

Dielectric relaxation and crystallization of nanophase separated 1-propanol-isoamylbromide mixture

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The effects of liquid-liquid phase separation on molecular relaxation of an apparently homogeneous mixture of 1-propanol and isoamylbromide has been studied by dielectric spectroscopy over a broad frequency and temperature range, and its crystallization kinetics investigated in real time. The mixture shows two widely separated relaxation processes, as before, with the faster relaxation due to the orientational diffusion of isoamylbromide and the slower due to that of 1-propanol. In the mixture, the scaled contribution to permittivity from orientation polarization, $\Delta\epsilon$, of isoamylbromide is about the same as in the pure state, but that of 1-propanol decreases by a factor of ~ 3 at 120 K. As the temperature is decreased, this difference remains constant. The relaxation time, τ , of isoamylbromide and its distribution parameter remains the same as for the pure liquid, but that of 1-propanol is longer and increases with decrease in T , becoming ~ 130 times the pure liquid's value at 119 K. This is in contrast to the finding for an isomeric heptanol, whose τ had decreased. Extrapolation suggests that at $T > 151$ K, τ of 1-propanol in the mixture may become less than that in the pure liquid (the isoamylbromide component crystallizes before this temperature could be reached). This indicates that T_g corresponding to τ of 10^3 s for 1-propanol in the mixture would be higher than in the pure liquid. Crystallization of the two components in the mixture occurs at different rates and 1-propanol remains partially uncrystallized while isoamylbromide completely crystallizes. τ of any remaining liquid isoamylbromide does not change in the presence of crystallized states while τ of residual liquid 1-propanol in the mixture is reduced. The mixture phase separates in submicron or nanosize aggregates of the alcohol in isoamylbromide, without affecting the latter's relaxation kinetics, while its own ϵ_s decreases and τ increases. Consequences of the finding for various relaxation mechanisms are briefly described. © 2007 American Institute of Physics. [DOI: 10.1063/1.2761898]

I. INTRODUCTION

Monohydroxy alcohols, and certain amides are a group of substances whose polarization decays according to a first order rate process and hence a single relaxation time. Water,¹⁻³ and solid crystalline ices^{3,4} at high temperatures also show a similar Debye-type relaxation spectra. Most liquids, whether hydrogen bonded or not, have shown a distribution of relaxation times⁵ for the α -relaxation process that represents structural fluctuations observed in viscous flow and whose kinetic freezing causes a liquid to vitrify and which have been related to the time scale of the Johari-Goldstein (JG) relaxation.⁶⁻⁹ A recent study has found that 1 wt % mixture of di-*n*-butylether in 3-methylpentane, in which intermolecular hydrogen bonding is absent shows a Debye-type spectra, and not a distribution of relaxation times.¹⁰ If verified, it would bear upon the manner in which the mechanism of Debye relaxation has so far been considered in terms of a first-order rate process of breaking and reforming of hydrogen bonds¹¹⁻¹⁴ and been explained^{13,14} in

terms of the theory of Anderson and Ullman¹⁵ which formally attributes the shape of a relaxation spectra to the relative rate of dipolar reorientation and its environment fluctuation.

On the basis of ionic solution studies,¹⁶ it had been confirmed that a Debye-type single relaxation process observed in 1-propanol, that contributes $>95\%$ of its total orientation polarization, is likely associated with the first order reaction rate process of breaking and reforming of intermolecular hydrogen bonds in the transitory linear chain structure in the liquid. The extent of hydrogen bonding in such liquids increases with decrease in the temperature and, at low temperatures, the activation energy for dipolar relaxation in these liquids tends to become much greater than the hydrogen-bond energy of 20–30 kJ/mol.

A variety of studies of binary solutions of alcohol in nonpolar liquids have found that monohydroxy alcohols show only one Debye-type relaxation process that carries most of their orientation polarization.¹⁷⁻²⁰ This has been interpreted to indicate a nonspecific character of the hydrogen bonding between alcohol molecules in the solution. Binary

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solutions of nonhydrogen bonded liquids have also shown only one relaxation process but with a distribution of relaxation times.^{21–23} In contrast binary solutions of alcohols in alkyl halides have shown two relaxation processes. Such a finding was first reported by Schallamach²⁴ who had performed dielectric relaxation measurements on dipolar (nonhydrogen bonded) liquids and alcohol mixtures. He had found that for fixed 9 MHz frequency measurements, binary mixtures of 1-propanol, citrol, geraniol, and of geranic acid in isoamylbromide showed separate dielectric loss peaks one for each component in the solution. In the geraniol-isoamylbromide mixture, the peak for the molecularly associated component had shifted to a lower temperature suggesting that the dielectric relaxation time, τ , of the alcohols was less in the solution than in the pure state.²⁴ He had concluded, “the hindering forces envisaged by Debye as well as the potential troughs of the so-called kinetic theory depend on the molecule and so give a separate relaxation time for each molecular species present.”²⁴ This suggested phase separation in the binary mixtures, undetectable in transmitted light, occurring already at high temperatures at which both components had τ of ~ 200 ns. Winslow *et al.*²⁵ had studied mixtures of different polar molecules in *o*-terphenyl and had concluded that dipole-dipole forces are not the dominant factor in determining the relaxation spectra’s shape which was asymmetric and more skewed at high than at low frequencies. Studies of 1-propanol-isoamylbromide and of 2-methylpentane-isoamylbromide mixtures were reported by Denney¹⁷ and Denney and Ring,²¹ who reached the same conclusions as Schallamach²⁴ and Winslow *et al.*²⁵

When there is intermolecular hydrogen bonding in the pure liquid and not in its binary solution, nanoscale aggregation of the component by phase separation leads to a set of changes in the dielectric and other properties. The effect of such aggregation on the features of α -relaxation process behavior was recently reported by studying a mixture of a long chain alcohol, 5-methyl-2-hexanol, with a slightly shorter molecule, isoamylbromide.²⁶ It was found that in the nanophase separated mixture, τ of the alcohol was shorter than the value measured for the pure liquid,²⁶ while τ of the isoamylbromide was slightly longer than measured for the pure liquid.²⁶ This is the opposite of the change in τ observed for 1-propanol-isoamylbromide mixture.^{17,24} In view of the interpretation of the Debye-type spectra in terms of the relaxation by hydrogen bond breaking and reforming,^{1–3,11–14,27,28} and our findings for the 5-methyl-2-hexanol mixture,²⁶ we have restudied the dielectric behavior of 1-propanol-isoamylbromide mixture in detail and have examined its crystallization behavior in real time by using broad band spectroscopy. Studies on their pure liquid states have been reported in earlier papers,^{16,22} and are used for comparison. We believe that in addition to the academic value, such studies are important for understanding certain biological process in which similar aggregation occurs, and in mixing of pharmaceuticals with a dipolar, nonhydrogen bonded liquid.

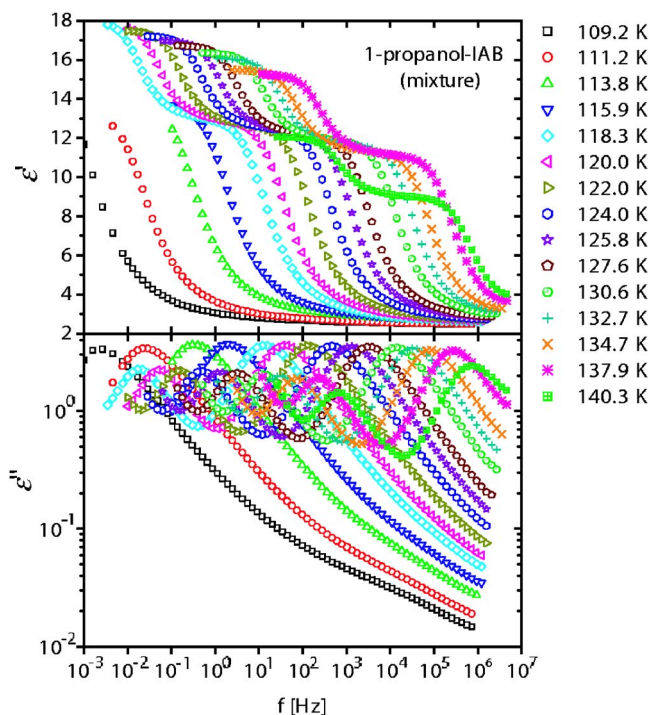


FIG. 1. (Top) Permittivity, ϵ' , and (bottom) loss, ϵ'' , spectra of the 20 mol % 1-propanol-isoamylbromide mixture between 1 mHz and 10 MHz at various temperatures.

II. EXPERIMENTAL METHODS

Samples of 1-propanol (Fluka AG, purum) used was from a stock used in an earlier study.¹⁶ Isoamylbromide (Aldrich, 96%) used was also from a sample used in an earlier study,²² which was redistilled prior to use. A mixture with the composition 1 mol of 1-propanol to 4 mol isoamylbromide (i.e., a 20 mol % solution of the 1-propanol in isoamylbromide) was prepared by accurate weighing. The spectra of the dielectric permittivity and loss, ϵ' and ϵ'' , were measured over the frequency range of 1 mHz–10 MHz and temperature range 91.7–140.3 K by means of a Novocontrol Alpha A frequency response analyzer and ZG4 dielectric interface in 2-wire mode, while the temperature of the sample was monitored at 20 s intervals during the electrical measurement. The capacitor (a 27 pF stainless steel variable multiplate capacitor with silver-plated electrodes) and a Pt 100 Ω resistance sensor for the temperature measurement were inserted into a glass vial containing the liquid mixture, ensuring no air bubbles were trapped. The sample was cooled from ambient temperature in liquid N_2 . The maximum deviation from the mean temperature was <0.2 K after stabilization. Since it was observed that the permittivity of the samples decreased quite abruptly at temperature above ~ 138 K (see Fig. 1), the crystallization behavior of the mixture was also briefly examined by heating a sample slowly (at ~ 0.1 K min^{-1}) from 131.7 to 140.1 K followed by cooling to 139.3 K while dielectric spectra were measured from 1 Hz to 10 MHz. These spectra took about 151 s to measure. The maximum temperature rise during a dielectric scan was <0.4 K. The reason for this somewhat unusual and awkward thermal history (see Fig. 7 for a full plot of temperature against time) was the inability of our liquid N_2 cryostat to

maintain a constant sample temperature while heat is evolved during the exothermic crystallization. This caused an overshoot of the sample temperature during the heating ramp.

III. RESULTS

For convenience of comparing the results, we have kept the same sequence for figures here as in the earlier paper on the study of 5-methyl-2-hexanol.²⁶ For brevity, the homogeneous solution of 1 mol of 1-propanol with 4 mol of isoamylbromide (i.e., a 20 mol % solution of the 1-propanol in isoamylbromide) studied here is referred to as the mixture. Its ϵ' and ϵ'' spectra are shown in Fig. 1 for the temperature range 109.2–140.3 K in which the dispersion and absorption features due to each component are clearly distinct. As seen in our study of 5-methyl-2-hexanol-iso-amylbromide mixture,²⁶ and as was observed previously by Denney¹⁷ for the 1-propanol-isoamylbromide mixture, the spectra show two dispersion regions in ϵ' and two peaks corresponding to these dispersions in ϵ'' . The lower frequency dispersion and the ϵ'' peak correspond to Brownian diffusion of 1-propanol while the higher frequency peak is associated with the isoamylbromide molecules. At the lowest temperature at which the isoamylbromide's ϵ' dispersion and ϵ'' peak appear in the frequency window of the experiment (109.2 K), τ of isoamylbromide estimated from the frequency of maximum loss would be ~ 67 s. At 109.2 K, 1-propanol in the mixture is vitrified [$T_g(10^3 \text{ s}) \sim 111.7$ K], and its extrapolated τ in the mixture is many orders of magnitude longer than that of the iso-amylbromide component and well below the frequency window of these measurements. This means that while the structure of the phase-separated 1-propanol becomes kinetically frozen at $T \leq 112$ K, diffusion of isoamylbromide molecules continues in the remainder of the ultraviscous phase in the regions surrounding the rigid 1-propanol in the mixture.

1-propanol has three relaxation processes, referred to as I, II, and III, of which I appears as a Debye peak (single relaxation time) in the ultraviscous state, which persists when hydrogen bonds are broken by addition of ionic salts to it, as described earlier.¹⁶ The other two are resolved from a fitting of the high-frequency ϵ' and ϵ'' data and show an asymmetric distribution of relaxation times. In contrast, isoamylbromide has two relaxation processes, both the lower frequency^{22,29} and higher frequency²² relaxations showing an asymmetric distribution of relaxation times. The fastest relaxation process in both isoamylbromide and 1-propanol has been regarded as the JG relaxation. To show their spectral positions and features in comparison to the spectra of the mixture, we have plotted the ϵ'' spectrum of the mixture at 125.1 K in Fig. 2(top) and spectra of pure isoamylbromide and 1-propanol at almost the same temperature (125.2 K) in Figs. 2(middle) and 2(bottom). The pure 1-propanol spectrum in Fig. 2(bottom) has been shifted downward in frequency so that the main loss peak coincides with that observed for the mixture. The pure isoamylbromide spectrum is unaltered. It is evident that some of the spectral features of the high frequency relaxation and the JG relaxation of

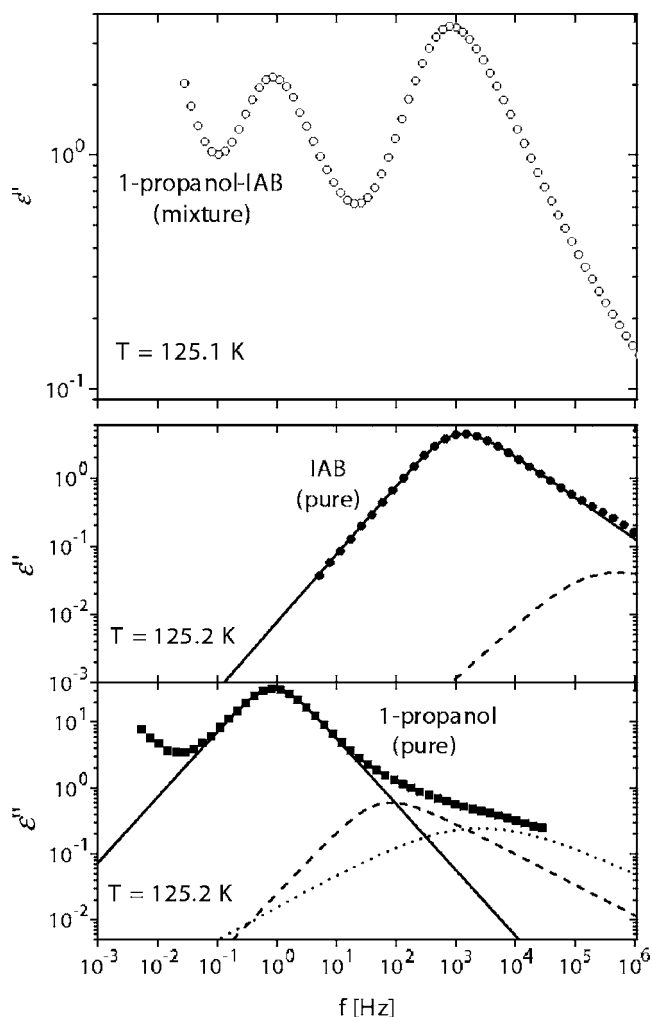


FIG. 2. (Top) Dielectric loss spectra of the 1-propanol-isoamylbromide mixture at 125.1 K. (Center) The corresponding spectra for pure isoamylbromide at 125.2 K. (Bottom) The spectra for pure 1-propanol at 125.2 K, showing the three relaxation processes I, II, and III in order of increasing frequency. The spectrum has been shifted so that the relaxation time of the Debye peak coincides with that for 1-propanol in the mixture at that temperature. The partial overlap of processes II and III of pure 1-propanol with the spectra of pure isoamylbromide leads to a slight overlap in the same spectral region of the mixture, which prevents an appropriate analysis of processes II and III of 1-propanol in the mixture. Complete characterization of the contribution of each substance to the mixture spectrum is not possible.

1-propanol overlap the isoamylbromide relaxations in the spectra measured here. Because of that, it is difficult to unambiguously resolve the ϵ' and ϵ'' spectra of the mixture into a total of five relaxation regions and dc conductivity. However, it is reasonable to assume the ϵ'' peak frequency of 1-propanol is not significantly affected by contributions to ϵ'' from the isoamylbromide component and that its high frequency relaxation processes,¹⁶ i.e., spectra II and III, also do not in turn significantly affect the ϵ'' peak position of isoamylbromide.²⁶ Therefore, instead of analyzing the spectra of the two liquids in the mixture into their respective components, we have determined the ϵ'' -peak frequency, f_m , from the spectra by fitting a high order polynomial to the points around f_m , and calculated the dielectric relaxation time from the relation, $\tau = (2\pi f_m)^{-1}$.

Figure 3 shows the resulting plots of τ on a logarithmic

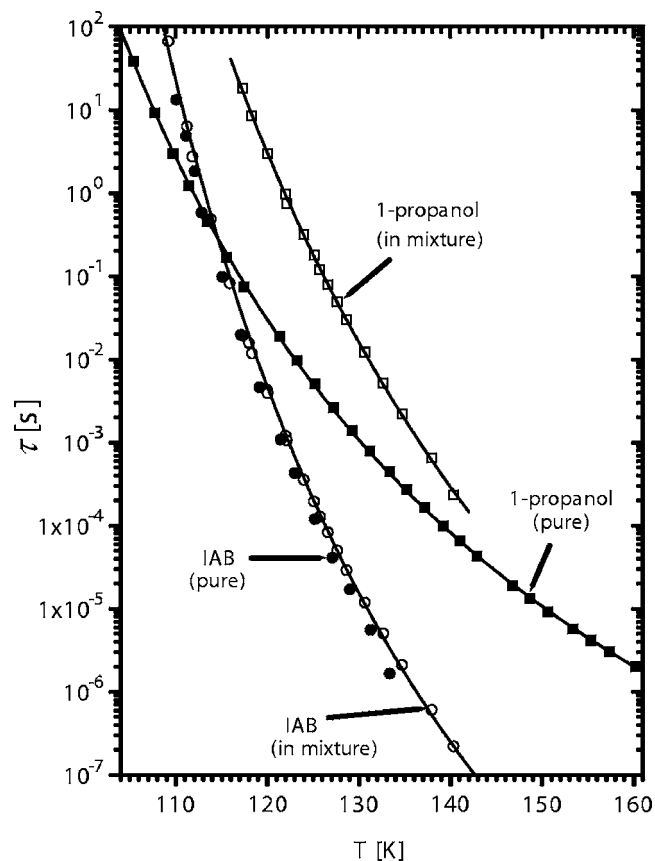


FIG. 3. Relaxation time obtained from the frequency of maximum loss of the components of the 1-propanol-isoamylbromide mixture is plotted against the temperature. For comparison, the data for pure 1-propanol (filled squares) and pure isoamylbromide (filled circles) are also plotted. The continuous lines are the fits to the equation, $\log_{10} \tau = A + [B/(T - T_0)]$, where $A = -17.61$, $B = 787$ K, and $T_0 = 68.5$ K for isoamylbromide in the mixture and the pure state. For 1-propanol in the mixture, $A = -16.45$, $B = 1088$ K, and $T_0 = 55.75$ K, and for pure 1-propanol $A = -12.71$, $B = 753.0$ K, and $T_0 = 52.68$ K.

scale against T for the relaxation due to Brownian diffusion of 1-propanol and that for that of isoamylbromide. For comparison, the plots for τ of pure 1-propanol taken from Ref. 16 and of isoamylbromide taken from data reported in Ref. 22 are also shown in Fig. 3. The Vogel-Fulcher-Tammann equation,³⁰⁻³² $\log \tau = -16.45 + [1088/(T - 55.8)]$, fits the data for 1-propanol in the mixture. From the earlier study of pure 1-propanol,¹⁶ $\log \tau = -12.71 + [753.0/(T - 52.68)]$. For isoamylbromide, τ values in the mixture and in the pure state are quite similar and are fitted reasonably well by the same relation as given before,²² $\log \tau = -17.61 + [787/(T - 68.5)]$ as seen by the line through the data in Fig. 3. As mentioned here earlier, and also found by Denney,¹⁷ τ of 1-propanol is longer in the mixture than in the pure state and that of the isoamylbromide is unaffected. This is in contrast to the behavior observed for a longer-chain alcohol, 5-methyl-2-hexanol whose τ becomes shorter in a mixture of the same concentration than in the pure state, that of the isoamylbromide increasing very slightly. That is, in both mixtures, τ of isoamylbromide and its temperature dependence remains almost the same, and τ of the alcohol component and isoamylbromide tend to converge with decrease in T , but it occurs slowly enough that the alcohol component still vitrifies at a

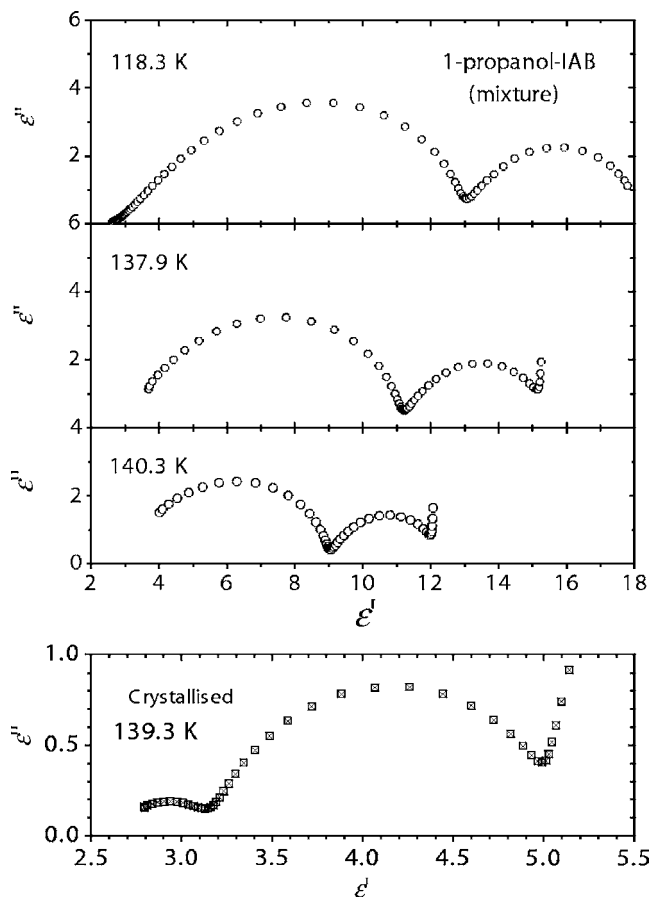


FIG. 4. Cole-Cole plots for 20 mol % 1-propanol-isoamylbromide at (top) 118.3 K, (center) 137.9 K, and (bottom) 140.3 K. The plot in the bottom panel is for a mixture that had partly crystallized after the thermal treatment of Fig. 7(bottom), i.e., a slow heating from 131.7 to 139.6 K at an average rate of ~ 0.1 K min^{-1} followed a slow heat to 140.1 K and cool to 139.3 K.

higher temperature than isoamylbromide in the mixture. Schallamach had also observed a decrease in the alcohol's τ and an increase in the isoamylbromide's τ in an equimolar geraniol-isoamylbromide mixture (see Fig. 5, Ref. 24).

To determine whether there is a change in the shape of the relaxation spectra of the mixture's components, we have shown the Cole-Cole³³ plots of the mixture in Fig. 4 at 118.3, 137.9, and 140.3 K. Of the two arcs seen at all three temperatures in Fig. 4, the one on the right hand side in the low-frequency range is due to the α -relaxation process of 1-propanol in the mixture. It appears approximately semicircular at the three temperatures as for the pure alcohol but fitting with a semicircular function shows that it is asymmetrically broadened at high frequencies. This behavior is somewhat different to that observed for 5-methyl-2-hexanol in its 20 mol % mixture with isoamylbromide where the corresponding arc for the alcohol was more clearly asymmetrically broadened relative to the semicircular Debye locus of the pure alcohol. The arc on the left hand side at high frequencies is due to the reorientational motion of isoamylbromide. It shows an asymmetric distribution of relaxation times of the Davidson-Cole³⁴ type. Figure 4 (bottom panel) shows the Cole-Cole plot at 139.3 K for a mixture sample that had been partially-crystallized. The isoamylbromide arc has be-

come extremely small, while the alcohol arc seems less affected. The crystallization results are discussed later here.

As shown in Fig. 2, and discussed here further, there would be a considerable ambiguity in resolving the relaxation spectra of 1-propanol in the mixture into three relaxation regions and determining the contribution of each to the dielectric strength, $\Delta\epsilon$. Despite the fact that τ is increased in the mixture, relaxation II and III of the 1-propanol spectra would still overlap part of the spectra of isoamylbromide. For this reason, we do not separate the spectral regions of 1-propanol in the mixture into its components I, II, and III to determine $\Delta\epsilon$, the orientational polarization contribution to its permittivity. Instead, we use the midpoint value of ϵ' as an estimate for the sum of the high frequency permittivity of the mixture, ϵ_{∞} , and for the orientational polarization contribution of the isoamylbromide component to the mixture's permittivity. Any remaining contribution to ϵ_s is then taken to be $\Delta\epsilon$ of 1-propanol. ϵ_{∞} was estimated from the high frequency limit of a spectrum measured at a low temperature where the contribution to the permittivity from relaxation processes should be minimal (91.7 K). Knowledge of ϵ_{∞} then allows us to estimate $\Delta\epsilon$ of isoamylbromide in the mixture. The $\Delta\epsilon$ for the mixture's components thus obtained are plotted against T in Fig. 5. For comparison, $\Delta\epsilon$ of pure 1-propanol and isoamylbromide are also plotted.

To gain an approximate idea of the distribution of relaxation times, the spectra were analyzed by fitting the sum of a Davidson-Cole³⁴ (with an asymmetric broadening parameter, β) and a Cole-Cole³³ relaxation term (the latter included to represent any JG relaxation contribution at the lower temperatures) to the isoamylbromide ϵ'' peak for each temperature in which it occurred within the measurement frequency window. The data on the low-frequency side of the peak were excluded, as these should contain the most influence from the higher frequency relaxations of 1-propanol. This contribution should be largest at lower temperatures because the τ values of isoamylbromide and 1-propanol in the mixture become closer as T is decreased (see Fig. 3) and the strength of process II increases. β is plotted against the temperature for the isoamylbromide component of the mixture in Fig. 6, where the data for pure isoamylbromide is also plotted for comparison. The difference in β is within experimental and analytical errors.

In the crystallization experiment, the sample had been quenched to liquid N₂ temperature, placed in the cryostat, and heated rapidly to the initial temperature of 131.7 K, a process that took roughly 30 min. Figures 7(top) and 7(middle) show the ϵ' and ϵ'' spectra of the mixture at ten points of the time and temperature during the slow heating followed by holding at temperatures close to where a spontaneous decrease in ϵ' indicating crystallization had been observed (see Fig. 1, the 140.3 K spectra). As a result of the inability of our cryostat system to hold a stable final temperature when extra heat is evolved during crystallization of the sample, we also show in Fig. 7(bottom), the sample's temperature as a function of time elapsed after the start of dielectric measurements. The sample was then heated from 132.0 K at 0.1 K min⁻¹ to \sim 139.1 K, more slowly to 140.1 K followed by a slight cooling to 139.3 K. The time-

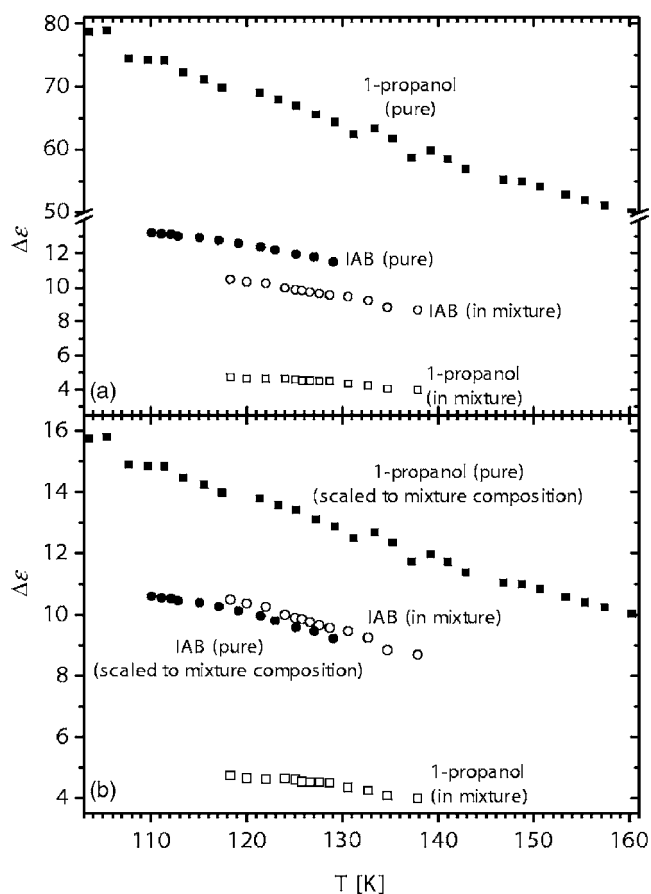


FIG. 5. (a) Contribution to the dielectric permittivity of the mixture from the orientational polarization of the 1-propanol and isoamylbromide components plotted as a function of temperature. The unscaled values measured for pure 1-propanol and isoamylbromide are shown for comparison. (b) The expected contribution to the dielectric permittivity of the mixture from the orientational polarization of 1-propanol and isoamylbromide is plotted against the temperature. This is shown by scaling the values for the pure substances to the mole fraction of each present in the mixture. The actual values measured for 1-propanol and isoamylbromide in the mixture are shown for comparison.

temperature positions in the sample history corresponding to the ten spectra of Figs. 7(top) and 7(middle) are marked.

IV. DISCUSSION

A. The dielectric relaxation behavior

In most respects, the results are qualitatively similar to that of 5-methyl-2-hexanol-isoamylbromide mixture.²⁶ Therefore, we only discuss the quantitative differences and their implications here. The plots in Fig. 5(a) show that the dielectric relaxation strength, $\Delta\epsilon$, of 1-propanol and isoamylbromide in the mixture are less than $\Delta\epsilon$ of their respective pure states, and the difference decreases slightly with increase in T . The lowering of measured $\Delta\epsilon$ in the mixture is of course expected because the amount of each component is a fraction of a mole and $\Delta\epsilon$ of each component would be obtained by scaling their respective pure state $\Delta\epsilon$ values by their mole fractions and square of the effective dipole moments. To investigate if there is an additional effect that alters the $\Delta\epsilon$ of the components in the mixture, we scaled the $\Delta\epsilon$ of pure liquids by multiplying by the mole fractions 0.2

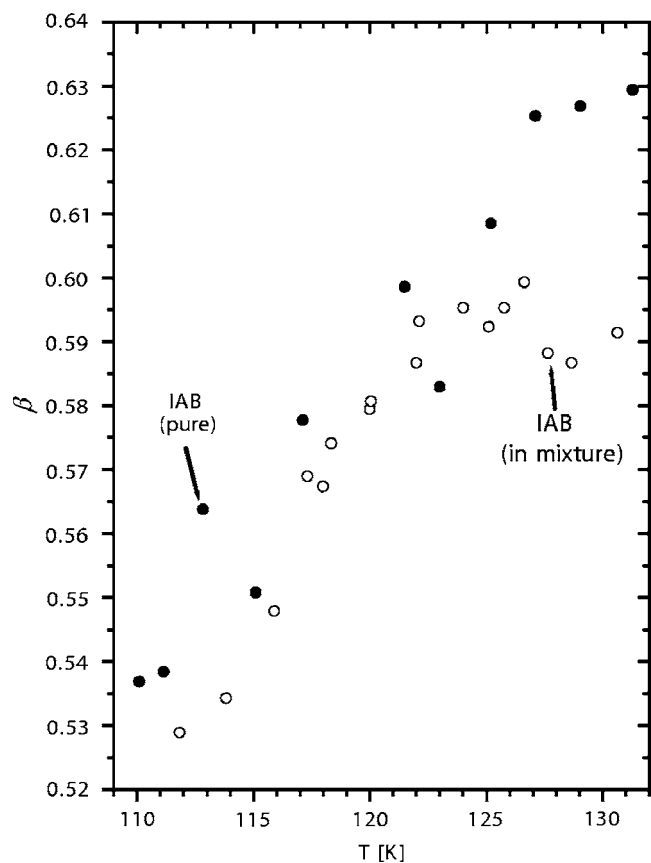


FIG. 6. Asymmetric (Davidson-Cole) distribution parameter, β , for isoamylbromide in the mixture and in the pure state plotted against the temperature. Maximum possible error in β at a single temperature for both data sets is $\sim \pm 2\%$.

(for 1-propanol) and 0.8 (for isoamylbromide), and have plotted it along with the mixture's measured $\Delta\epsilon$ in Fig. 5(b). It is evident that for 1-propanol at 120 K, the measured $\Delta\epsilon$ is lower, $\sim 35\%$ of the scaled $\Delta\epsilon$, and the two are the same for isoamylbromide at 120 K. In the 5-methyl-2-hexanol-isoamylbromide mixture at 155 K, the measured $\Delta\epsilon$ for 5-methyl-2-hexanol was also lower, $\sim 35\%$ of the scaled $\Delta\epsilon$, but that of isoamylbromide was higher, by $\sim 15\%$ at 130 K.²⁶ Thus there is a factor of 3 decrease in $\Delta\epsilon$ of the alcohols from their pure state values to those in the mixture.

For 1-propanol, this decrease may indicate a decrease in the molecular density in the nanophase-separated clusters and/or a decrease in the dipolar orientational correlation from its value in the pure state. Hydrogen-bond and strong dipole-dipole interactions in liquids and solids have been known to change the $\Delta\epsilon$, which has been quantitatively interpreted in terms of an orientational correlation factor g in the Onsager,³⁵ Kirkwood,³⁶ and Fröhlich³⁷ theory. If the effective dipole moment of 1-propanol were to remain unchanged, then its scaled $\Delta\epsilon$ would be close to the measured value. The decrease in $\Delta\epsilon$, therefore, reflects a significant decrease in g . This may occur if constraints to intermolecular hydrogen bonding become prominent in the phase separated state or else some of the molecules become hydrogen bonded in an antiparallel manner into dimers or multimers such that the net effective dipole moment is decreased.^{38–41}

In the same composition mixture, τ of 1-propanol clus-

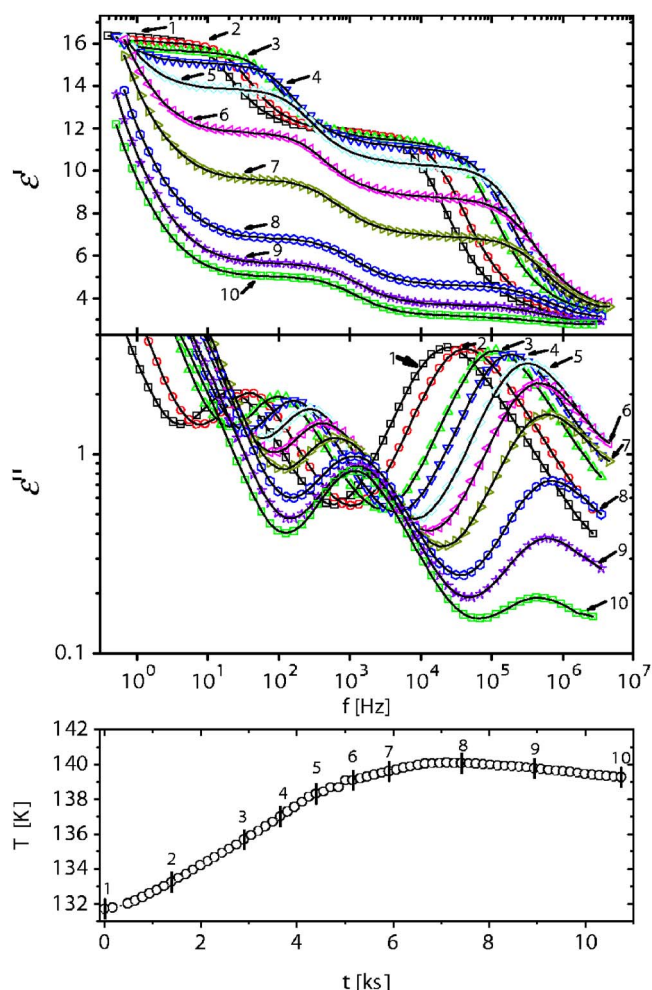


FIG. 7. (Top) ϵ' and (middle) ϵ'' of the 1-propanol-isoamylbromide mixture at various points (1–10) along the temperature vs time (from first measurement) sample history shown in the bottom panel. The sample was heated at an average rate of ~ 0.1 K min^{-1} from 131.7 K (1) to 139.6 K (7). Heat evolved during crystallization then caused the sample temperature to rise further to 140.1 K (8), after which it slowly fell to 139.3 K (10) over ~ 4 ks.

ters has been found to be longer than in the pure 1-propanol.^{17,24} The viscosity, η , of pure 1-propanol is 1.93 cP (Ref. 42) at 298 K and that of isoamylbromide is also low, but not known.⁴³ Were their respective η values to determine their molecular dynamics at 298 K, their structural relaxation time ($=\eta/G_\infty$, $G_\infty=1 \times 10^{10}$ dynes cm^{-2}) would be nearly the same, i.e., ~ 1.93 ps. This would presumably be the case for τ also. In Fig. 3, τ of 1-propanol at 140 K is about 2.5 decades longer than τ of isoamylbromide. Because of the already large difference at 140 K it would seem that τ would decrease more rapidly with increase in T for 1-propanol than for isoamylbromide, as τ approaches its nanosecond value at 298 K. In comparison, η of 5-methyl-2-hexanol is higher than of isoamylbromide at 298 K and there is an immeasurably high difference between their respective τ at 140 K (pure 5-methyl-2-hexanol is vitrified below 149 K).²⁶ A more remarkable difference appears in the τ value of 1-propanol in the mixture and in the pure state. The τ value in the mixture at 119 K is ~ 130 times the value measured for the pure state and at 140 K, it is only ~ 4 times. An extrapolation indicates that the same value of $\tau=8.3$

$\times 10^{-6}$ s for 1-propanol in the mixture and the pure state would be reached and their plots against T in Fig. 3 would either merge or most likely cross. This would not suggest that clusters have ceased to exist at $T > 151$ K. It would only indicate that structure of the 1-propanol clusters at the crossing temperature differs little from the structure in the pure state and that depending upon the thermal energy, τ of alcohol clusters may be higher than in the pure state, equal to it, or lower. This was not observed for 5-methyl-2-hexanol. We conclude that the behavior of monohydroxy alcohols of different chain lengths in nanophase separated states differ.

For isoamylbromide, β in Fig. 6 for the mixture and the pure state remains the same showing no effect of phase separation on β . This is in contrast to the 5-methyl-2-hexanol mixture for which β of isoamylbromide decreased from 0.61 to 0.52. Fitting of a Debye relaxation to the Cole-Cole plots in Fig. 4 is poor at high frequencies and the relaxation has become slightly skewed, as found for the 5-methyl-2-hexanol mixture where the effect was far larger.²⁶ As β has been related to the steepness index^{44,45} of the approach of $\log \tau$ to T_g in the known (Oldekop) plot⁴⁶ against T/T_g [later named the “fragility” or m (Ref. 45)], this means that m for 1-propanol and isoamylbromide does not change on phase separation. In terms of the dynamic heterogeneity conjecture,^{47,48} presence of nanoscopic heterogeneity of a different constituent does not add to the dynamic heterogeneity of the component phases.

There are several indications that the 1-propanol-isoamylbromide mixture is inhomogeneous at a submicrometer scale. As they are similar to those found for the 5-methyl-2-hexanol-isoamylbromide mixture, we mention these only briefly here. One anticipates that a *homogeneous* mixture would show one relaxation process and not the two observed, and the viscosity of the mixture would be different from that of the pure state. Also, τ of isoamylbromide in the mixture would differ from that in the pure state, but the two are the same within the experimental and analytical uncertainty. (Viscosity of other binary mixtures have shown a monotonic decrease as 1-bromobutane is added to an alkanol.⁴⁹) This means that τ and β of isoamylbromide are not affected by the presence of 1-propanol, i.e., when 1-propanol clusters form, isoamylbromide is left in a relatively pure state in the mixture. Lastly, the refractive index of 1-propanol is 1.385 and of isoamylbromide is 1.441 at ambient temperature.⁵⁰ According to the Fresnel equation, this difference is sufficient to produce an optical contrast in the mixture to make it somewhat opaque. But the mixture at ambient temperature is found to be optically transparent, which indicates that 1-propanol clusters are smaller than the wavelength of light, despite that the mixture shows two dielectric relaxation processes.

At ~ 119 K, τ of 1-propanol clusters is 130 times that for the pure liquid, which is the opposite of the finding for 5-methyl-2-hexanol clusters in isoamylbromide, whose τ was several orders of magnitude *lower*. We suggest that the smaller size of the 1-propanol molecule relative to 5-methyl-2-hexanol would cause less steric hindrance to hydrogen bonding and the reorientation of the OH group, and there would be a relatively larger number of molecules in its

nanometer-size cluster, i.e., the extent of hydrogen bonding in the 1-propanol clusters would be significantly greater than in 5-methyl-2-hexanol clusters. The presumably spherical or curved shape of the cluster that is needed to minimize its surface energy would further constrain alignment of OH groups necessary for the hydrogen bonding. Since each molecule forms two hydrogen bonds, one as a donor of proton and another as an acceptor, the number of hydrogen bonds that need to break before a reference dipole and its dipolar environment can orient would be a maximum of two. We propose that the increase in τ of 1-propanol in the mixture reflects an increase in the number of intermolecular H bonds.

The relaxation rate of oligomers (dimer and trimer) of confined propylene glycol changes in a nonmonotonic manner with change in the nanopore size.⁵¹ In mesopores (7.5–2.5 nm) of a sol-gel glass matrix this rate either decreases or increases depending on whether the pores are treated with hexamethyldisiloxane (this replaces dangling –OH groups on the pore walls with trimethylsilyl groups) or not.^{52,53} In the untreated pores, H-bonding interactions between the SiO₂ pore walls and propylene glycol are strong, which increases τ , but weaker in the treated pores and τ then becomes slightly shorter than in the bulk. A more recent differential scanning calorimetry (DSC) study has shown that T_g of another H-bonded liquid, glycerol, confined to hexagonal mesoporous silica with pore sizes of 26.4–2.6 nm (untreated to maintain formation of interfacial –OH bonds) increases with decreasing pore size as a result of increasing importance of these interface effects, while T_g of a non-H bonded liquid (*o*-terphenyl) is reduced by ~ 20 K for the smallest pore size.⁵⁴ In relevance to our study, interaction between the alcohol molecules on the cluster-liquid interface could also be a factor in determining whether τ increases in the mixture or not. For 1-propanol the effect also depends upon the thermal energy, as its variation with T in Fig. 3 shows. The change of τ of the 1-propanol component on partial crystallization of the isoamylbromide matrix substantiates that interfacial interaction of the clusters with the matrix is also important (see next section).

As discussed earlier,²⁶ the findings have consequences for (i) the use of the Debye-Stokes-Einstein equation between the dc conductivity and τ because it is not certain which of the two relaxation processes observed should be related to the dc conductivity, (ii) the mechanism of the Debye relaxation, (iii) the restricted Brownian diffusion within the nanoclusters and the liquid containing the clusters, and (iv) the use of entropy concepts for the relaxation process.

B. Crystallization kinetics

The spectra of ϵ' and ϵ'' in Fig. 7 show that, as expected, the ϵ'' spectra shift toward a higher frequency as T increases. Also, there are large decreases in ϵ' for spectra labeled 5–10, indicating crystallization, which mainly affect the isoamylbromide ϵ' dispersion and ϵ'' peak. The spectra of ϵ' and ϵ'' at different T and time during the heating of the mixture from ~ 132 to ~ 140 K over a period of ~ 11 ks show that the spectral features of the 1-propanol component (as represented by τ associated with its relaxation peak) shift to a

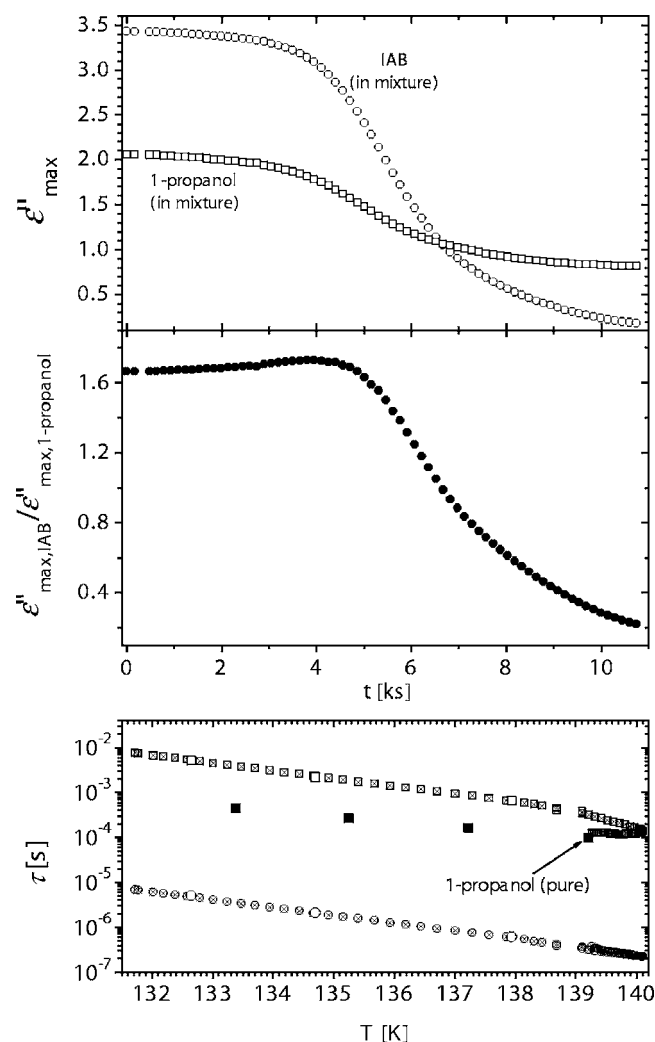


FIG. 8. (Top) ϵ''_{\max} for the loss peaks of the isoamylbromide and 1-propanol components of the mixture plotted as a function of time as it undergoes the thermal treatment shown previously in the temperature-time plot of Fig. 7 (bottom). (Middle) the ratio of ϵ''_{\max} for the isoamylbromide and 1-propanol components vs time. The ratio decreases sharply above 5 ks due to the onset of crystallization, primarily of the iso-amylbromide component. (Bottom) The corresponding relaxation times for the 1-propanol (crossed squares) and isoamylbromide (crossed circles) components as a function of temperature. When crystallization occurs, the relaxation time for the 1-propanol component of the mixture decreases towards the pure value, causing a hysteresis. The four filled squares correspond to pure 1-propanol. The open symbols correspond to data for the mixture from Fig. 3 while the filled squares are relaxation times for pure 1-propanol.

higher frequency and the ϵ' plateau and the ϵ''_{\max} value associated with both components decreases. This occurs even when T remains close to 139 K over the time period of 6 to ~ 11 ks (Fig. 8, bottom). To analyze the data more accurately, we have shown the plots of ϵ''_{\max} against the time in Fig. 8 (top), bearing in mind that T is not constant. The plots for 1-propanol and isoamylbromide in the mixture show the ϵ''_{\max} for isoamylbromide decreases to a value of ~ 0.18 more rapidly than that for the 1-propanol component decreases to a value of ~ 0.82 . The limiting low value of ϵ''_{\max} is expected to be zero for the orientationally ordered crystallized state. But this value is not reached for either of the two components, indicating that a significant amount of 1-propanol, $\sim 40\%$ ($0.82 \times 100/2.1$), remains uncrystallized while only $\sim 5.3\%$

($0.18 \times 100/3.4$) of isoamylbromide remains uncrystallized. Pure 1-propanol did not show crystallization at these temperatures but pure isoamylbromide had a tendency to crystallize when heated above 129 K,²² as found here for the mixture. The large decrease in ϵ''_{\max} for each component onsets at 2.5 ks and the relative decrease of ϵ''_{\max} is far larger for isoamylbromide.

If after a certain instant of time both components were to crystallize to the same extent, then the ratio ($\epsilon''_{\max, \text{isoamylbromide}}/\epsilon''_{\max, \text{1-propanol}}$) would be equal to 1.6 at all times during the crystallization, provided it did not change with T . However, it slightly increases up to t of 4 ks and thereafter decreases sharply after 4.5 ks as crystallization proceeds and appears to be reaching completion at long times. The increase indicates a relatively higher sensitivity of $\epsilon''_{\max, \text{1-propanol}}$ to T and/or an increased crystallization of 1-propanol that would reduce $\epsilon''_{\max, \text{1-propanol}}$ relatively more. The sigmoid shape decrease thereafter mainly indicates a slower crystallization of 1-propanol relative to isoamylbromide. Evidently, the interfacial and/or intermolecular interactions have an effect on the crystallization of nanophase separated clusters of 1-propanol.

The τ of the two components determined during the course of crystallization is plotted against T in Fig. 8 (bottom panel), where the data obtained by cooling the mixture from 140.1 to ~ 139 K are also plotted. The plots show that τ agrees with those measured from the spectra of uncrystallized components in Figs. 1–3. The main feature is that τ of 1-propanol decreases more rapidly with increase in T in the 139–140.1 K range and then on cooling its original value of 0.29 ms is not recovered at 139.3 K, while the τ value of 0.30 μs for isoamylbromide is recovered. This indicates that crystallization of the mixture produces a state of 1-propanol whose τ is reduced. In fact, τ in the crystallized mixture at 139.3 K has almost returned to the value for pure 1-propanol¹⁶ at 139.3 K, as seen by the solid square symbols in Fig. 8(c). This would suggest that interfacial interactions between the liquid isoamylbromide and 1-propanol clusters, which disappear on crystallization may also be partly responsible for the large increase in τ of 1-propanol in the mixture, which is in addition to the nanoconfinement effect mentioned above. The relatively high value of 0.82 for $\epsilon''_{\max, \text{1-propanol}}$ at ~ 11 ks of crystallization time also indicates that either 1-propanol is incompletely crystallized and/or the remaining liquid's τ is reduced compared to the mixture. This would be possible if the state of 1-propanol at the crystal interfaces or grain junctions was molecular or less than two-hydrogen bonded, i.e., more free to reorient.

V. CONCLUSION

The dielectric relaxation spectra of 1-propanol mixed with isoamylbromide (1:4 mol/mol ratio) shows two relaxation regions attributable to the reorientation of the alcohol and of isoamylbromide molecules at different rates. This indicates that 1-propanol phase separates most likely into nanometer-size regions. The dynamics of 1-propanol in the mixture becomes slower by a factor ~ 130 at 119 K. The gap

between the relaxation rates is reduced at higher temperatures with a possible crossover at 151 K. The dynamics of isoamylbromide does not change. The relaxation of 1-propanol remains Debye-type while that of isoamylbromide has a distribution of times which remains the same in the mixture. The contribution to permittivity due to orientation polarization of 1-propanol decreases by a factor of 14.6 (at 120 K) from pure to the mixed state and that due to isoamylbromide decreases by a factor of 1.20, when scaling for the mole fraction of each component is not taken into account. When scaling from the pure state to the mixture composition is used, the contribution expected for 1-propanol remains much higher than was actually measured in the mixture, indicating a considerable decrease in the orientation polarization as a result of change in the density and/or short-range dipolar orientation. But it remains the same for isoamylbromide in the pure state and the mixture. The results show that phase separation may lead to an increase in the relaxation time as the extent of hydrogen bonding increases and as the aggregates reach a nanoscale size in which interfacial effects distort the hydrogen-bond arrangement.

The study also raises the issue of how the dielectric relaxation times of the alcohol and isoamylbromide can be related to the macroscopic viscosity of the solution through the equality of shear and dielectric relaxation times or else can be related to the continuum model of high-frequency shear moduli of the clusters and of the liquid matrix, which seems to have found recent support from experiments.^{55,56} It is also difficult to see how this behavior may be interpreted in terms of the configurational entropy theory.⁵⁷

During the crystallization of the mixture, isoamylbromide crystallizes relatively faster and reaches completion before 1-propanol. This may be related to the faster Brownian diffusion or relaxation time of isoamylbromide. The relaxation time of the uncrystallized isoamylbromide fraction does not change from its value in the nanophase separated state of isoamylbromide. The relaxation time of the 1-propanol is reduced towards the value in the bulk pure liquid at the final stages of crystallization indicating that the dynamics of the interfacial liquid at the crystal grain junctions is different from that in the nanophase separated mixture.

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