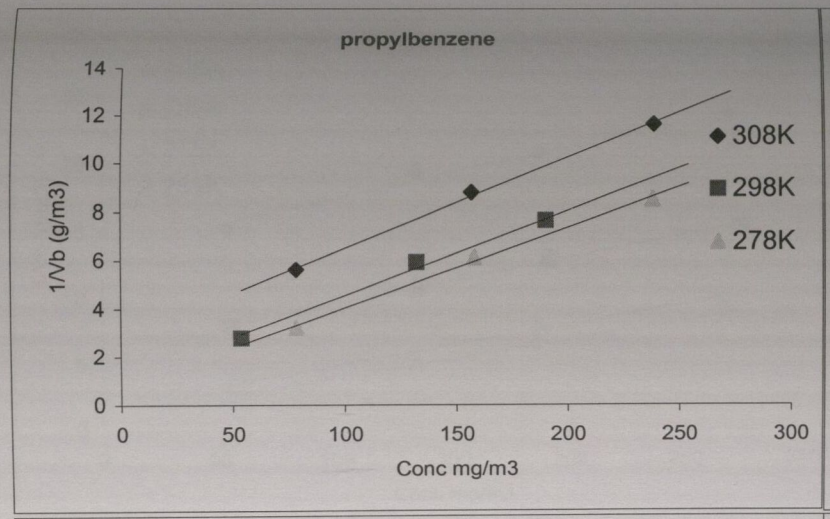

Toluene on Carbotrap 20ppbv
y = 64.953x + 952.09
ng Toluene adsorbed
Volume sampled (L/g)
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
0
500
1000
1500

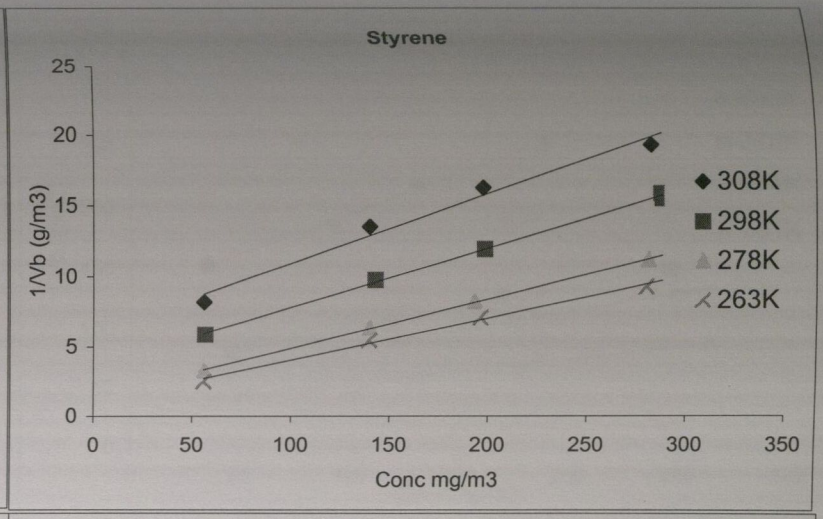

o-Xylene on Carbotrap 11ppbv
y = 49.604x - 408.29
µg adsorbed/g adsorbent
Volume Sampled (L/g)
0
20000
40000
60000
80000
100000
120000
140000
0
500
1000
1500
2000
2500

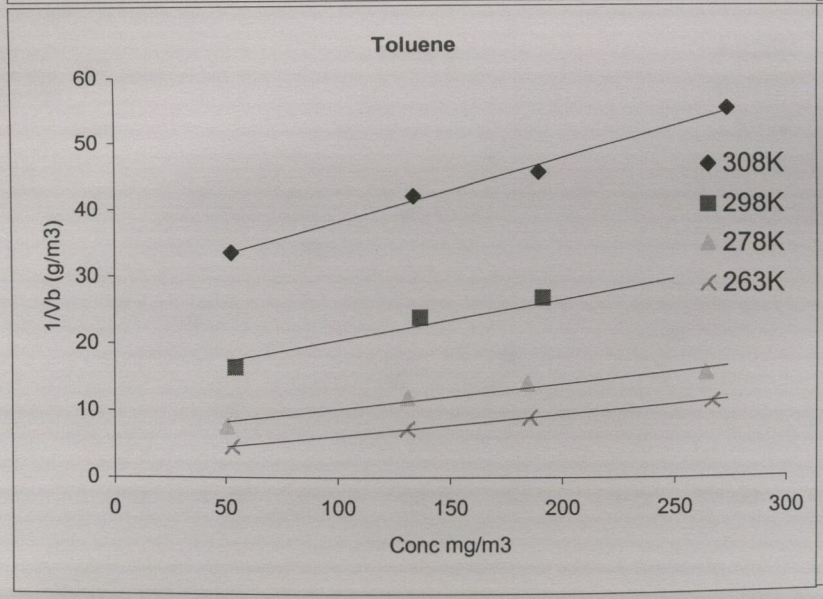

Benzene on Carbotrap 12ppbv at 263K
y = 48.223x + 153.07
ng Benzene adsorbed
Volume sampled (L/g)
0
5000
10000
15000
20000
25000
0
100
200
300
400
500

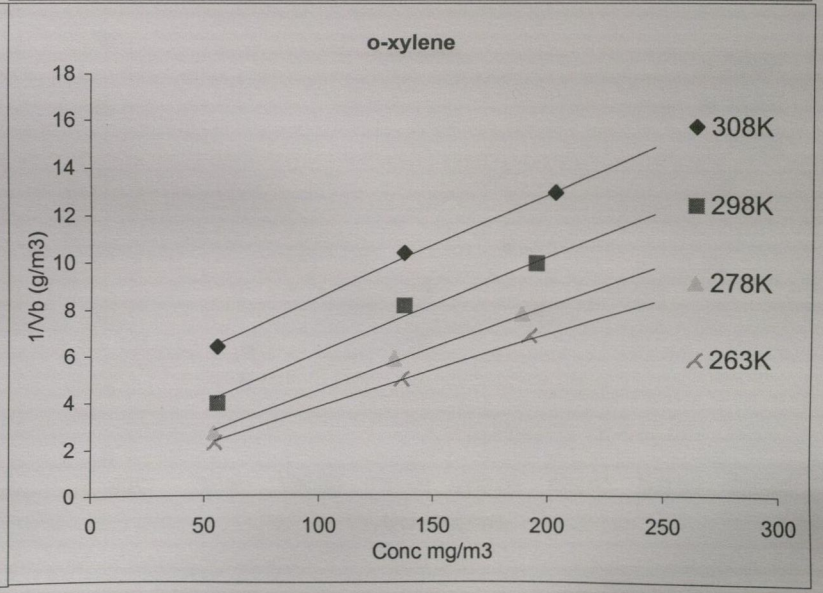
# APPENDIX VII

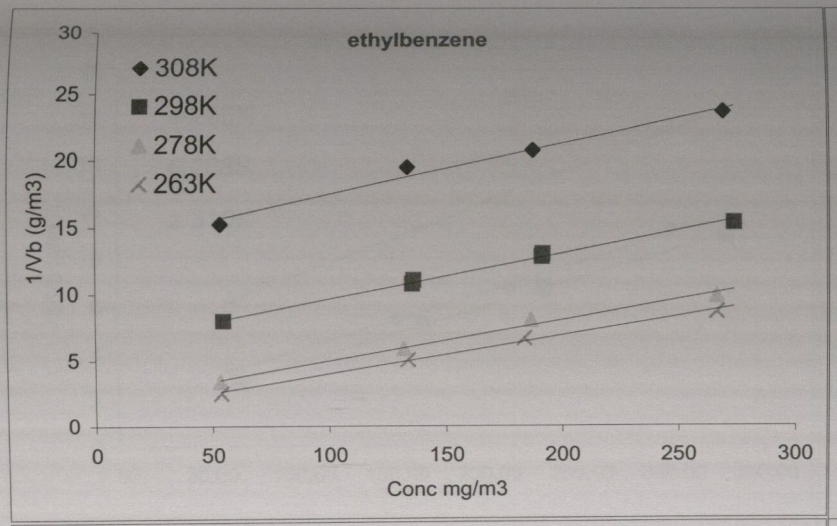
**Linear Langmuir isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the mg/m$^3$ concentration range on Carbotrap-B at different temperatures**

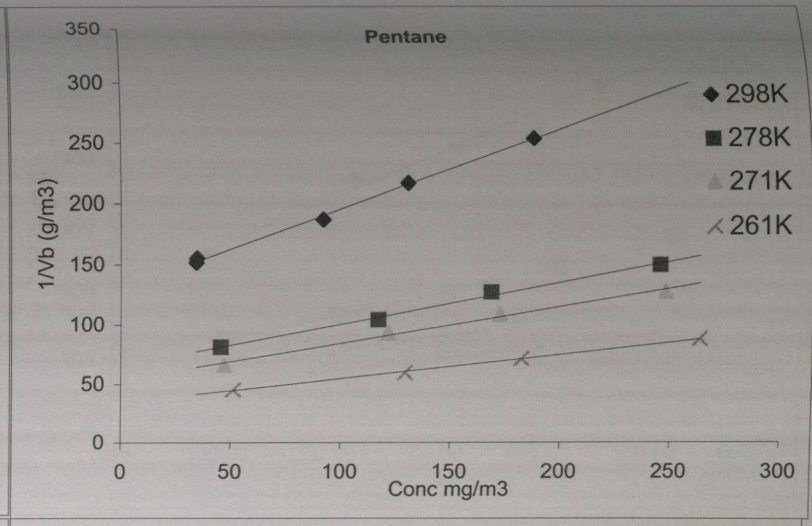

propylbenzene
1/Vb (g/m3)
Conc mg/m3
308K
298K
278K
0
2
4
6
8
10
12
14
0
50
100
150
200
250
300

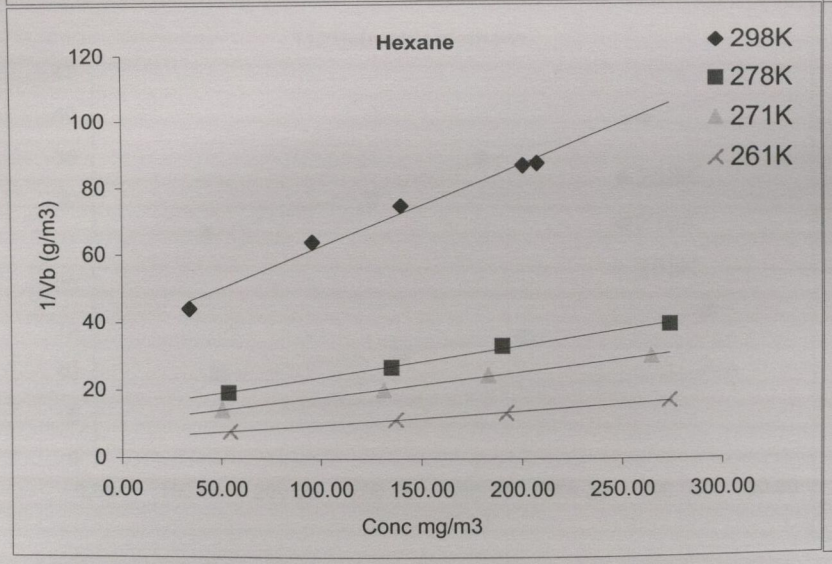

Styrene
1/Vb (g/m3)
Conc mg/m3
308K
298K
278K
263K
0
5
10
15
20
25
0
50
100
150
200
250
300
350

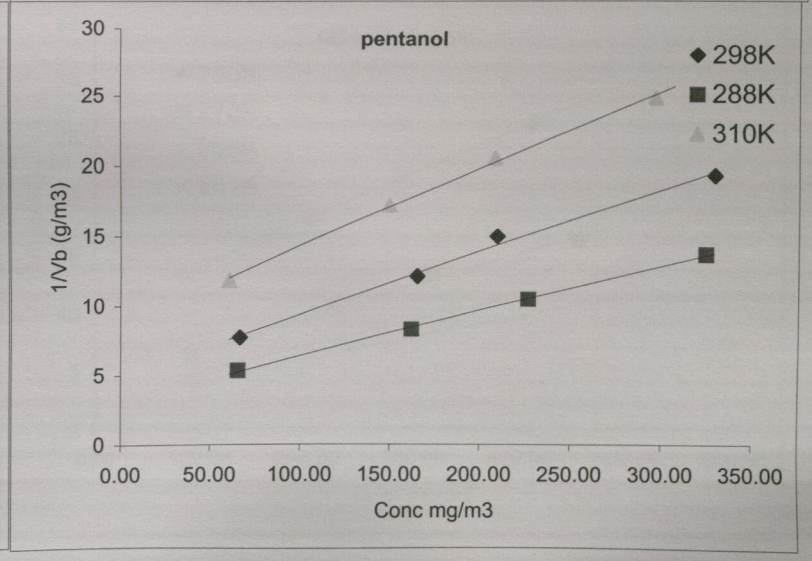

Toluene
1/Vb (g/m3)
Conc mg/m3
308K
298K
278K
263K
0
10
20
30
40
50
60
0
50
100
150
200
250
300

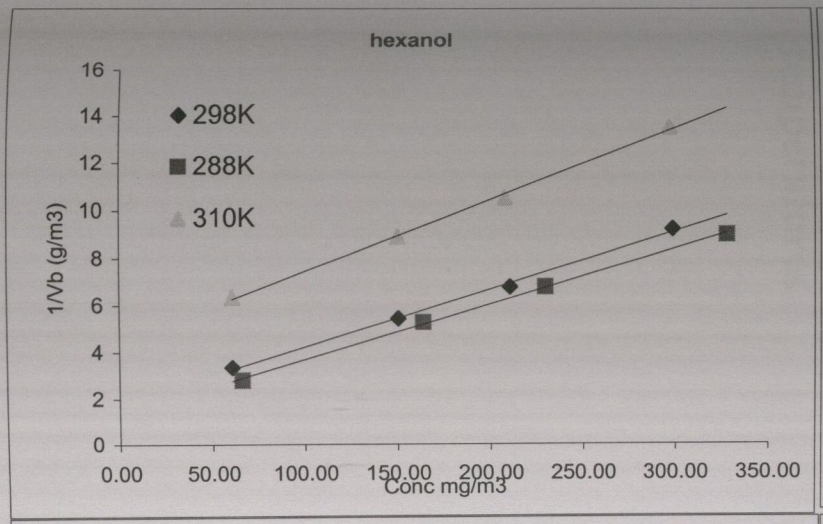

o-xylene
1/Vb (g/m3)
Conc mg/m3
308K
298K
278K
263K
0
2
4
6
8
10
12
14
16
18
0
50
100
150
200
250
300

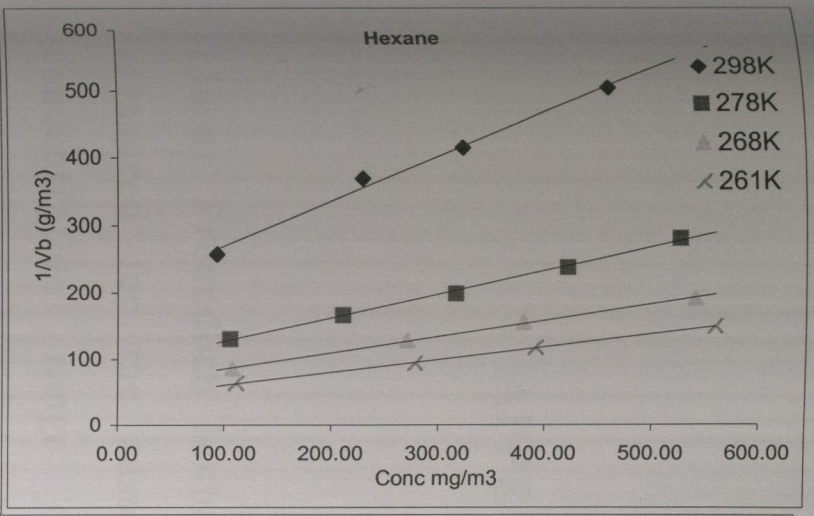

ethylbenzene
308K
298K
278K
263K
1/Vb (g/m3)
Conc mg/m3
0
5
10
15
20
25
30
0
50
100
150
200
250
300

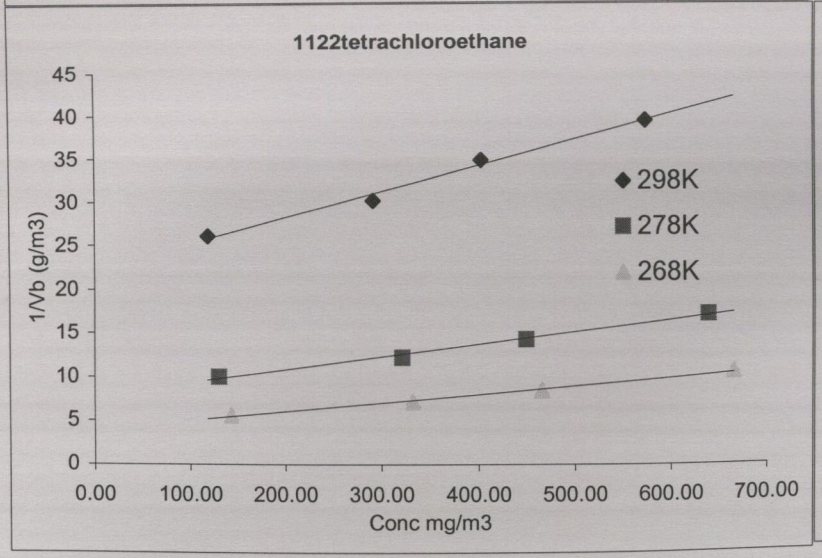

Pentane
298K
278K
271K
261K
1/Vb (g/m3)
Conc mg/m3
0
50
100
150
200
250
300
350
0
50
100
150
200
250
300

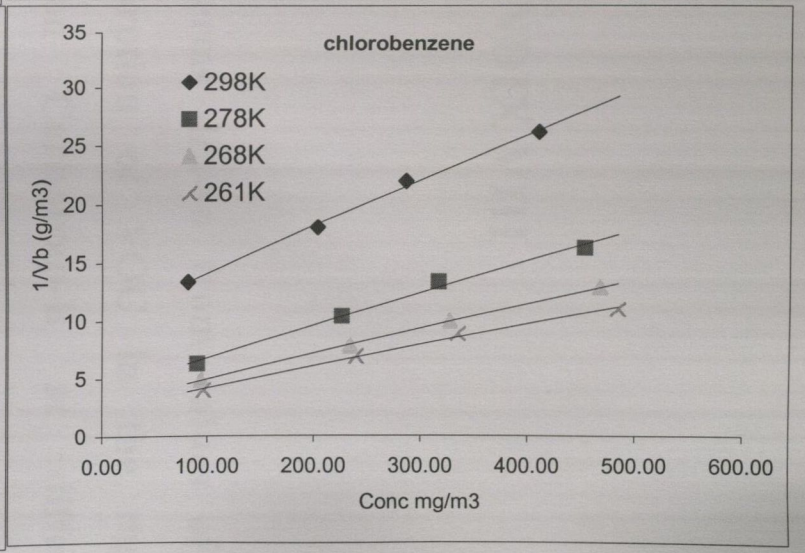

Hexane
298K
278K
271K
261K
1/Vb (g/m3)
Conc mg/m3
0
20
40
60
80
100
120
0.00
50.00
100.00
150.00
200.00
250.00
300.00


pentanol
298K
288K
310K
1/Vb (g/m3)
Conc mg/m3
0
5
10
15
20
25
30
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00


hexanol
298K
288K
310K
1/Vb (g/m3)
Conc mg/m3
0
2
4
6
8
10
12
14
16
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00

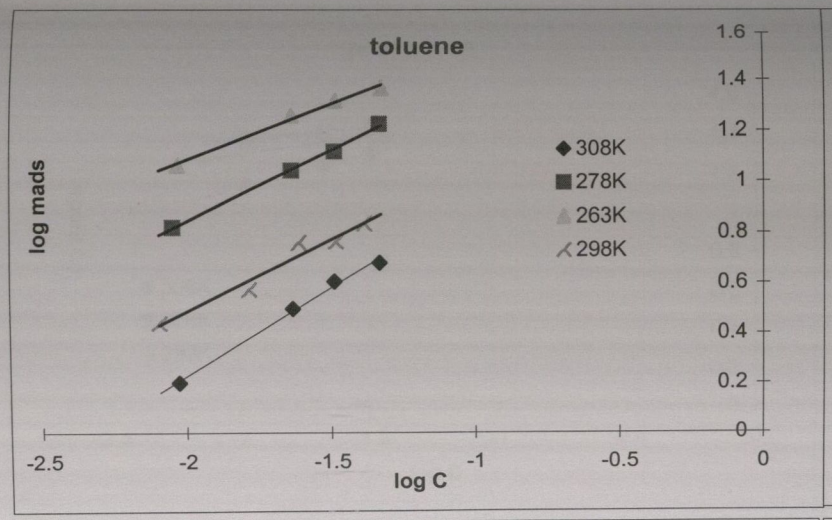

Hexane
298K
278K
268K
261K
1/Vb (g/m3)
Conc mg/m3
0
100
200
300
400
500
600
0.00
100.00
200.00
300.00
400.00
500.00
600.00

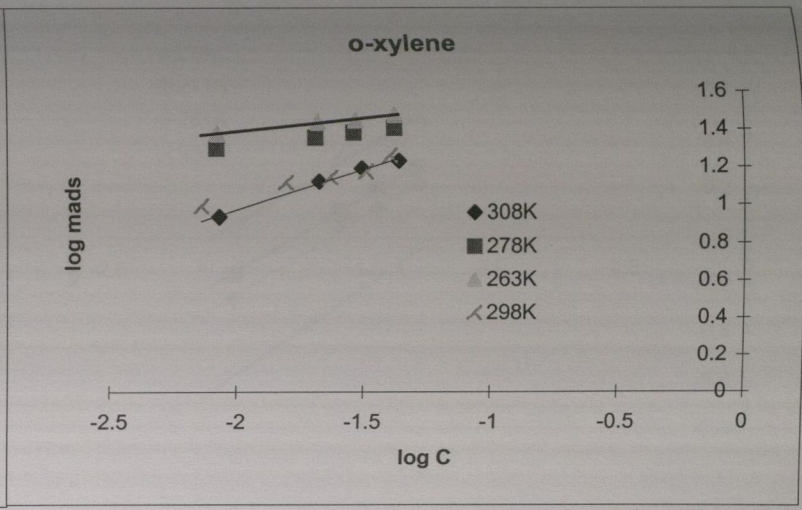

1122tetrachloroethane
298K
278K
268K
1/Vb (g/m3)
Conc mg/m3
0
5
10
15
20
25
30
35
40
45
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00

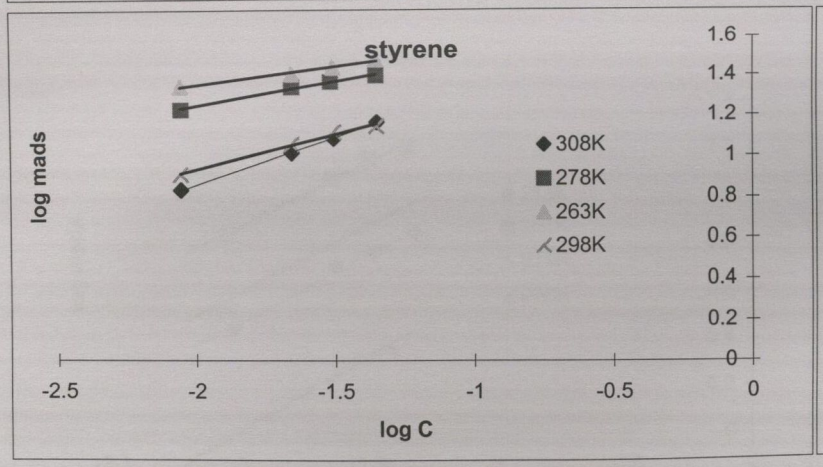

chlorobenzene
298K
278K
268K
261K
1/Vb (g/m3)
Conc mg/m3
0
5
10
15
20
25
30
35
0.00
100.00
200.00
300.00
400.00
500.00
600.00

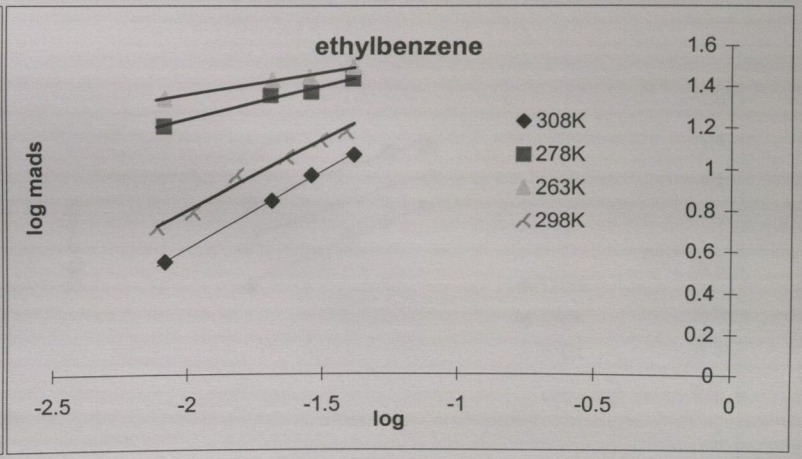
# APPENDIX VIII

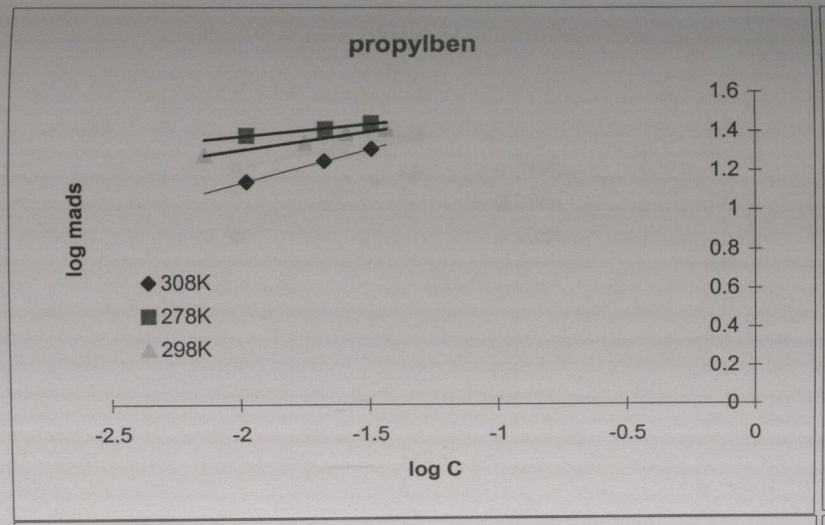
**Linear Freundlich isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the mg/m$^3$ concentration range on Carbotrap-B at different temperatures**

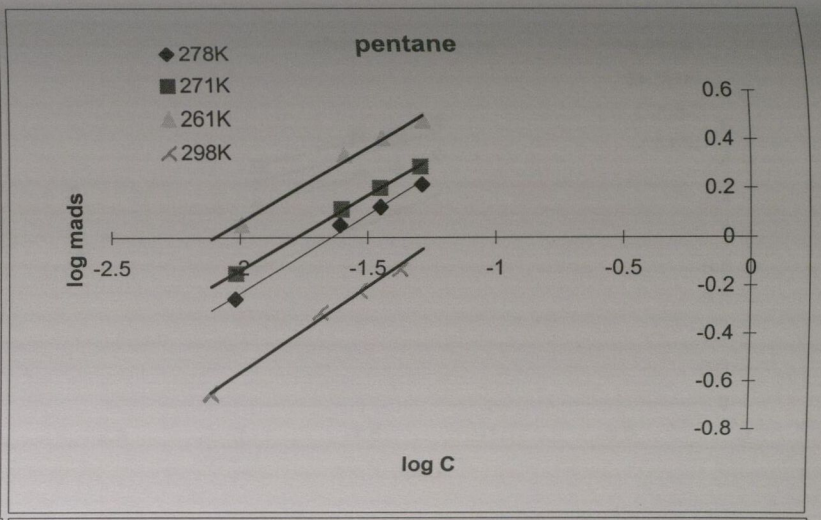

toluene
log mads
log C
308K
278K
263K
298K
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

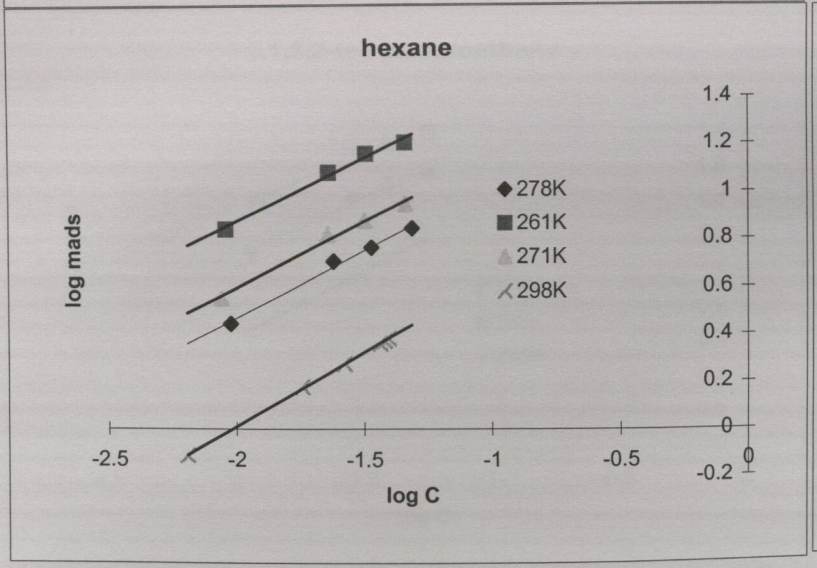

o-xylene
log mads
log C
308K
278K
263K
298K
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

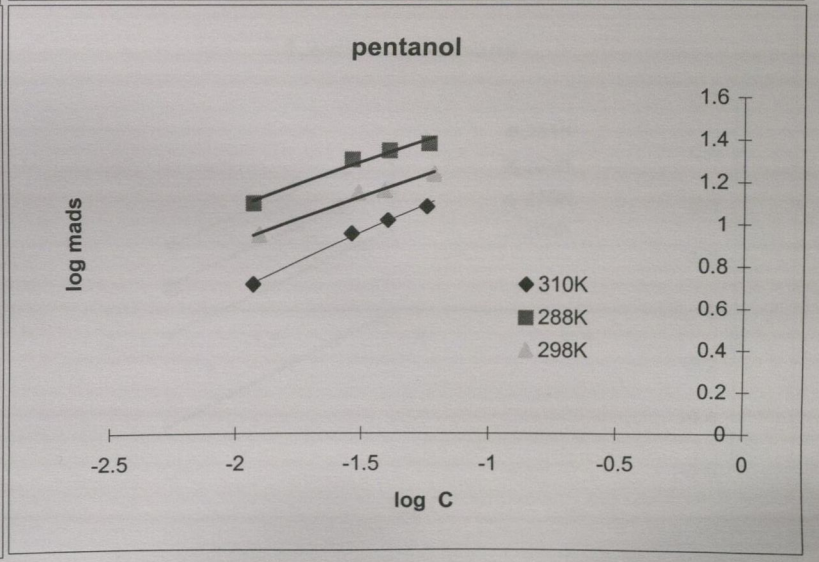

styrene
log mads
log C
308K
278K
263K
298K
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

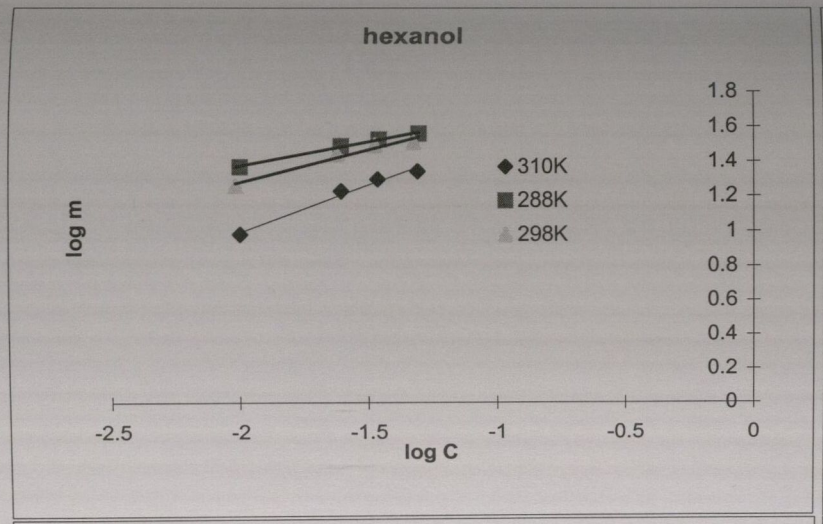

ethylbenzene
log mads
log
308K
278K
263K
298K
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

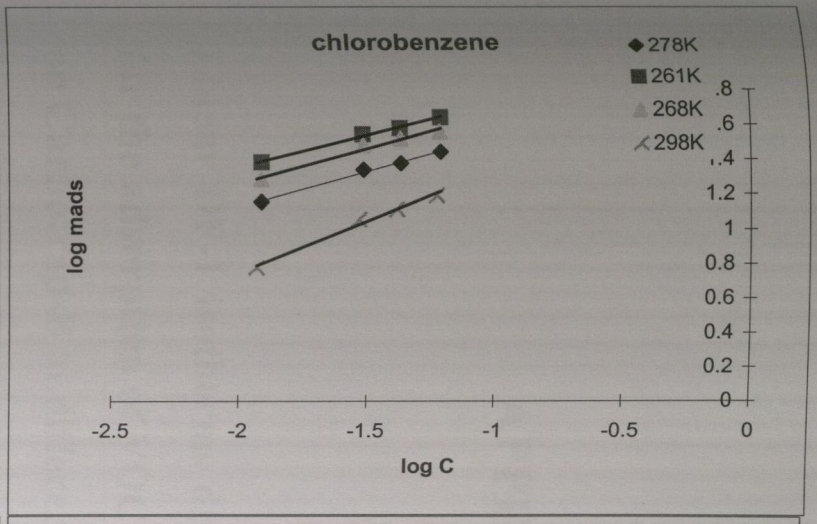

propylben
log mads
log C
308K
278K
298K
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

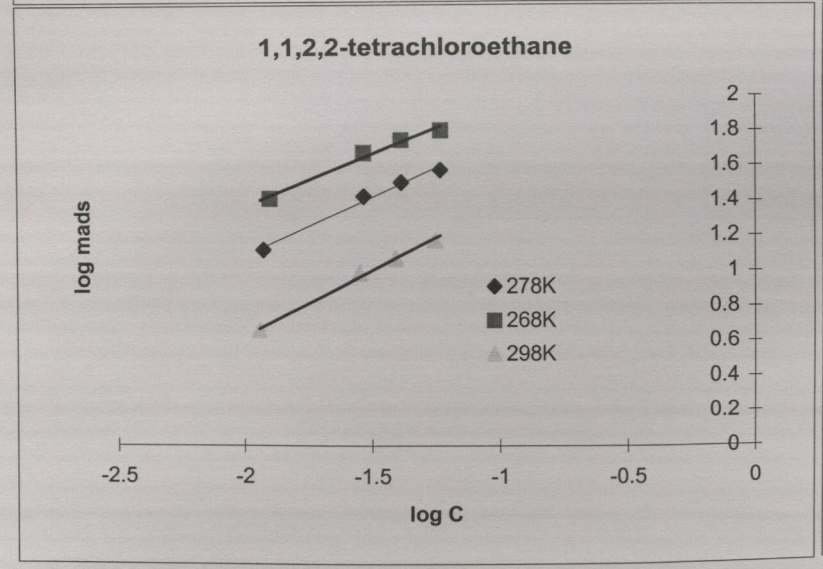

pentane
278K
271K
261K
298K
log mads
log C
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-2.5
-1.5
-1
-0.5
0

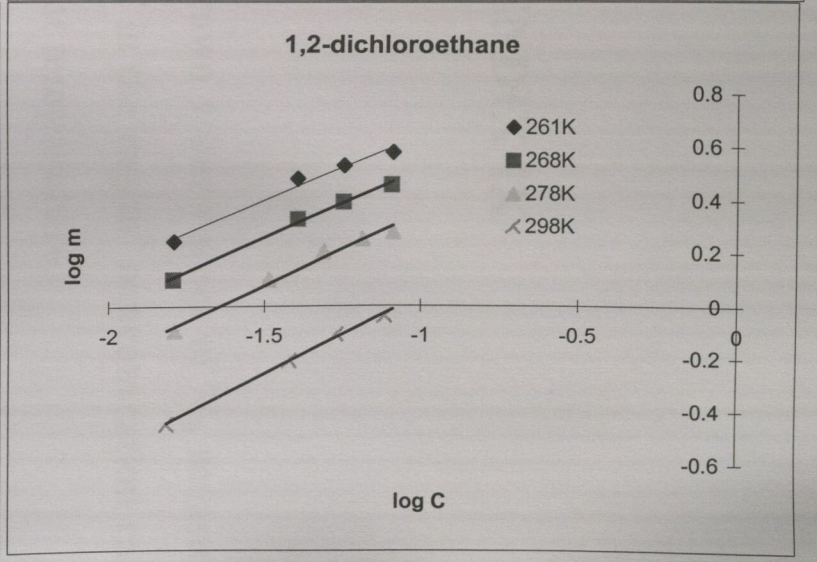

hexane
log mads
log C
278K
261K
271K
298K
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-2.5
-2
-1.5
-1
-0.5
0


pentanol
log mads
log C
310K
288K
298K
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0


hexanol
log m
log C
310K
288K
298K
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

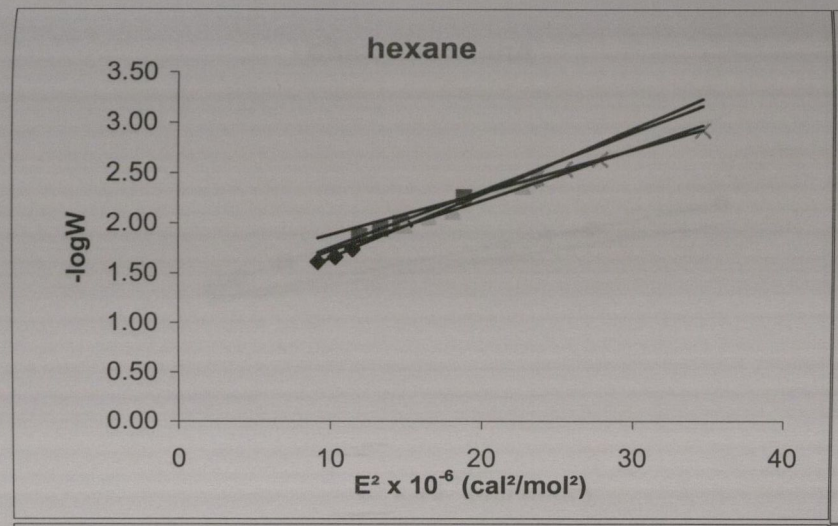

chlorobenzene
log mads
log C
278K
261K
268K
298K
.8
.6
.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

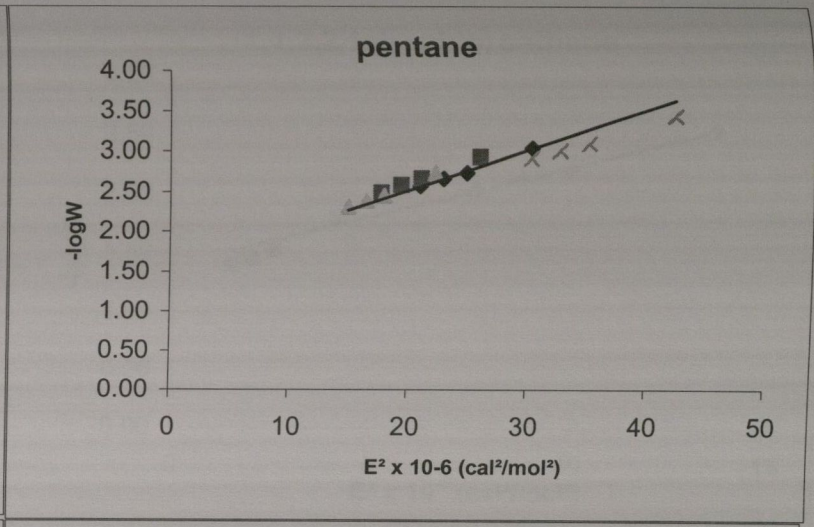

1,1,2,2-tetrachloroethane
log mads
log C
278K
268K
298K
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-2.5
-2
-1.5
-1
-0.5
0

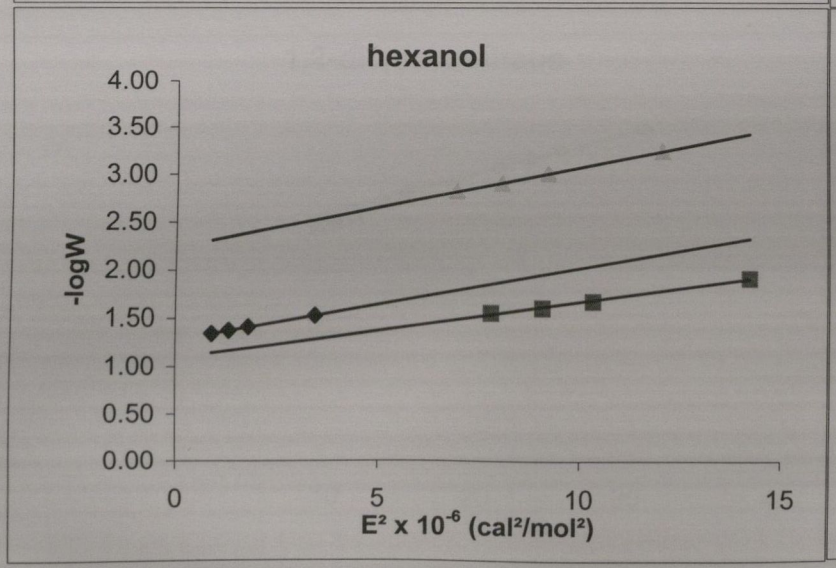

1,2-dichloroethane
log m
log C
261K
268K
278K
298K
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-2
-1.5
-1
-0.5
0

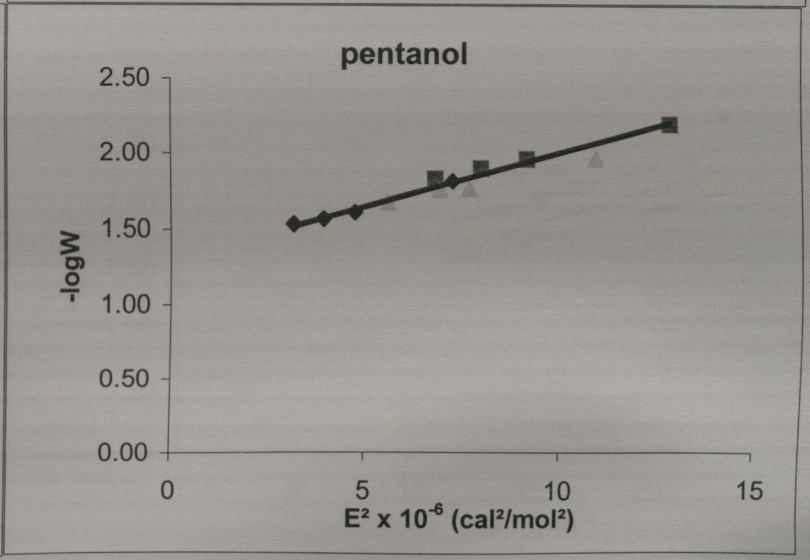
# APPENDIX IX

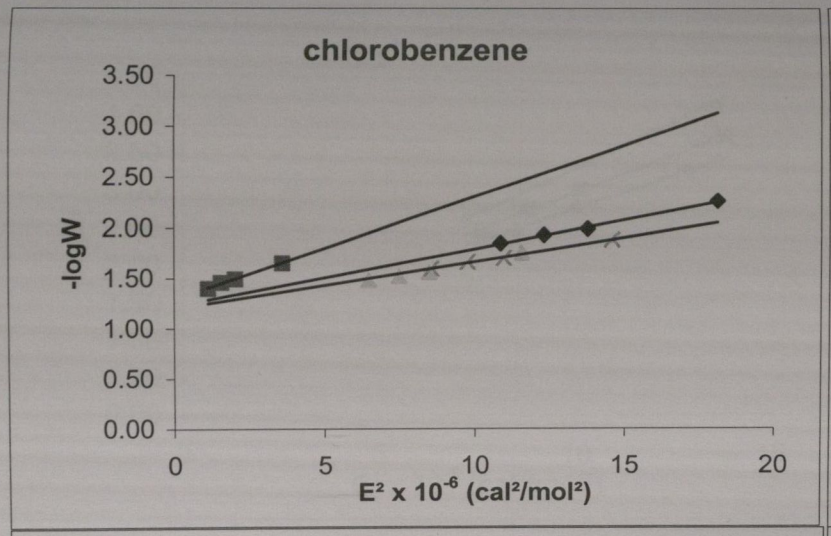
**Linear DP-1 isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the mg/m$^3$ concentration range on Carbotrap-B at different temperatures**

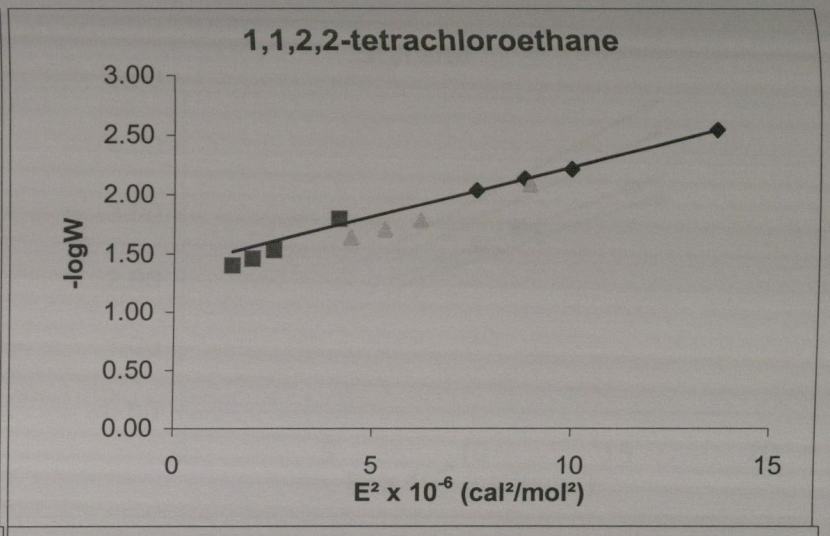

hexane
-logW
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
10
20
30
40
E² x 10⁻⁶ (cal²/mol²)

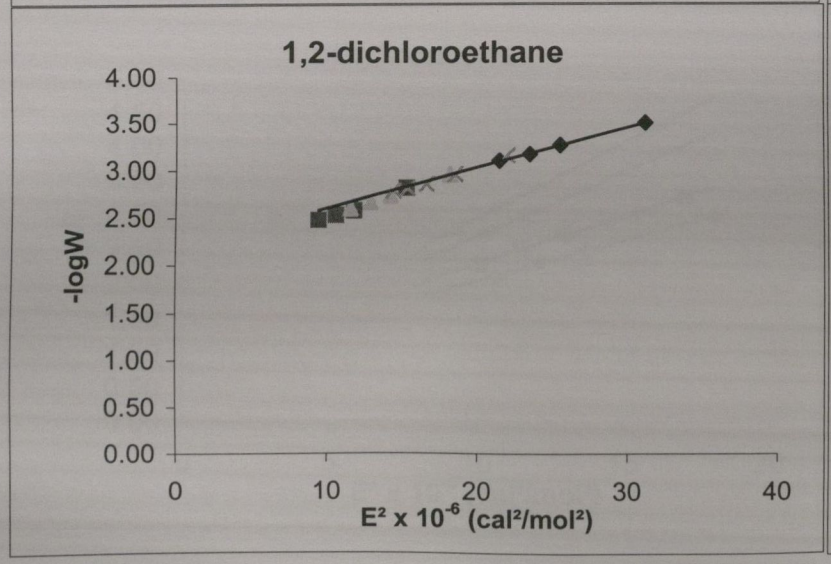

pentane
-logW
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
10
20
30
40
50
E² x 10-6 (cal²/mol²)

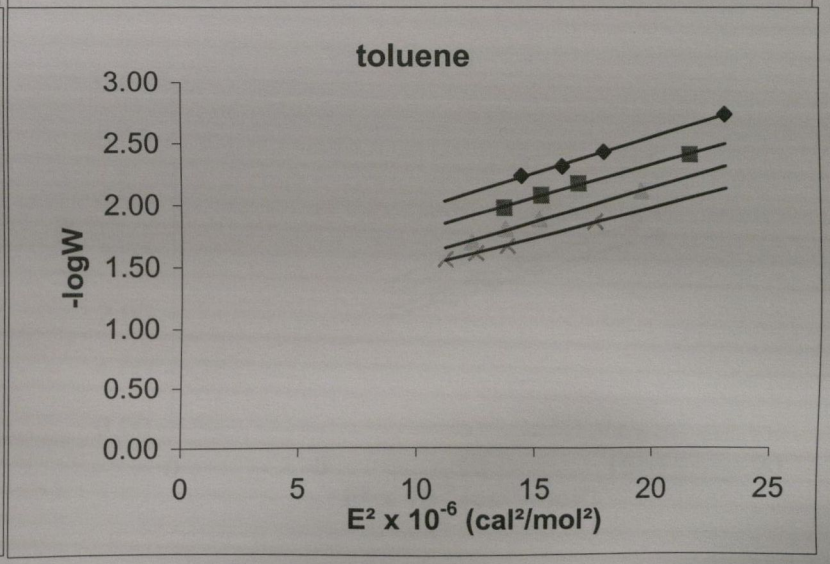

hexanol
-logW
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
E² x 10⁻⁶ (cal²/mol²)

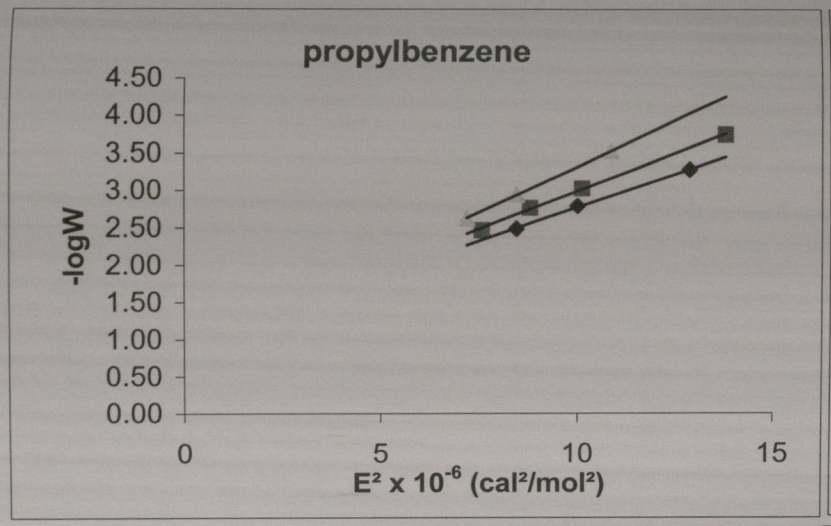

pentanol
-logW
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
E² x 10⁻⁶ (cal²/mol²)

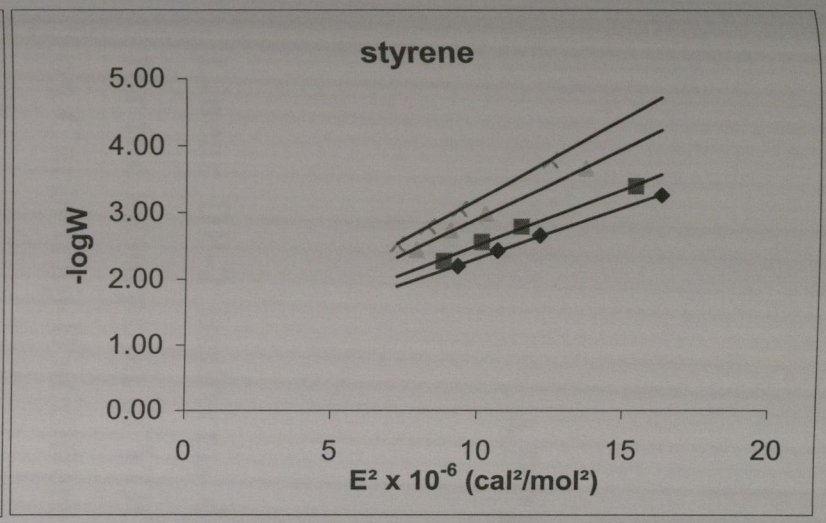

chlorobenzene
-logW
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

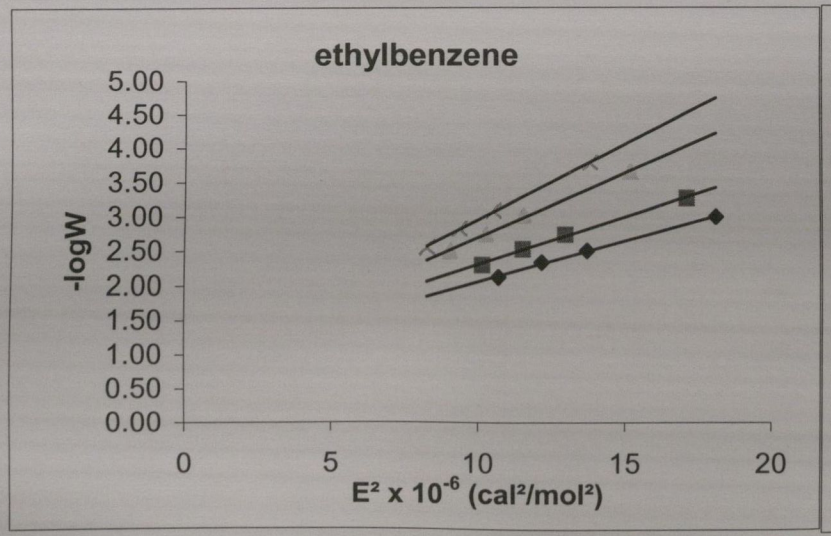

1,1,2,2-tetrachloroethane
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
E² x 10⁻⁶ (cal²/mol²)

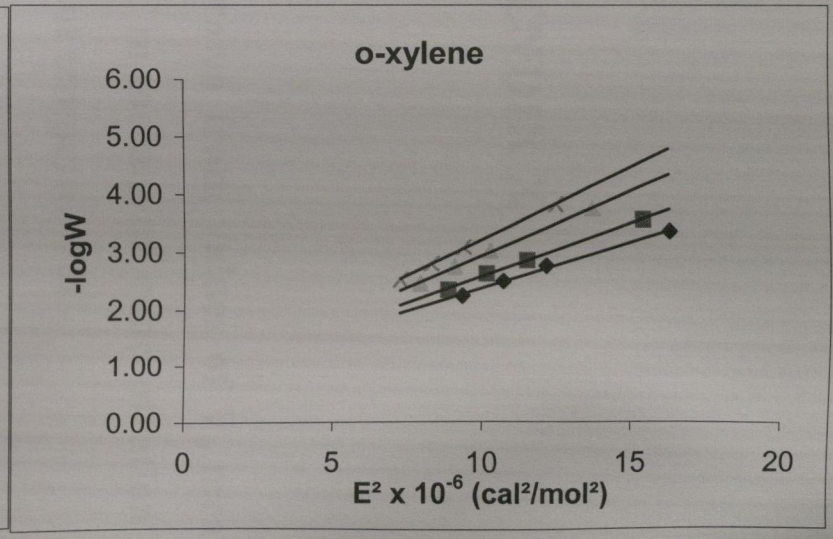

1,2-dichloroethane
-logW
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
10
20
30
40
E² x 10⁻⁶ (cal²/mol²)


toluene
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
20
25
E² x 10⁻⁶ (cal²/mol²)


propylbenzene
-logW
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
E² x 10⁻⁶ (cal²/mol²)

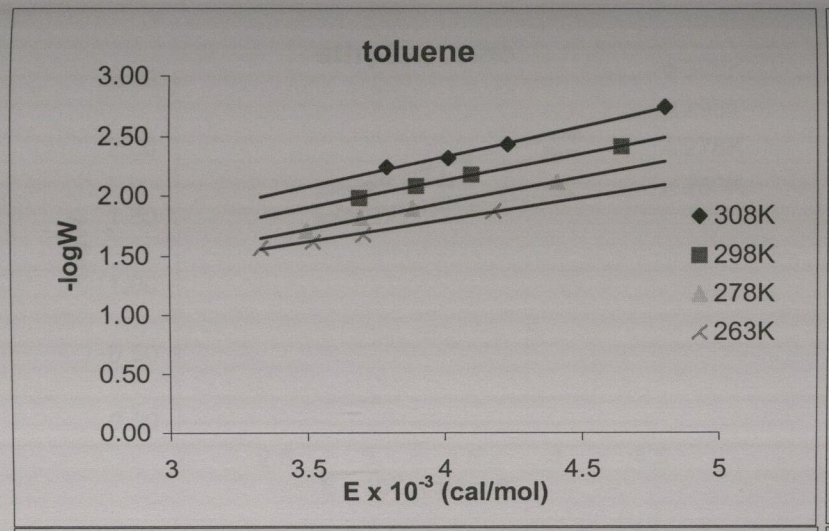

styrene
-logW
5.00
4.00
3.00
2.00
1.00
0.00
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

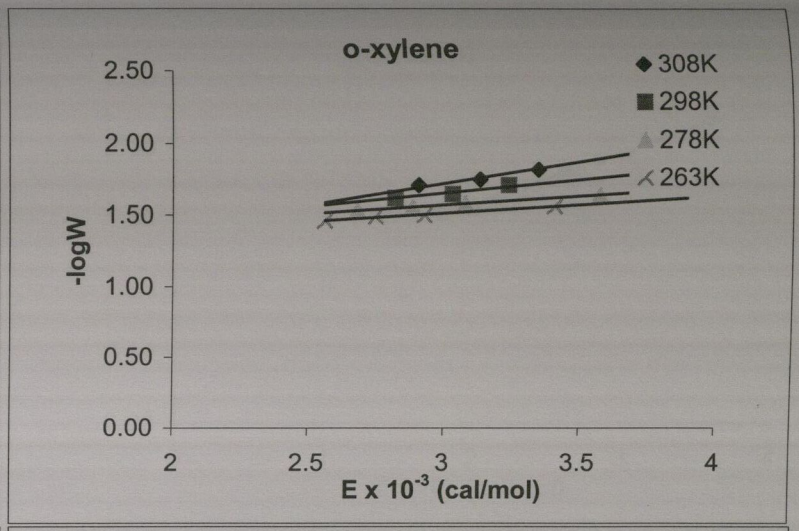

ethylbenzene
-logW
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

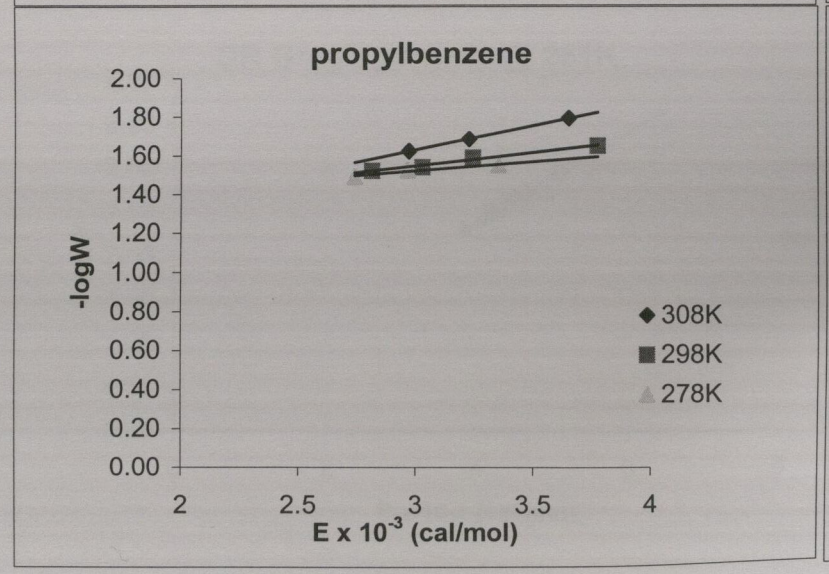

o-xylene
-logW
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0
5
10
15
20
E² x 10⁻⁶ (cal²/mol²)

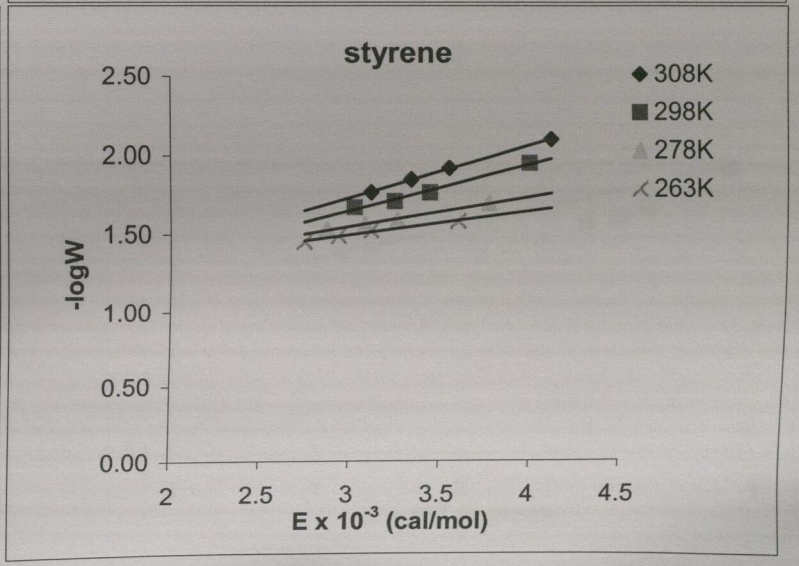
# APPENDIX X

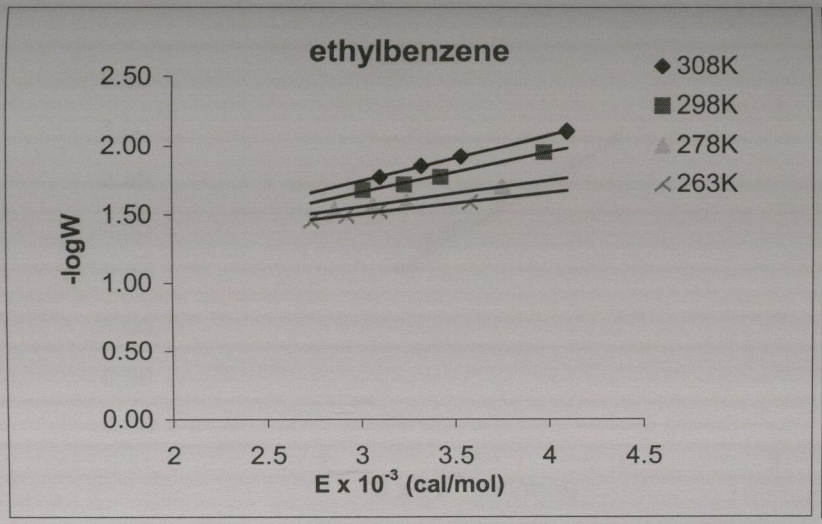
**Linear DP-2 isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the mg/m$^3$ concentration range on Carbotrap-B at different temperatures**

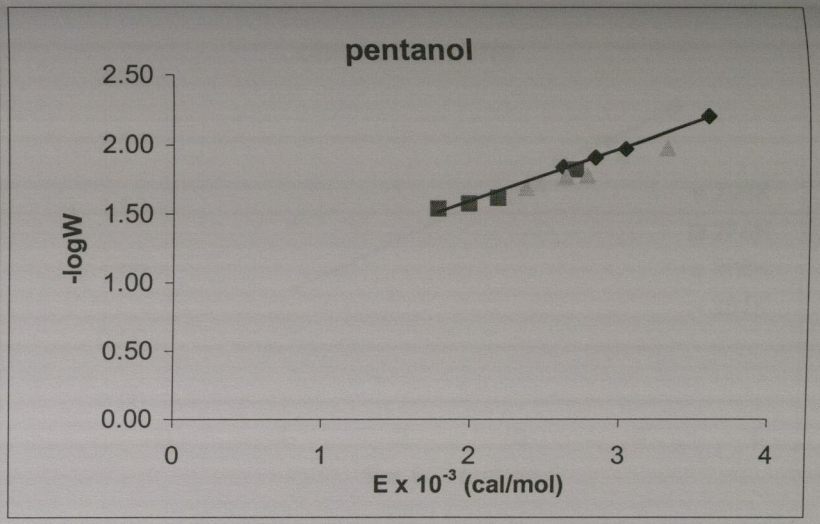

toluene
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
3
3.5
4
4.5
5
E x 10-3 (cal/mol)
308K
298K
278K
263K

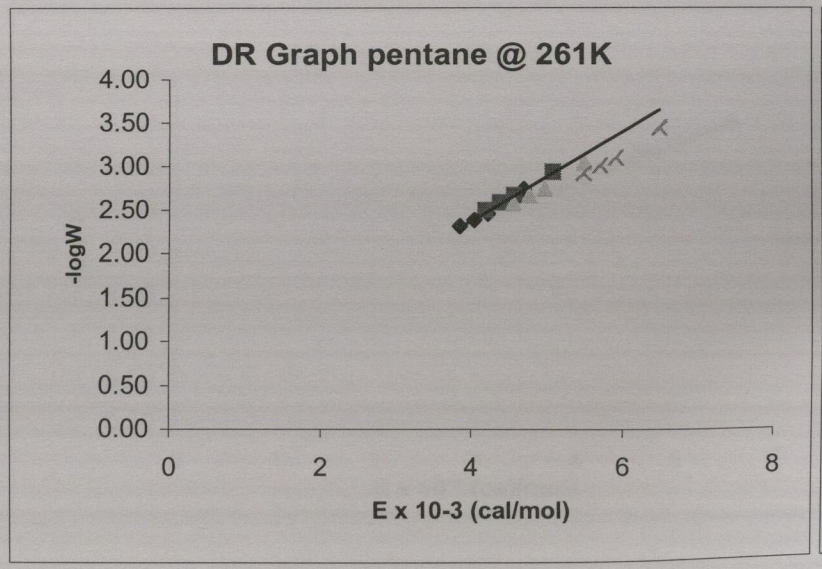

o-xylene
-logW
2.50
2.00
1.50
1.00
0.50
0.00
2
2.5
3
3.5
4
E x 10-3 (cal/mol)
308K
298K
278K
263K

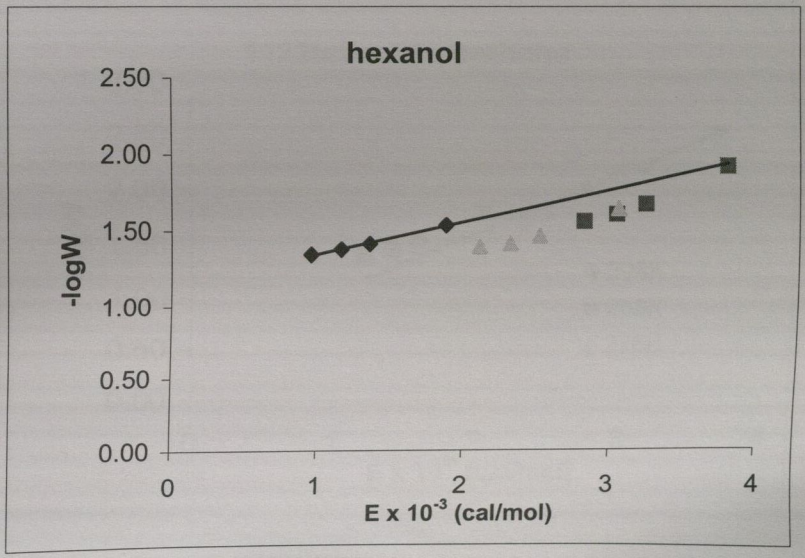

propylbenzene
-logW
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
2
2.5
3
3.5
4
E x 10-3 (cal/mol)
308K
298K
278K

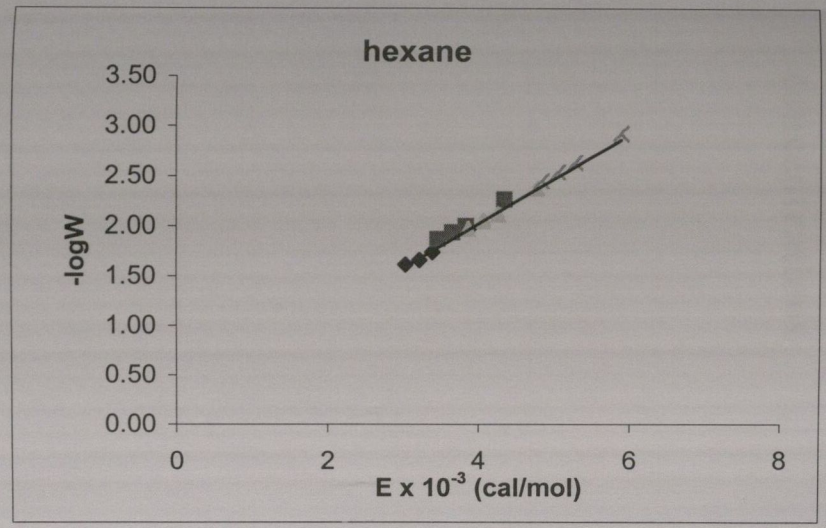

styrene
-logW
2.50
2.00
1.50
1.00
0.50
0.00
2
2.5
3
3.5
4
4.5
E x 10-3 (cal/mol)
308K
298K
278K
263K

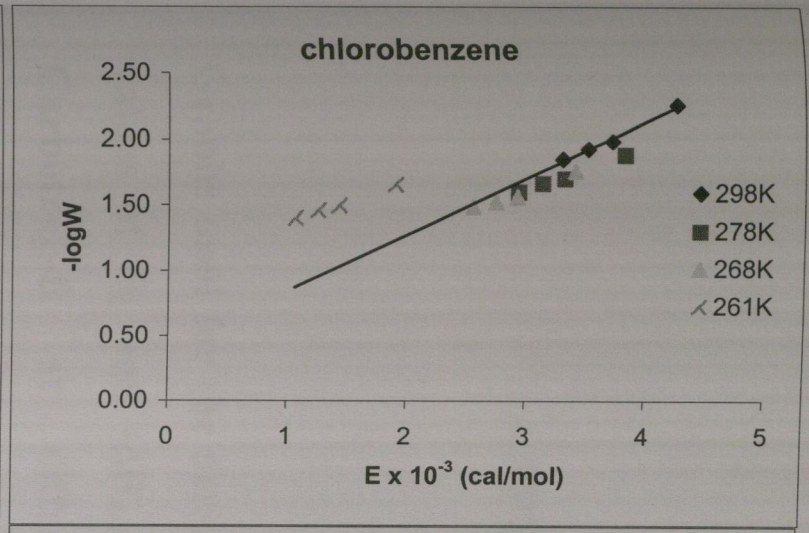

ethylbenzene
308K
298K
278K
263K
-logW
2.50
2.00
1.50
1.00
0.50
0.00
2
2.5
3
3.5
4
4.5
E x 10-3 (cal/mol)

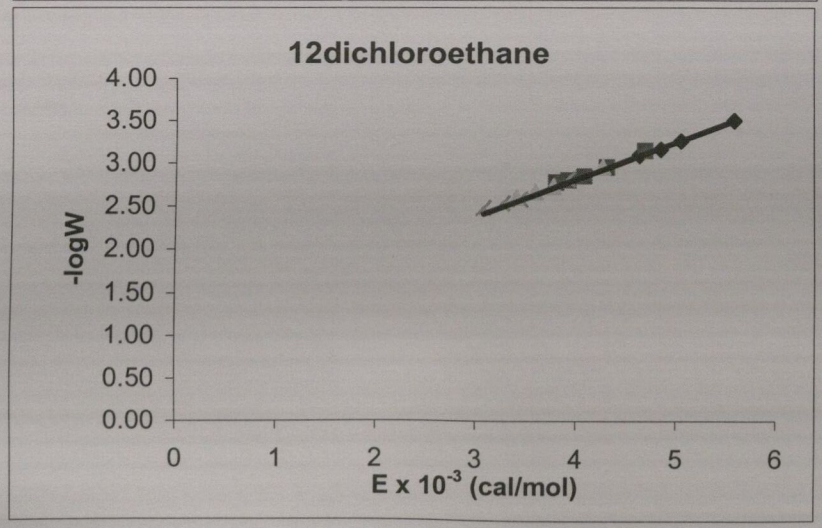

pentanol
-logW
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
E x 10-3 (cal/mol)

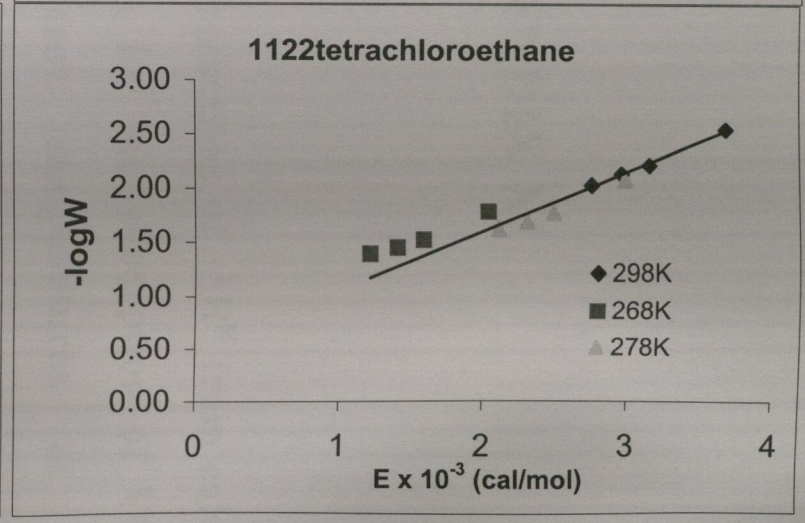

DR Graph pentane @ 261K
-logW
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
2
4
6
8
E x 10-3 (cal/mol)


hexanol
-logW
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
E x 10-3 (cal/mol)


hexane
-logW
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
2
4
6
8
E x 10-3 (cal/mol)

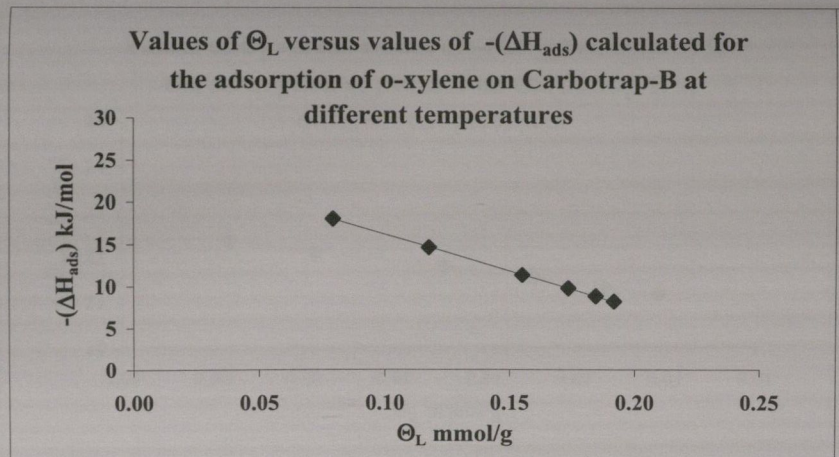

chlorobenzene
-logW
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
5
E x 10-3 (cal/mol)
298K
278K
268K
261K

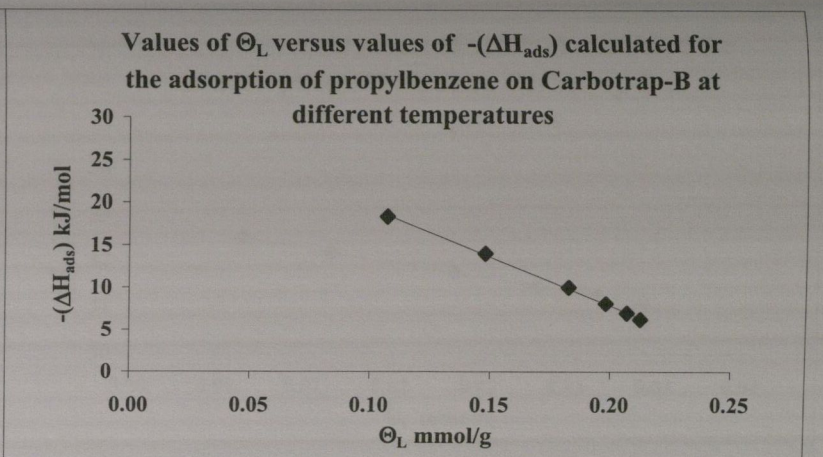

12dichloroethane
-logW
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
5
6
E x 10-3 (cal/mol)

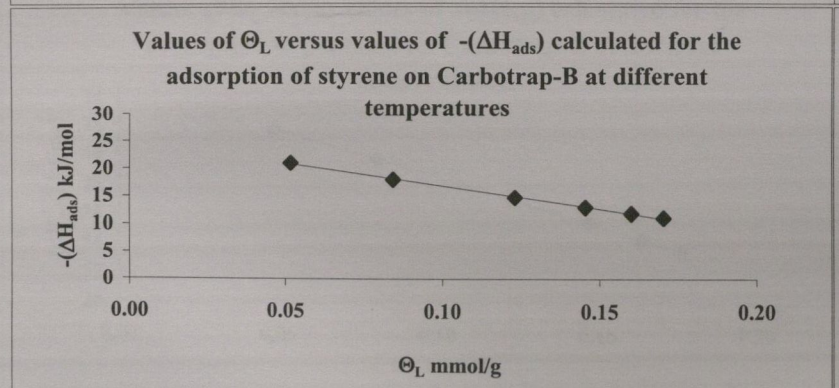

1122tetrachloroethane
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
1
2
3
4
E x 10-3 (cal/mol)
298K
268K
278K

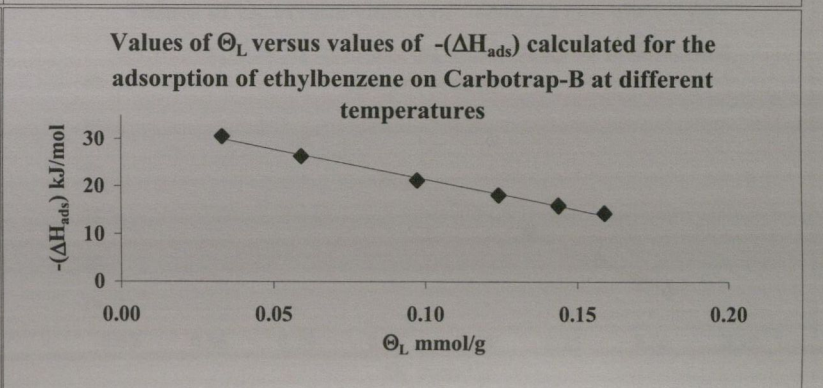
# APPENDIX XI

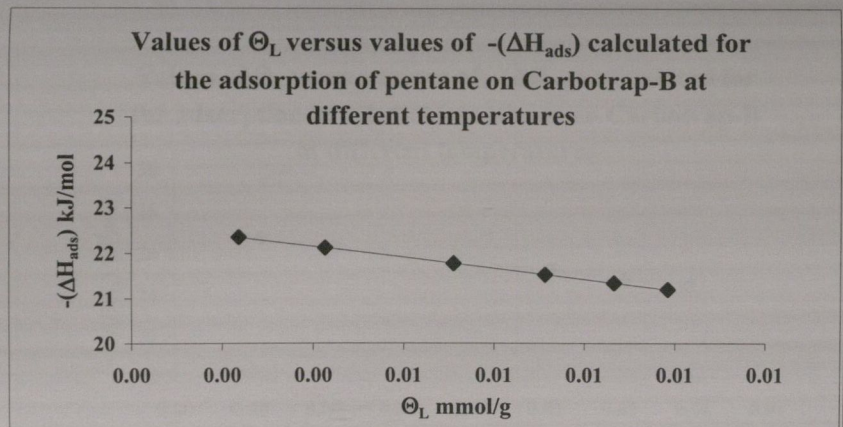
**Graphs used for the determination of $-\Delta H^{st}$ from calculated values of $\Theta_L$ and $-\Delta H_{ads}$ for the adsorption of VOC on Carbotrap-B at different temperatures at $mg/m^3$ concentrations**

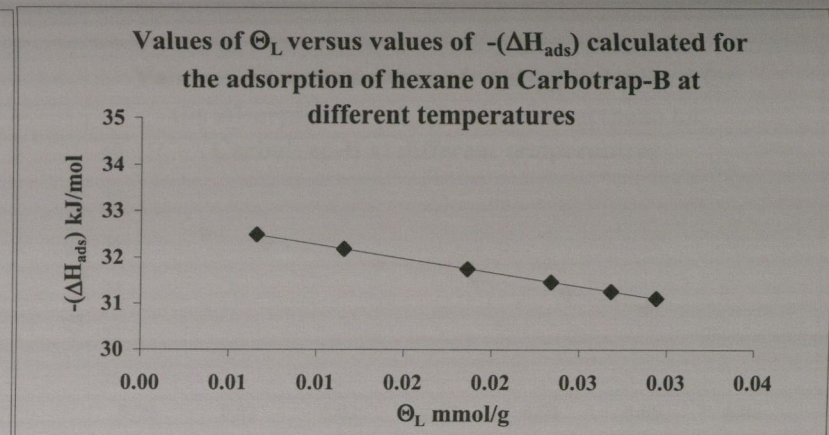

Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of o-xylene on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
30
25
20
15
10
5
0
0.00
0.05
0.10
0.15
0.20
0.25
$\Theta_L$ mmol/g

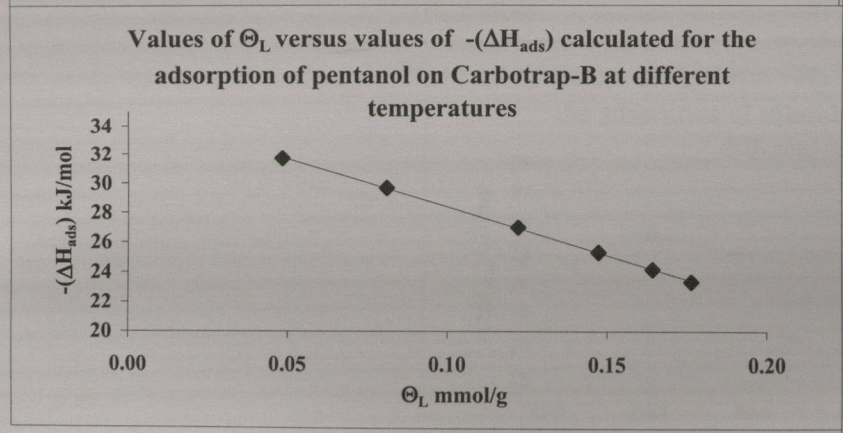

Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of propylbenzene on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
30
25
20
15
10
5
0
0.00
0.05
0.10
0.15
0.20
0.25
$\Theta_L$ mmol/g

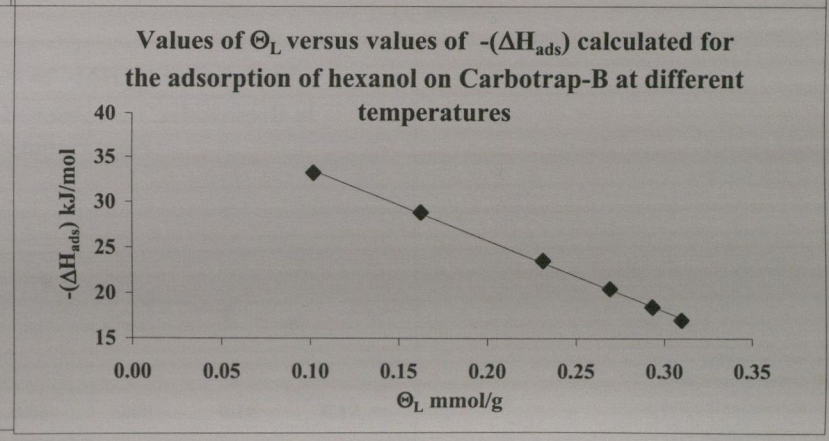

Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of styrene on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
30
25
20
15
10
5
0
0.00
0.05
0.10
0.15
0.20
$\Theta_L$ mmol/g

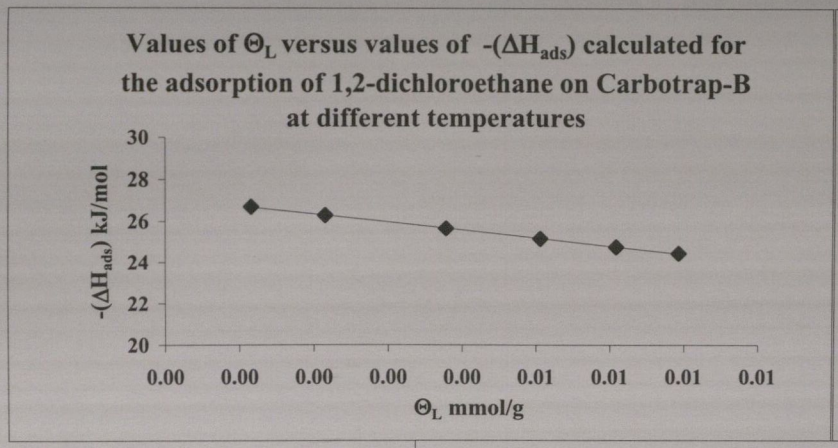

Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of ethylbenzene on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
30
20
10
0
0.00
0.05
0.10
0.15
0.20
$\Theta_L$ mmol/g

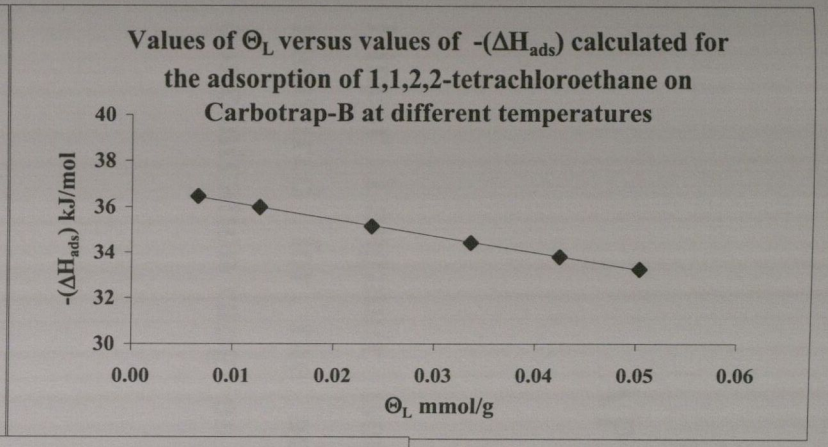

Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of pentane on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
25
24
23
22
21
20
0.00
0.00
0.00
0.01
0.01
0.01
0.01
0.01
$\Theta_L$ mmol/g

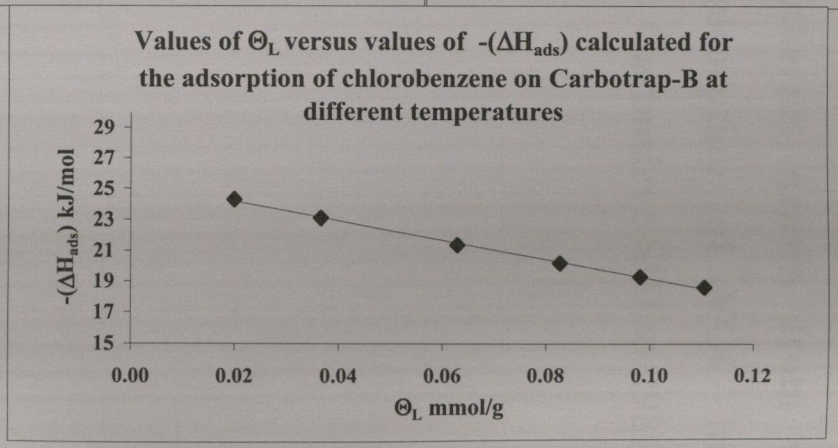

Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of hexane on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
35
34
33
32
31
30
0.00
0.01
0.01
0.02
0.02
0.03
0.03
0.04
$\Theta_L$ mmol/g


Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of pentanol on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
34
32
30
28
26
24
22
20
0.00
0.05
0.10
0.15
0.20
$\Theta_L$ mmol/g


Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of hexanol on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
40
35
30
25
20
15
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
$\Theta_L$ mmol/g

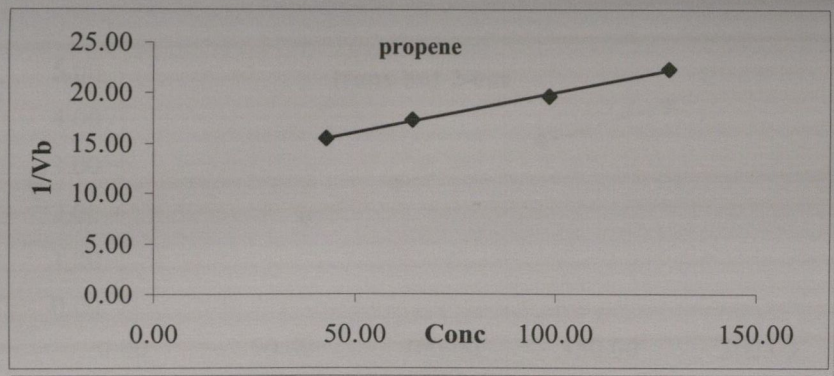

Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of 1,2-dichloroethane on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
30
28
26
24
22
20
0.00 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.01
$\Theta_L$ mmol/g

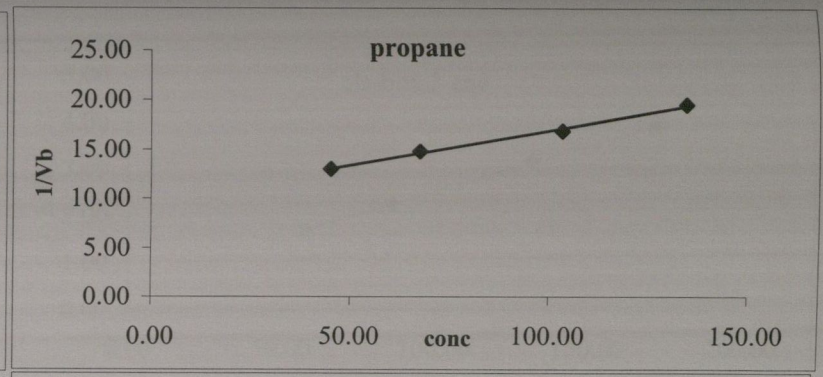

Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of 1,1,2,2-tetrachloroethane on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
40
38
36
34
32
30
0.00 0.01 0.02 0.03 0.04 0.05 0.06
$\Theta_L$ mmol/g

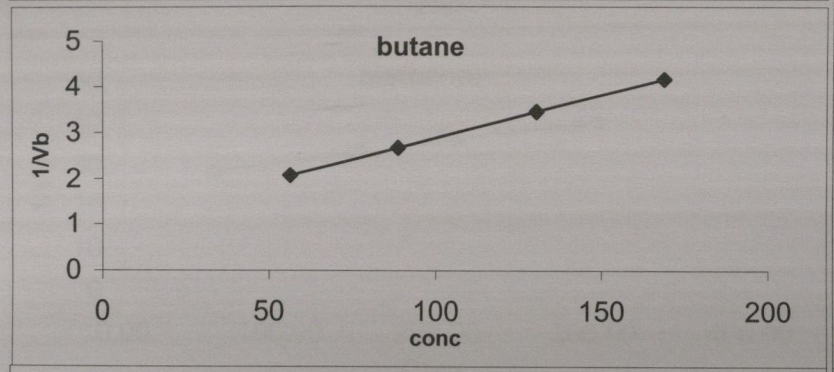

Values of $\Theta_L$ versus values of $-(\Delta H_{ads})$ calculated for the adsorption of chlorobenzene on Carbotrap-B at different temperatures
$-(\Delta H_{ads})$ kJ/mol
29
27
25
23
21
19
17
15
0.00 0.02 0.04 0.06 0.08 0.10 0.12
$\Theta_L$ mmol/g

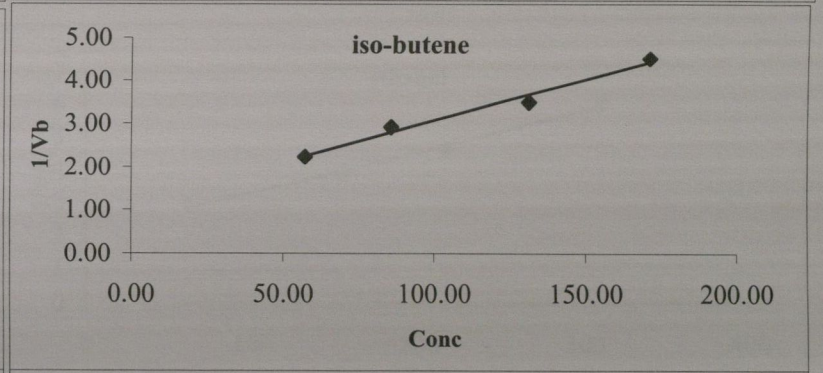
# APPENDIX XII

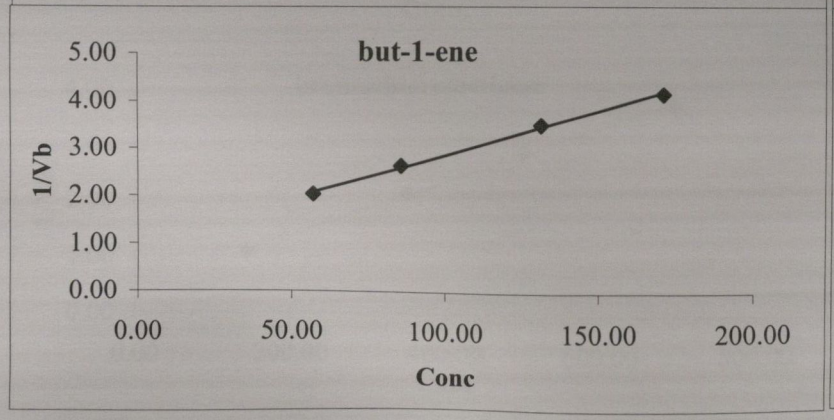
**Linear Langmuir isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the $mg/m^3$ concentration range on Carbosieve SIII at 298K**

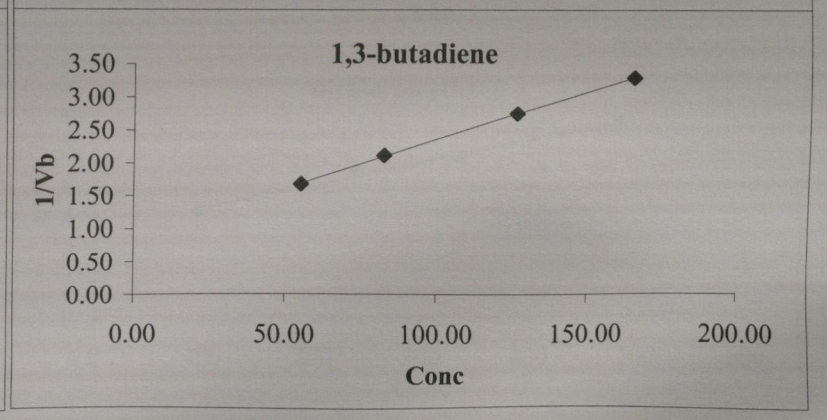

propene
25.00
20.00
15.00
10.00
5.00
0.00
1/Vb
0.00
50.00
Conc
100.00
150.00

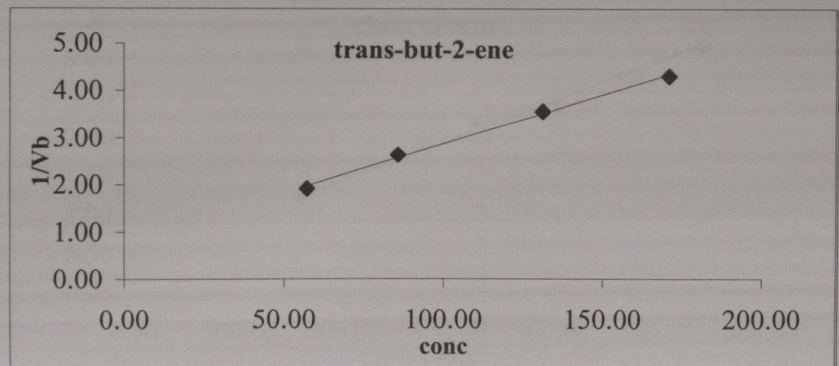

propane
25.00
20.00
15.00
10.00
5.00
0.00
1/Vb
0.00
50.00
conc
100.00
150.00

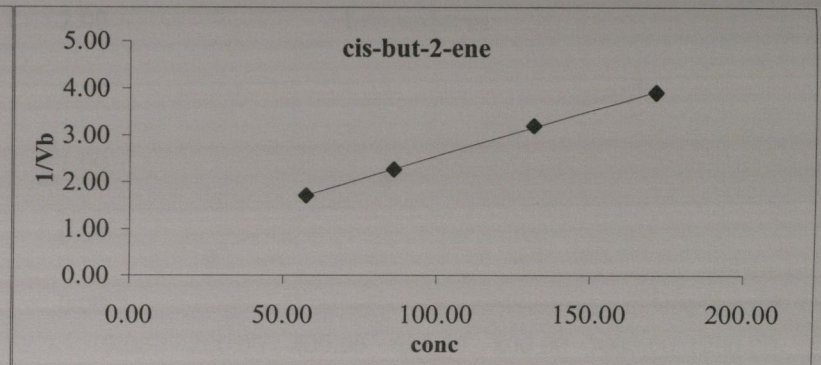

butane
5
4
3
2
1
0
1/Vb
0
50
100
150
200
conc

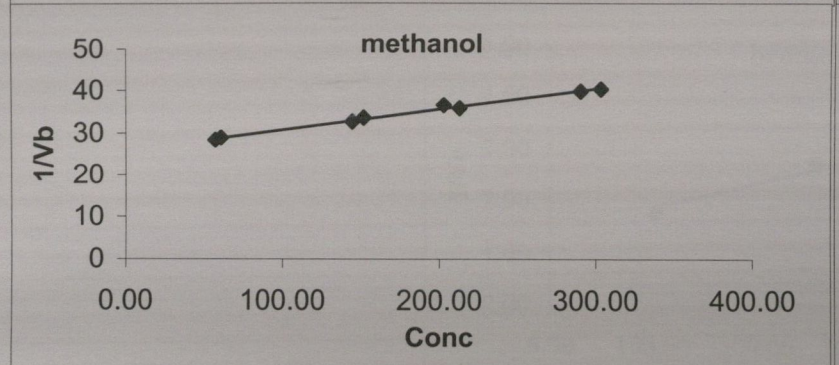

iso-butene
5.00
4.00
3.00
2.00
1.00
0.00
1/Vb
0.00
50.00
100.00
150.00
200.00
Conc

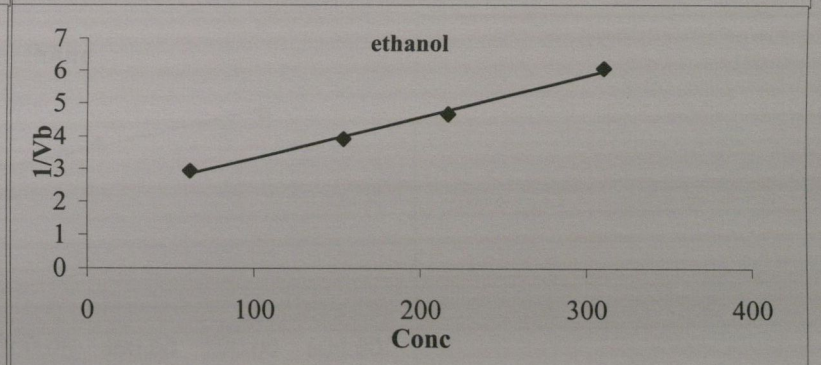

but-1-ene
5.00
4.00
3.00
2.00
1.00
0.00
1/Vb
0.00
50.00
100.00
150.00
200.00
Conc

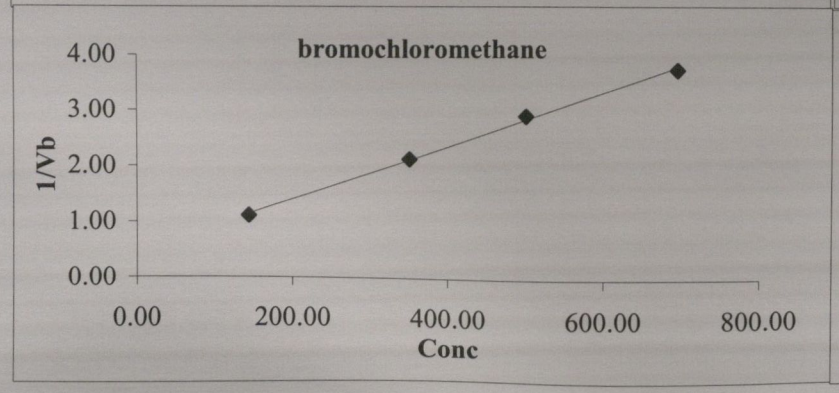

1,3-butadiene
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
1/Vb
0.00
50.00
100.00
150.00
200.00
Conc

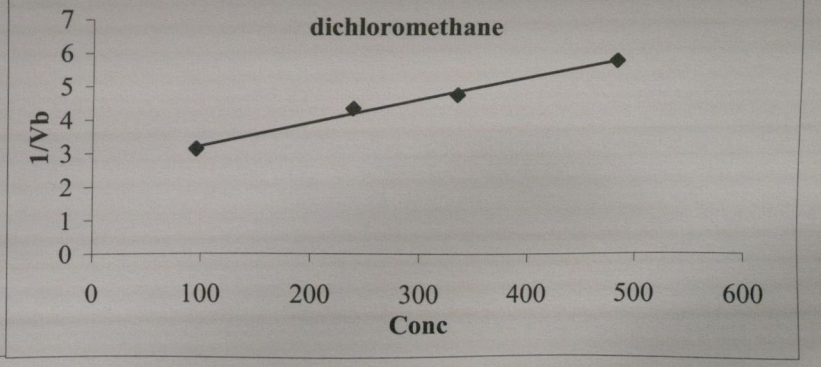

trans-but-2-ene
1/Vb
5.00
4.00
3.00
2.00
1.00
0.00
0.00
50.00
100.00
150.00
200.00
conc

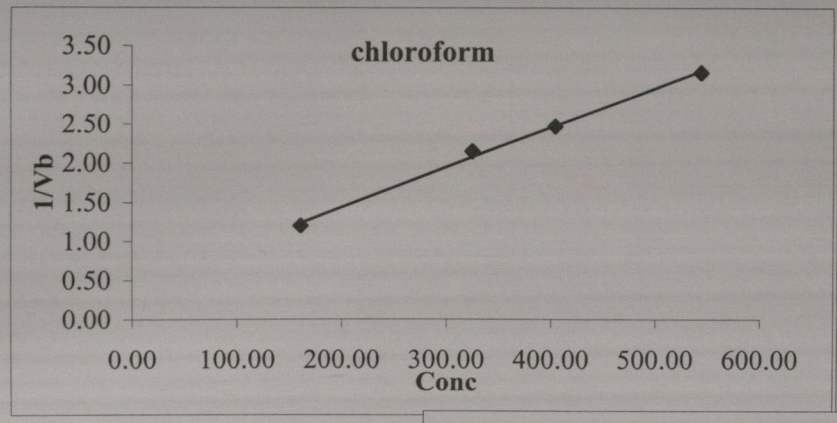

cis-but-2-ene
1/Vb
5.00
4.00
3.00
2.00
1.00
0.00
0.00
50.00
100.00
150.00
200.00
conc

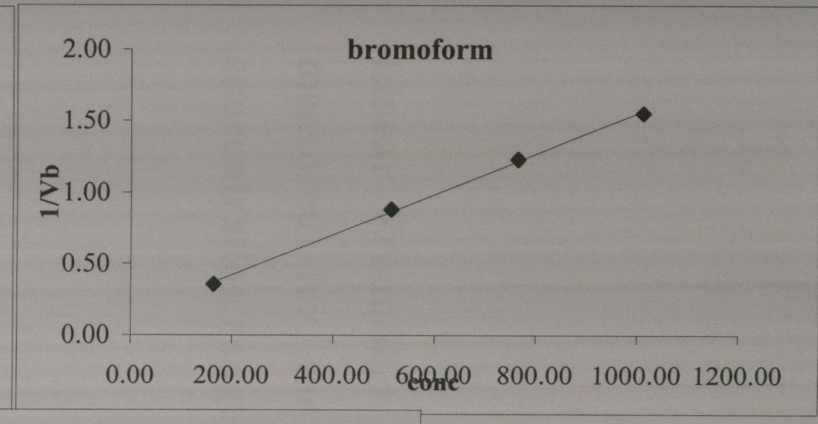

methanol
1/Vb
50
40
30
20
10
0
0.00
100.00
200.00
300.00
400.00
Conc

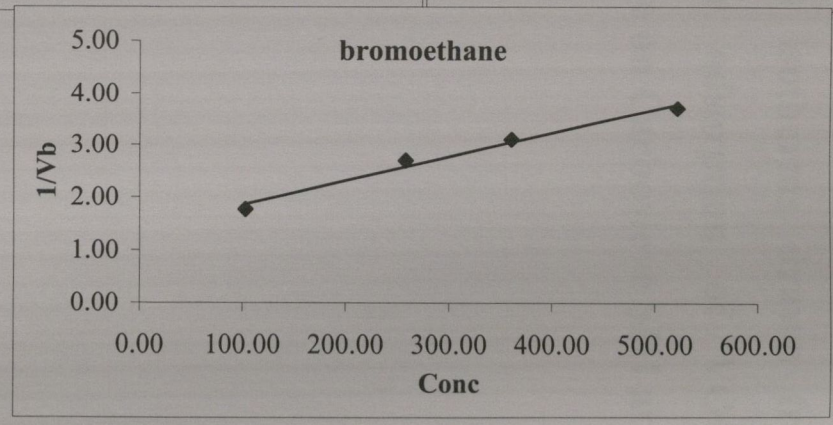

ethanol
1/Vb
7
6
5
4
3
2
1
0
0
100
200
300
400
Conc


bromochloromethane
1/Vb
4.00
3.00
2.00
1.00
0.00
0.00
200.00
400.00
600.00
800.00
Conc


dichloromethane
1/Vb
7
6
5
4
3
2
1
0
0
100
200
300
400
500
600
Conc

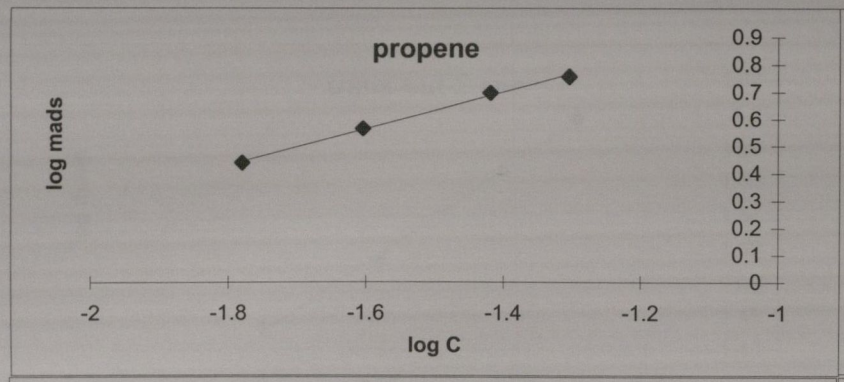

chloroform
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
1/Vb
0.00
100.00
200.00
300.00
400.00
500.00
600.00
Conc

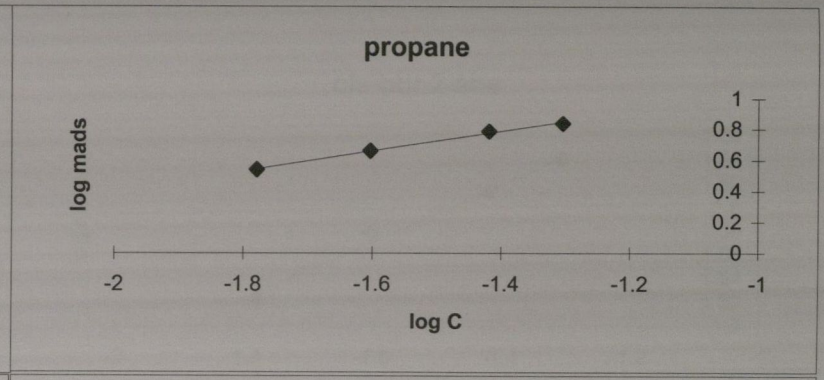

bromoform
2.00
1.50
1.00
0.50
0.00
1/Vb
0.00
200.00
400.00
600.00
800.00
1000.00
1200.00
conc

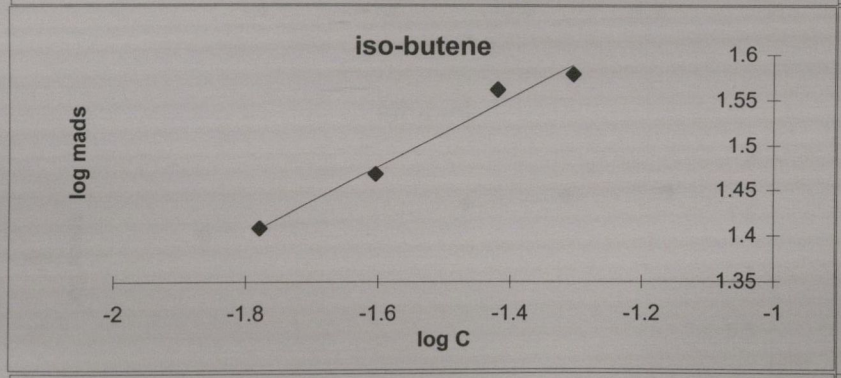

bromoethane
5.00
4.00
3.00
2.00
1.00
0.00
1/Vb
0.00
100.00
200.00
300.00
400.00
500.00
600.00
Conc

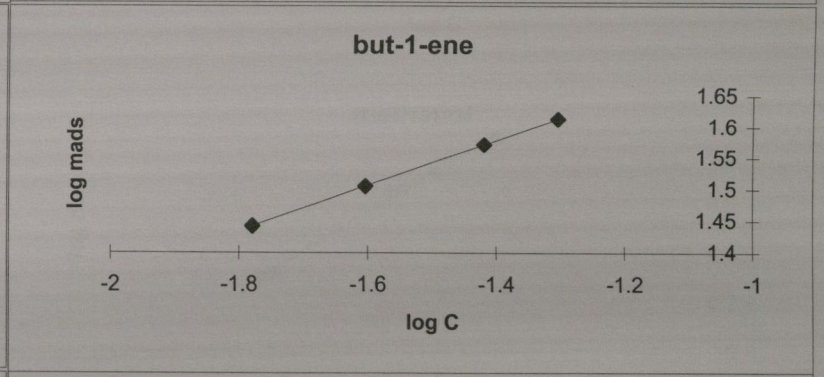
# APPENDIX XIII

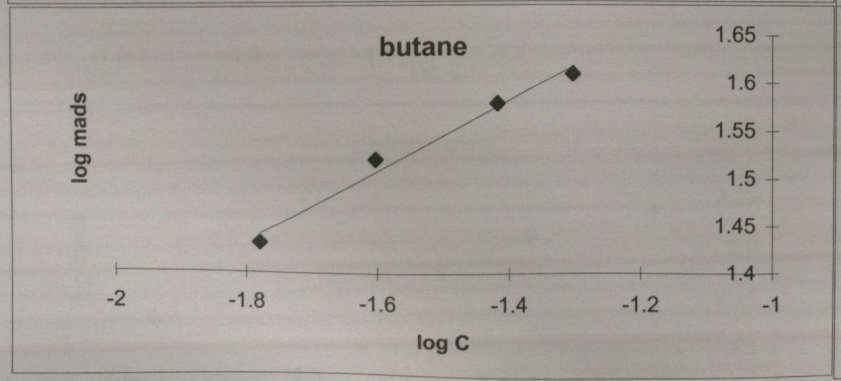
**Linear Freundlich isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the $mg/m^3$ concentration range on Carbosieve SIII at 298K**

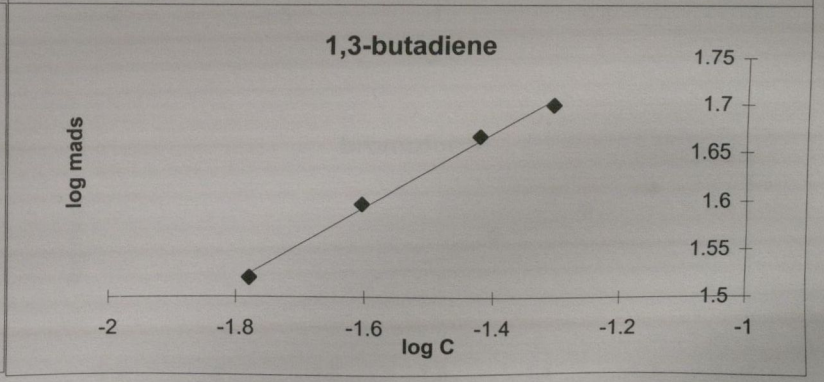

propene
log mads
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-2
-1.8
-1.6
-1.4
-1.2
-1
log C

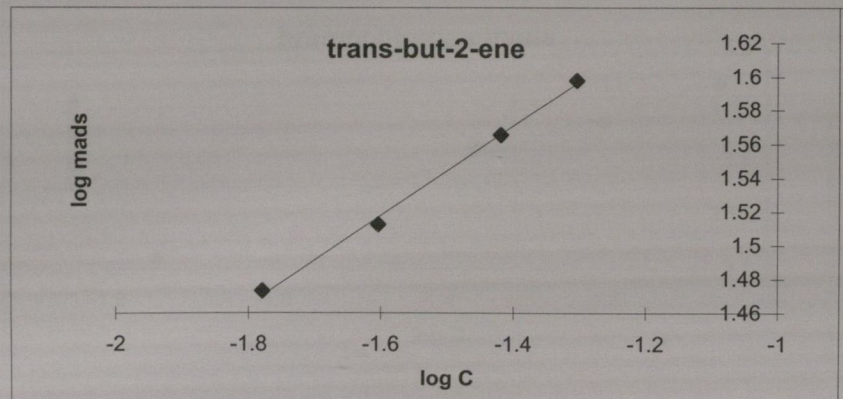

propane
log mads
1
0.8
0.6
0.4
0.2
0
-2
-1.8
-1.6
-1.4
-1.2
-1
log C

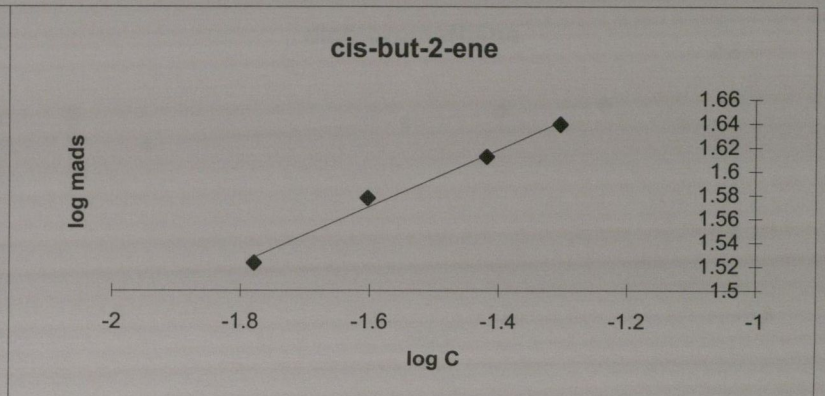

iso-butene
log mads
1.6
1.55
1.5
1.45
1.4
1.35
-2
-1.8
-1.6
-1.4
-1.2
-1
log C

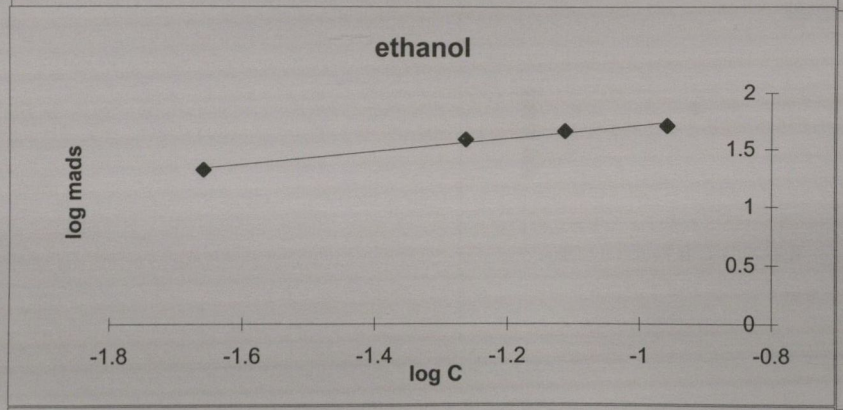

but-1-ene
log mads
1.65
1.6
1.55
1.5
1.45
1.4
-2
-1.8
-1.6
-1.4
-1.2
-1
log C

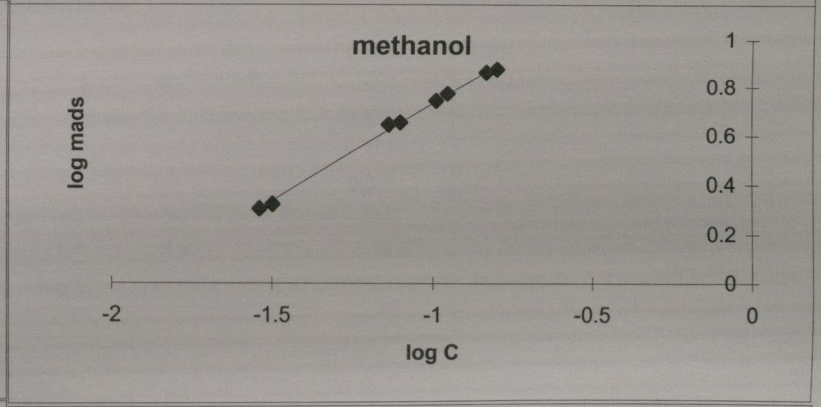

butane
log mads
1.65
1.6
1.55
1.5
1.45
1.4
-2
-1.8
-1.6
-1.4
-1.2
-1
log C

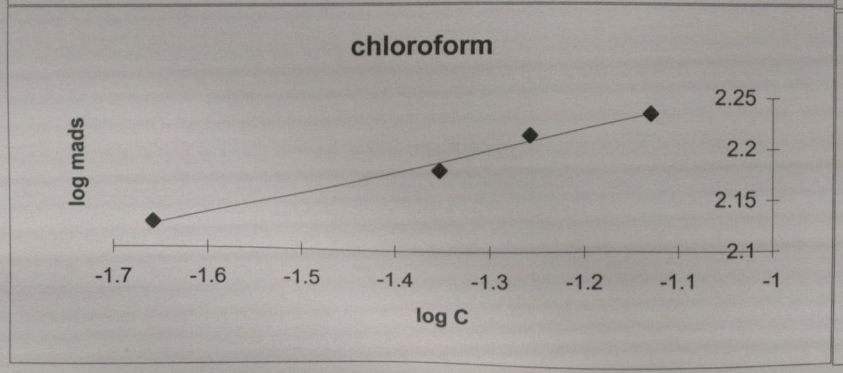

1,3-butadiene
log mads
1.75
1.7
1.65
1.6
1.55
1.5
-2
-1.8
-1.6
-1.4
-1.2
-1
log C

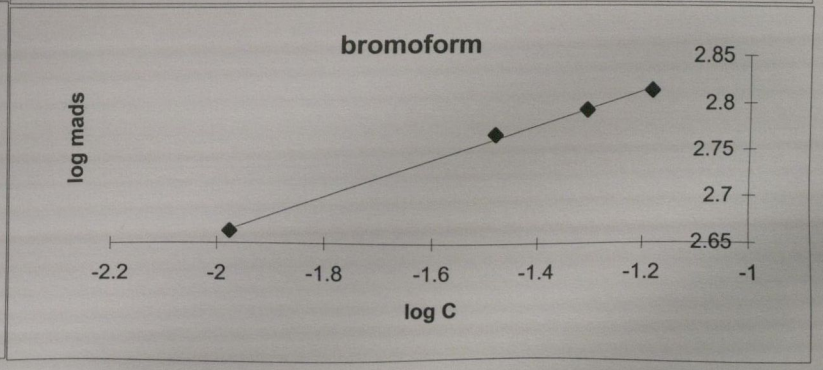

trans-but-2-ene
log mads
log C
1.62
1.6
1.58
1.56
1.54
1.52
1.5
1.48
1.46
-2
-1.8
-1.6
-1.4
-1.2
-1

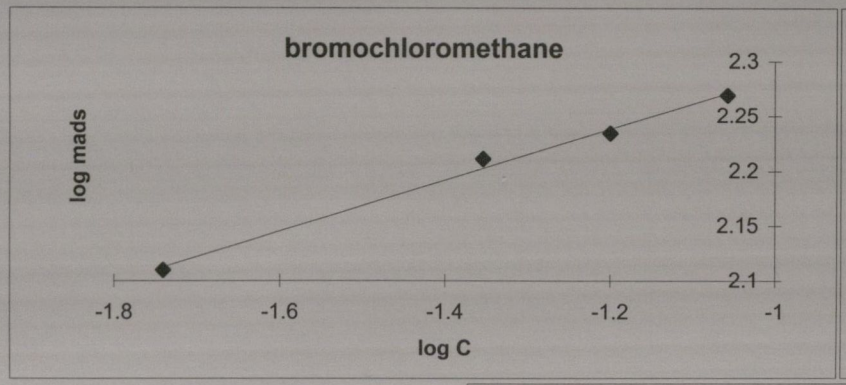

cis-but-2-ene
log mads
log C
1.66
1.64
1.62
1.6
1.58
1.56
1.54
1.52
1.5
-2
-1.8
-1.6
-1.4
-1.2
-1

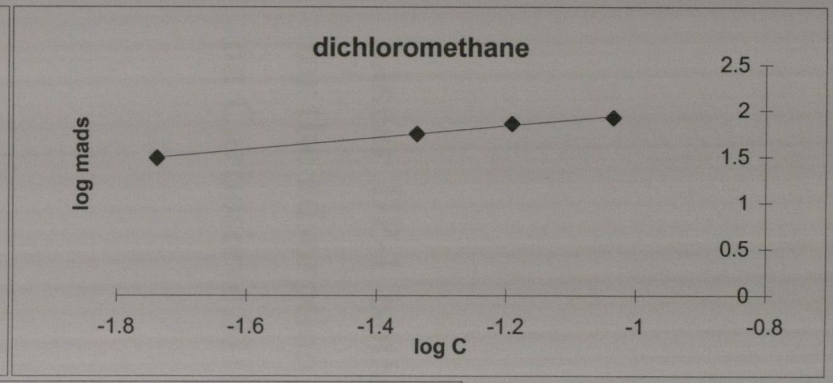

ethanol
log mads
log C
2
1.5
1
0.5
0
-1.8
-1.6
-1.4
-1.2
-1
-0.8

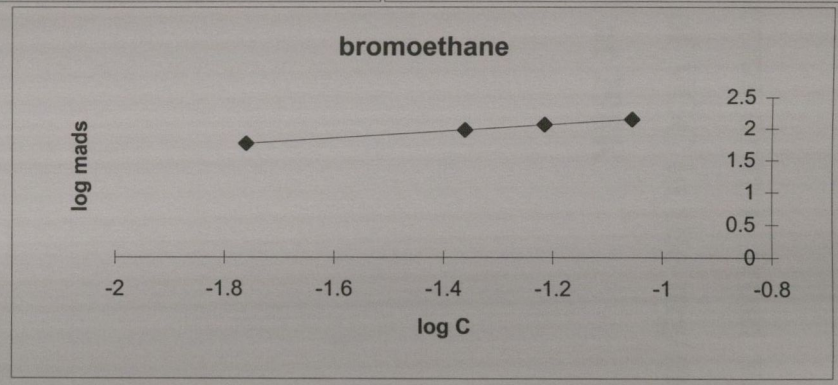

methanol
log mads
log C
1
0.8
0.6
0.4
0.2
0
-2
-1.5
-1
-0.5
0


chloroform
log mads
log C
2.25
2.2
2.15
2.1
-1.7
-1.6
-1.5
-1.4
-1.3
-1.2
-1.1
-1


bromoform
log mads
log C
2.85
2.8
2.75
2.7
2.65
-2.2
-2
-1.8
-1.6
-1.4
-1.2
-1

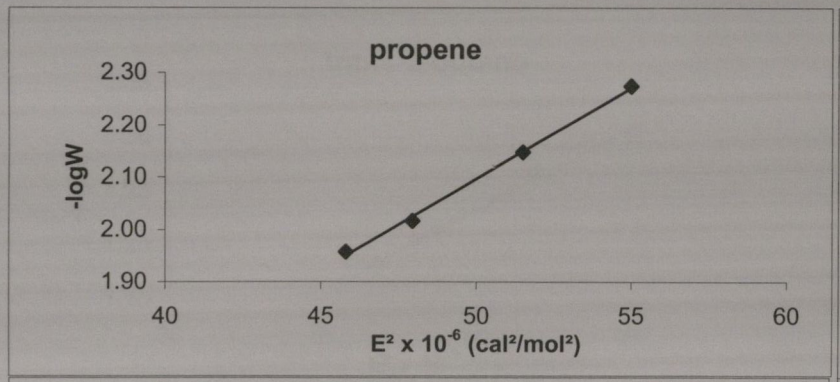

bromochloromethane
log mads
2.3
2.25
2.2
2.15
2.1
-1.8
-1.6
-1.4
-1.2
-1
log C

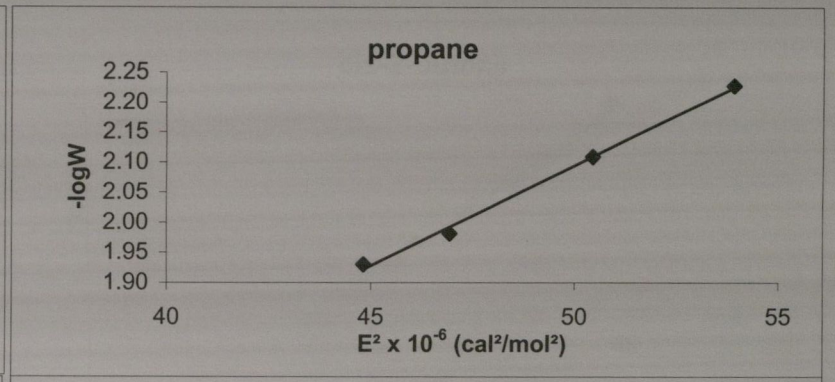

dichloromethane
log mads
2.5
2
1.5
1
0.5
0
-1.8
-1.6
-1.4
-1.2
-1
-0.8
log C

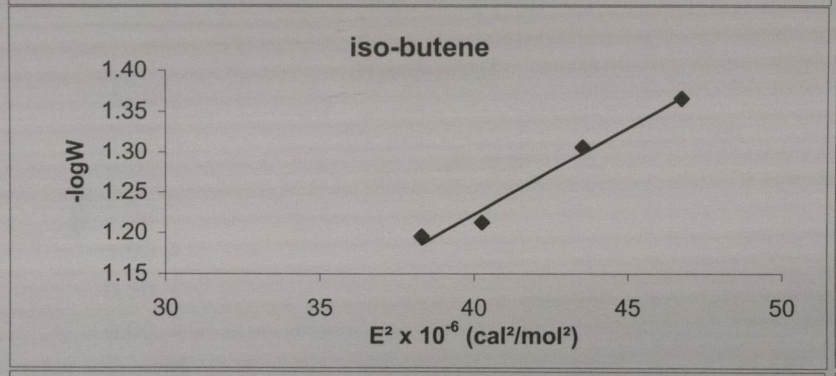

bromoethane
log mads
2.5
2
1.5
1
0.5
0
-2
-1.8
-1.6
-1.4
-1.2
-1
-0.8
log C

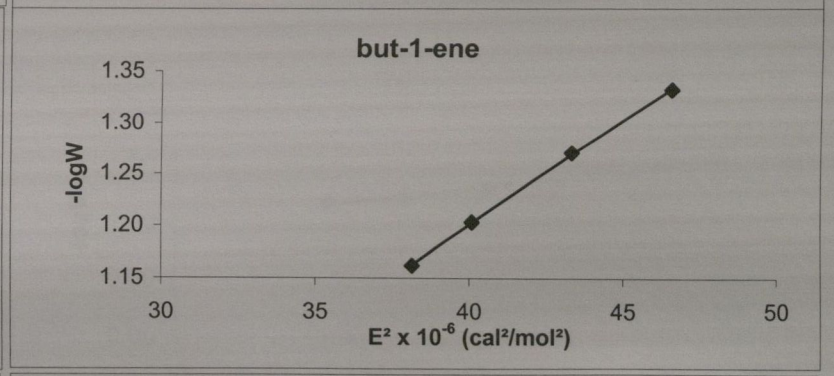
# APPENDIX XIV

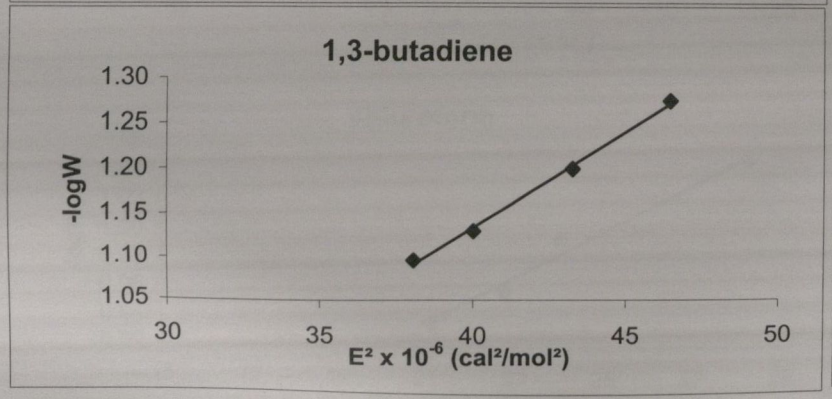
**Linear DP-1 isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the mg/m$^3$ concentration range on Carbosieve SIII at 298K**

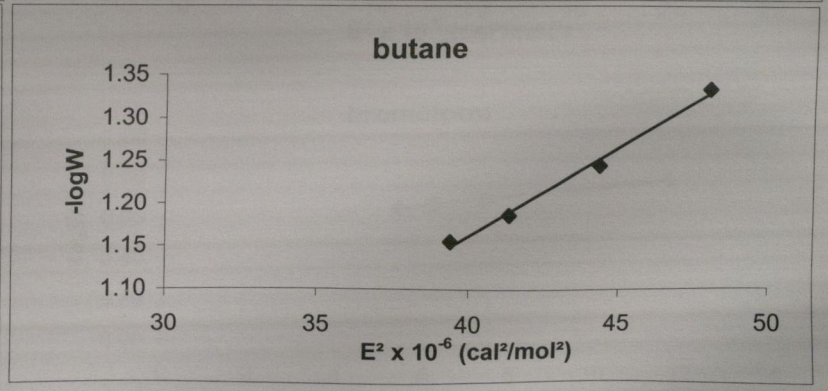

propene
-logW
2.30
2.20
2.10
2.00
1.90
40
45
50
55
60
E² x 10⁻⁶ (cal²/mol²)

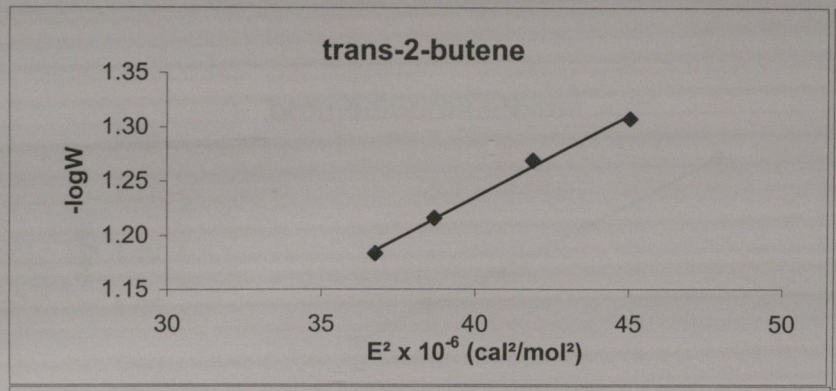

propane
-logW
2.25
2.20
2.15
2.10
2.05
2.00
1.95
1.90
40
45
50
55
E² x 10⁻⁶ (cal²/mol²)

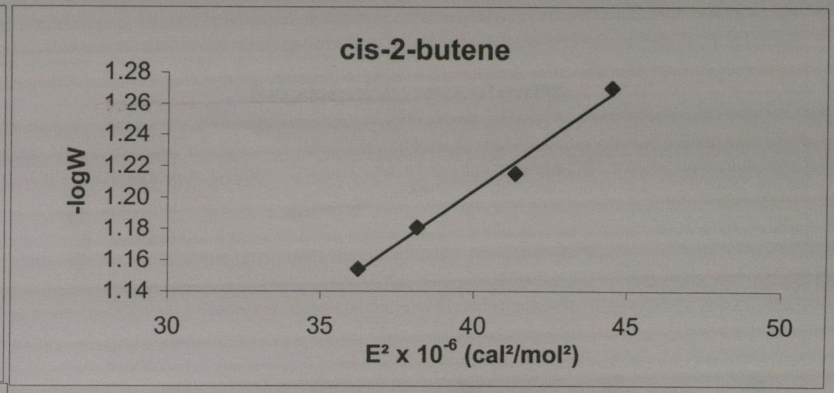

iso-butene
-logW
1.40
1.35
1.30
1.25
1.20
1.15
30
35
40
45
50
E² x 10⁻⁶ (cal²/mol²)

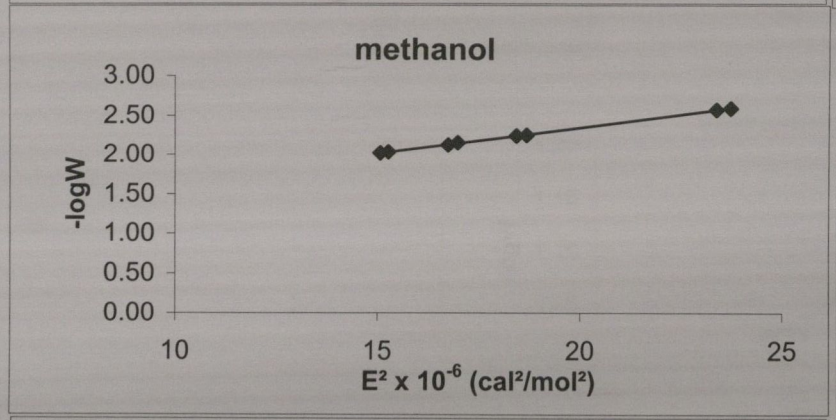

but-1-ene
-logW
1.35
1.30
1.25
1.20
1.15
30
35
40
45
50
E² x 10⁻⁶ (cal²/mol²)

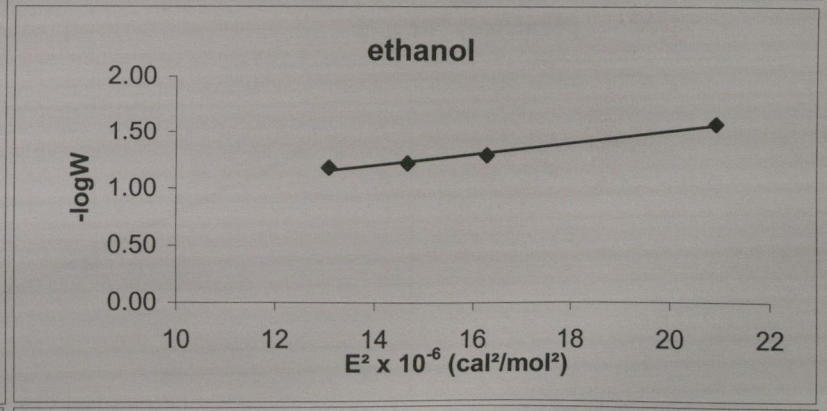

1,3-butadiene
-logW
1.30
1.25
1.20
1.15
1.10
1.05
30
35
40
45
50
E² x 10⁻⁶ (cal²/mol²)

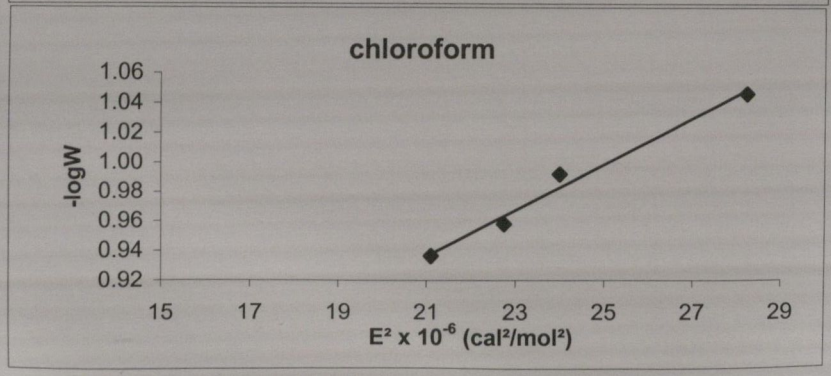

butane
-logW
1.35
1.30
1.25
1.20
1.15
1.10
30
35
40
45
50
E² x 10⁻⁶ (cal²/mol²)

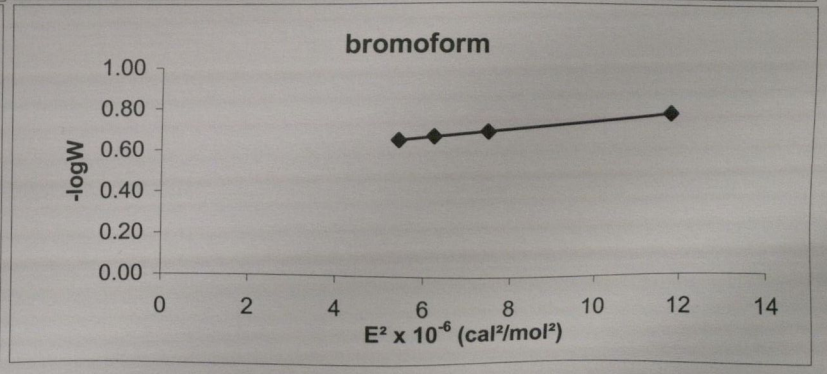

trans-2-butene
-logW
1.35
1.30
1.25
1.20
1.15
30
35
40
45
50
E² x 10⁻⁶ (cal²/mol²)

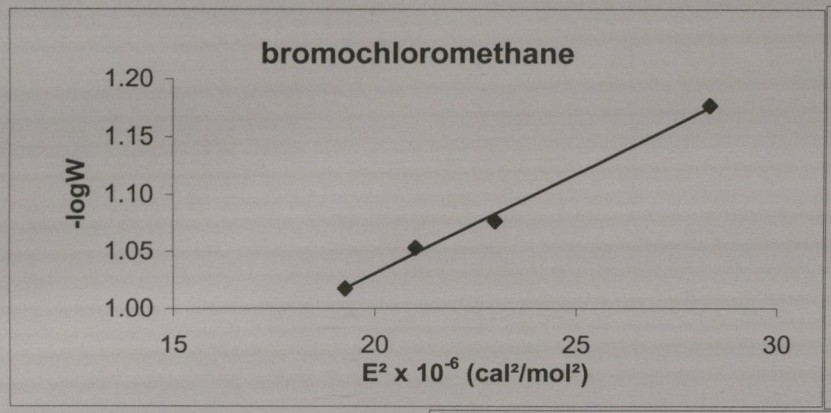

cis-2-butene
-logW
1.28
1.26
1.24
1.22
1.20
1.18
1.16
1.14
30
35
40
45
50
E² x 10⁻⁶ (cal²/mol²)

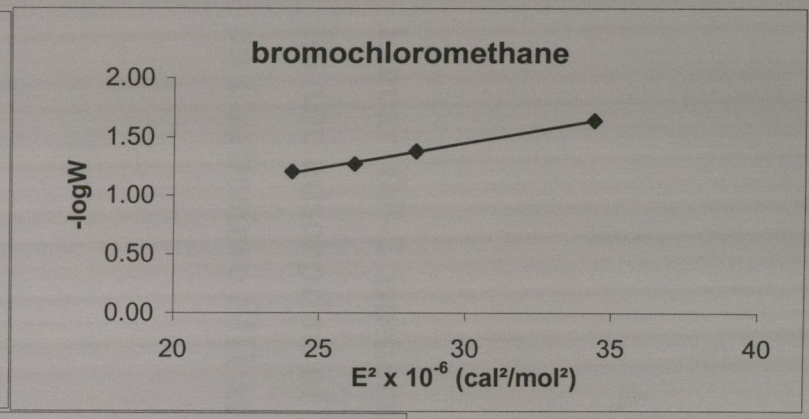

methanol
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
10
15
20
25
E² x 10⁻⁶ (cal²/mol²)

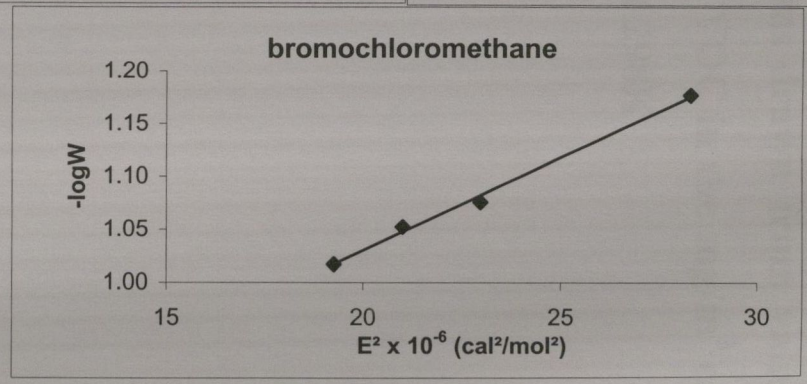

ethanol
-logW
2.00
1.50
1.00
0.50
0.00
10
12
14
16
18
20
22
E² x 10⁻⁶ (cal²/mol²)


chloroform
-logW
1.06
1.04
1.02
1.00
0.98
0.96
0.94
0.92
15
17
19
21
23
25
27
29
E² x 10⁻⁶ (cal²/mol²)


bromoform
-logW
1.00
0.80
0.60
0.40
0.20
0.00
0
2
4
6
8
10
12
14
E² x 10⁻⁶ (cal²/mol²)

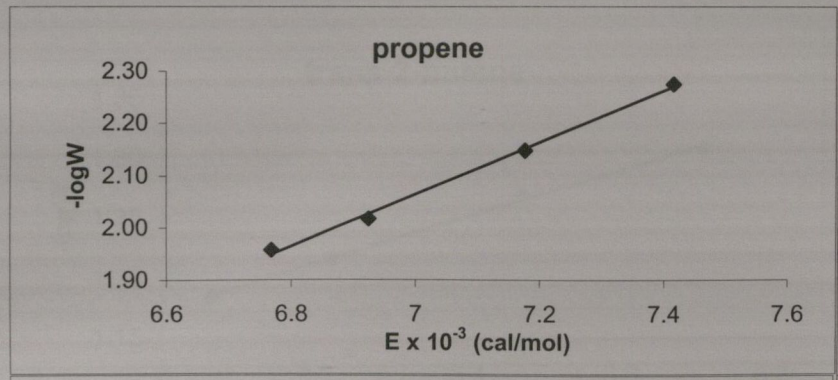

bromochloromethane
-logW
1.20
1.15
1.10
1.05
1.00
15
20
25
30
E² x 10⁻⁶ (cal²/mol²)

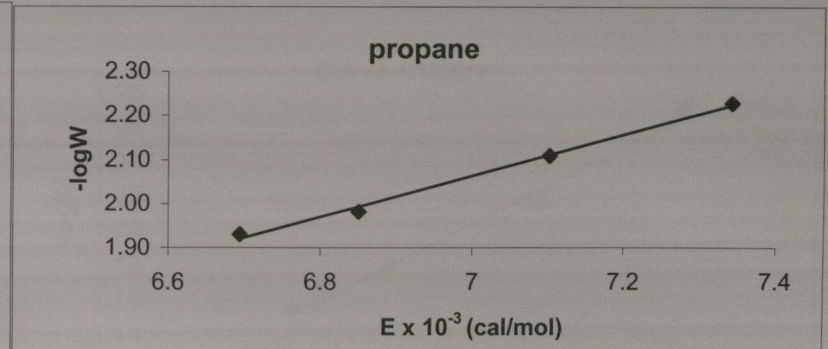

bromochloromethane
-logW
2.00
1.50
1.00
0.50
0.00
20
25
30
35
40
E² x 10⁻⁶ (cal²/mol²)

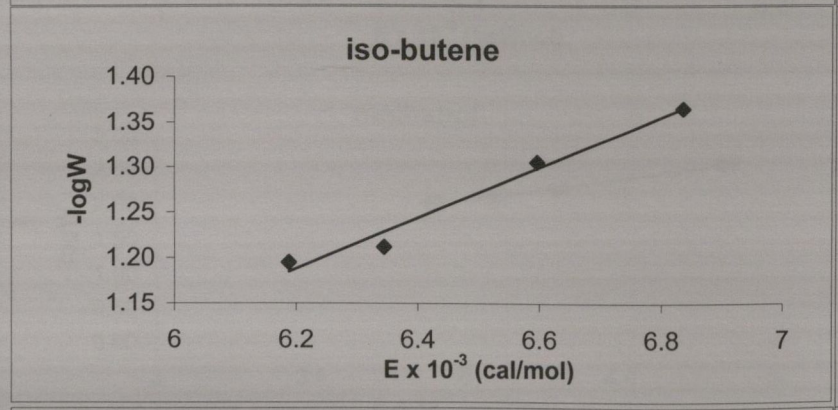

bromochloromethane
-logW
1.20
1.15
1.10
1.05
1.00
15
20
25
30
E² x 10⁻⁶ (cal²/mol²)

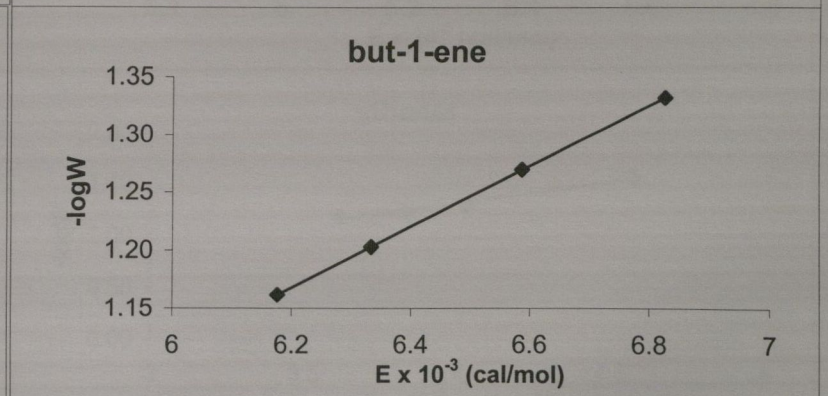
# APPENDIX XV

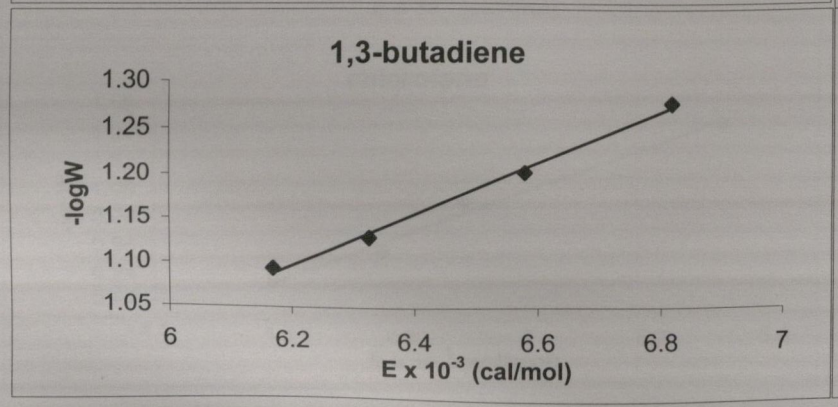
**Linear DP-2 isotherms drawn from values of $V_b$ measured for the adsorption of VOC in the mg/m$^3$ concentration range on Carbosieve SIII at 298K**

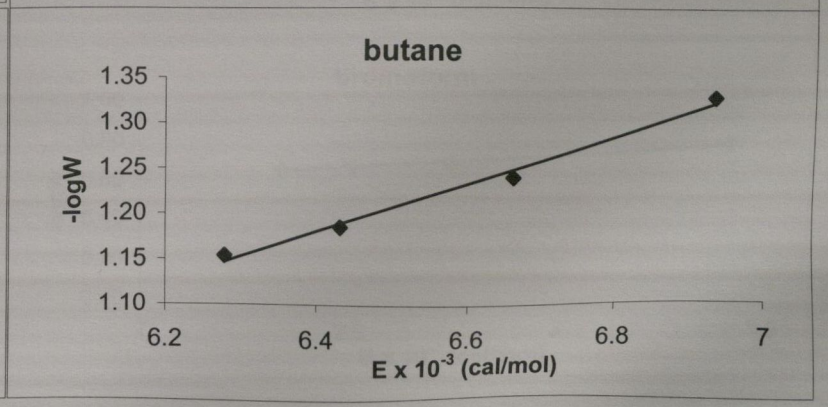

propene
-logW
2.30
2.20
2.10
2.00
1.90
6.6
6.8
7
7.2
7.4
7.6
E x 10-3 (cal/mol)

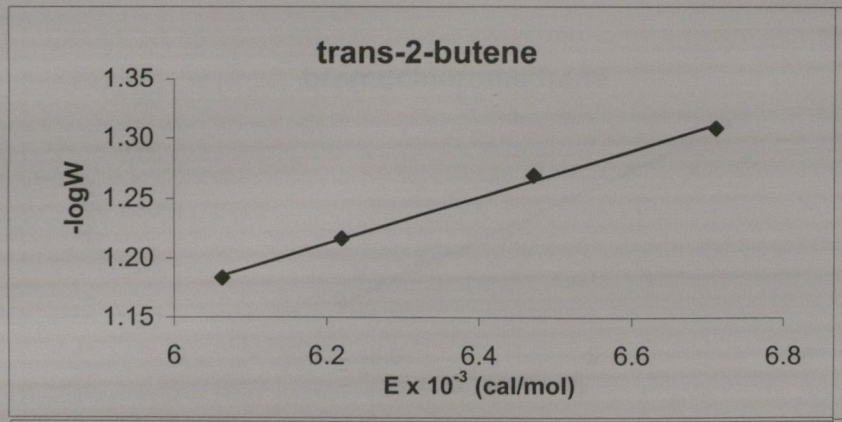

propane
-logW
2.30
2.20
2.10
2.00
1.90
6.6
6.8
7
7.2
7.4
E x 10-3 (cal/mol)

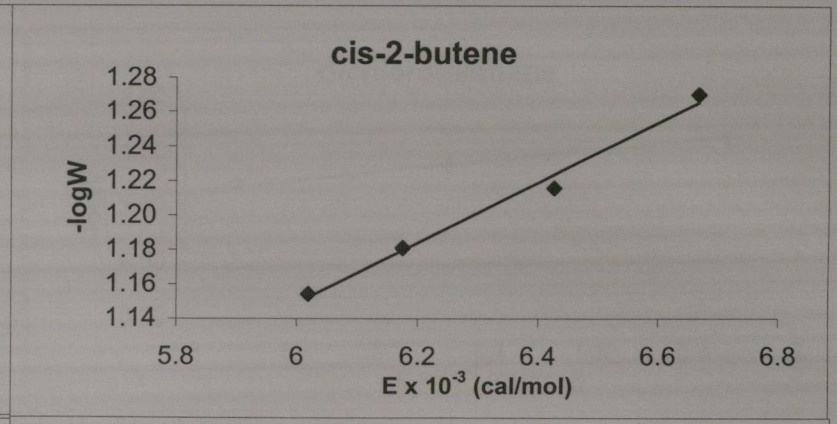

iso-butene
-logW
1.40
1.35
1.30
1.25
1.20
1.15
6
6.2
6.4
6.6
6.8
7
E x 10-3 (cal/mol)

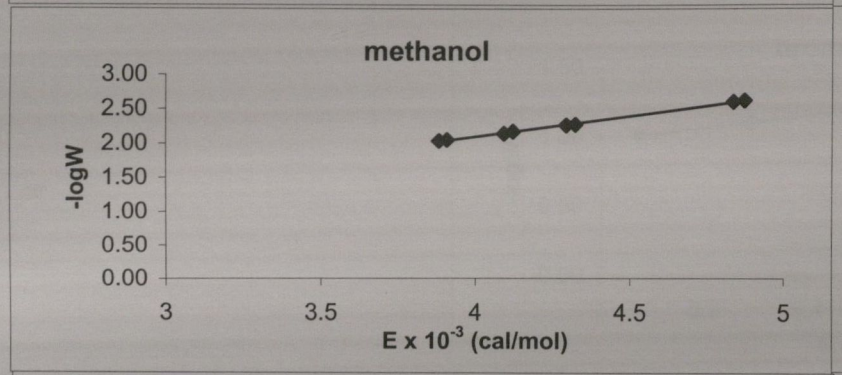

but-1-ene
-logW
1.35
1.30
1.25
1.20
1.15
6
6.2
6.4
6.6
6.8
7
E x 10-3 (cal/mol)

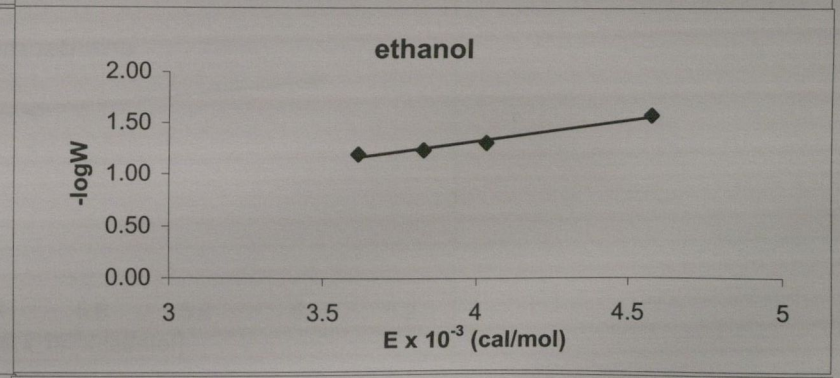

1,3-butadiene
-logW
1.30
1.25
1.20
1.15
1.10
1.05
6
6.2
6.4
6.6
6.8
7
E x 10-3 (cal/mol)

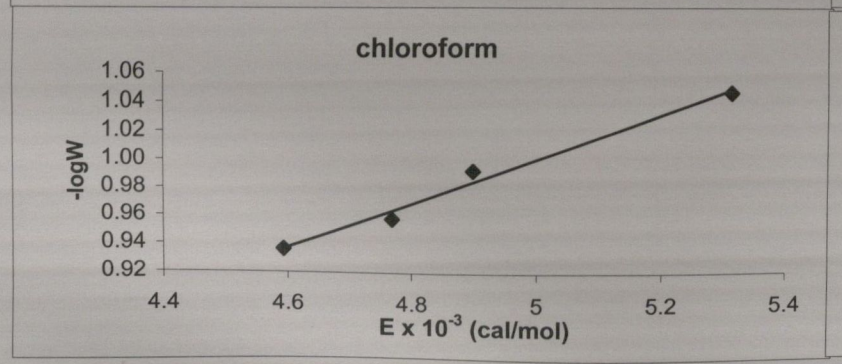

butane
-logW
1.35
1.30
1.25
1.20
1.15
1.10
6.2
6.4
6.6
6.8
7
E x 10-3 (cal/mol)

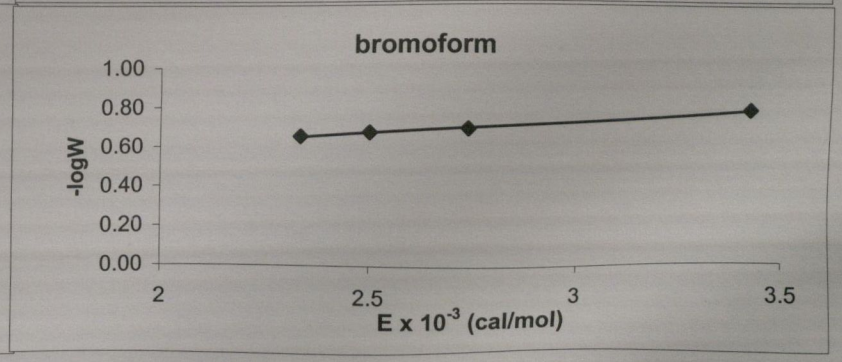

trans-2-butene
-logW
1.35
1.30
1.25
1.20
1.15
6
6.2
6.4
6.6
6.8
E x 10-3 (cal/mol)

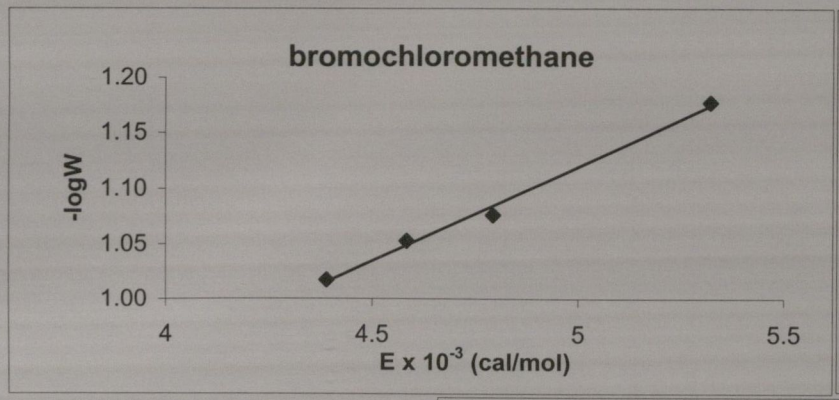

cis-2-butene
-logW
1.28
1.26
1.24
1.22
1.20
1.18
1.16
1.14
5.8
6
6.2
6.4
6.6
6.8
E x 10-3 (cal/mol)

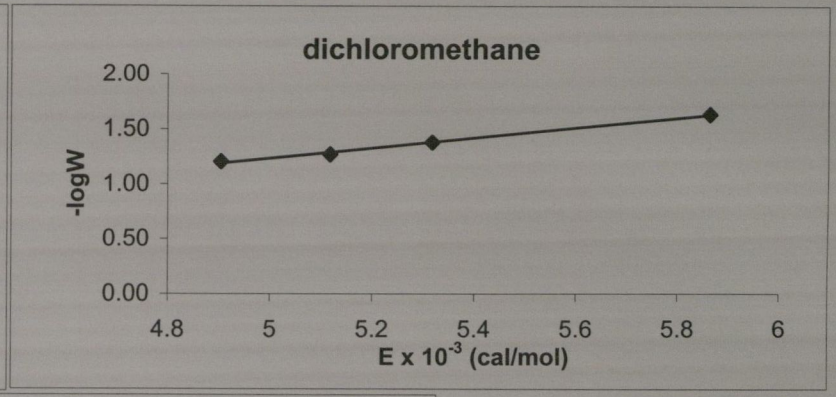

methanol
-logW
3.00
2.50
2.00
1.50
1.00
0.50
0.00
3
3.5
4
4.5
5
E x 10-3 (cal/mol)

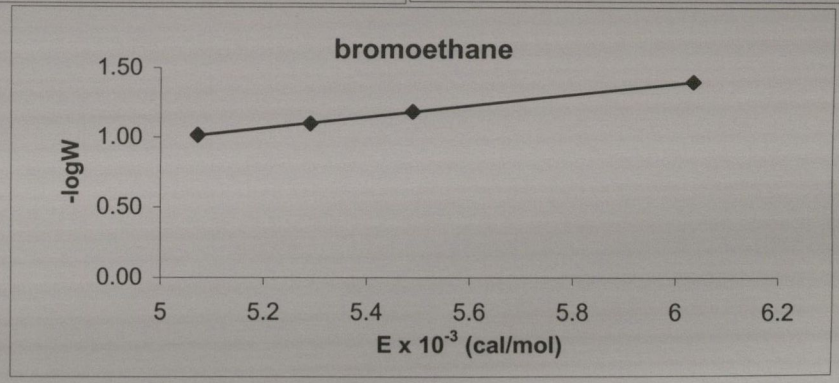

ethanol
-logW
2.00
1.50
1.00
0.50
0.00
3
3.5
4
4.5
5
E x 10-3 (cal/mol)


chloroform
-logW
1.06
1.04
1.02
1.00
0.98
0.96
0.94
0.92
4.4
4.6
4.8
5
5.2
5.4
E x 10-3 (cal/mol)


bromoform
-logW
1.00
0.80
0.60
0.40
0.20
0.00
2
2.5
3
3.5
E x 10-3 (cal/mol)


bromochloromethane
-logW
1.20
1.15
1.10
1.05
1.00
4
4.5
5
5.5
E x 10-3 (cal/mol)


dichloromethane
-logW
2.00
1.50
1.00
0.50
0.00
4.8
5
5.2
5.4
5.6
5.8
6
E x 10-3 (cal/mol)


bromoethane
-logW
1.50
1.00
0.50
0.00
5
5.2
5.4
5.6
5.8
6
6.2
E x 10-3 (cal/mol)