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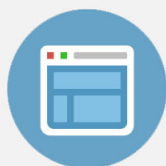
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## Debye process and dielectric state of an alcohol in a nonpolar solvent

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To investigate the origin of the first order molecular kinetics of the most prominent, Debye-type polarization, a detailed dielectric relaxation study of 66.5, 40, and 20 mole% solutions of 5-methyl-2-hexanol in 2-methylpentane (2:1, 0.67:1, and 0.25:1 molar ratios) was performed. The Debye-type polarization remains prominent in the solutions, despite the extensive loss of intermolecular hydrogen bonds. At high temperatures, its contribution to permittivity extrapolates close to the statistically scaled values for the 2:1 solution. For others, the measured values of its contribution crossover the scaled values in a temperature plane. The faster relaxation process of about 4% magnitude has an asymmetric distribution of times in the solutions and, relative to those of the pure alcohol, their values decrease on heating more at high temperatures and less at low. This is attributed to an increase in the alcohol cluster size by consumption of monomers as well as the growth of smaller clusters as the solution is cooled. It is argued that structural fluctuation in solutions, as in the pure alcohol, is determined by the rates of both the Debye-type and the faster polarizations in the ultraviscous state.

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### I. INTRODUCTION

Nearly 95% of electrical polarization in many monohydroxy alcohols<sup>1,2</sup> and alkyl amides<sup>3,4</sup> follows the first order kinetics of exponential decay with time, or a single, Debye-type relaxation. In contrast, the majority of ultraviscous liquids and most alcohols, including some monohydroxy alcohols, have shown a distribution of relaxation times, or a non-exponential decay of polarization.<sup>5</sup> Anderson and Ullman<sup>6</sup> had discussed these two types of relaxations in terms of fluctuation of a dipole relative to its environment. Accordingly, a Debye-type relaxation is observed when the rate of “free volume” or environmental fluctuation is much faster than the rate of dipolar reorientation. In contrast, a relaxation time distribution is observed when the rate of dipole reorientation is comparable to or much faster than the rate of environment fluctuation.<sup>6</sup> They implied that there is a spectrum of structures in a liquid with varying abilities to undergo reorientation and are all in dynamic equilibrium with one another. This variation in the environment of the local order may be seen to correspond to diffusion in the “fluctuating free volume.”<sup>6</sup>

In an extensively hydrogen-bonded liquid, an H-bond must break before a dipole may reorient. After an H-bond has broken, the molecule may either form an H-bond with the same neighbor without reorienting, or it may form an H-bond with another neighbor. In the first case, no dipolar reorientation occurs, and in the second case dipolar reorientation occurs. Thus there are two processes, first breaking of an H-bond and then orientation diffusion. Dipolar reorientation would occur during the time period an H-bond remains broken. Accordingly, one may consider a consecutive reaction,

$A \rightarrow B \rightarrow C$ ;  $A \rightarrow B$  for H-bond fluctuations and  $B \rightarrow C$  for the dipolar reorientation. In a case when the process  $A \rightarrow B$  is slower than the process  $B \rightarrow C$  the H-bond fluctuations would not only determine the Brownian diffusion but also the dipolar reorientation kinetics. As these fluctuations follow the first-order kinetics, the dielectric relaxation has a single relaxation time, as for the single Debye-type process.

Most liquids show an asymmetric distribution of relaxation times, which may indicate dynamic heterogeneity.<sup>7-9</sup> Conceptually, it represents a multiplicity of Debye-type single relaxation processes, as originally described mathematically by Majumdar<sup>10</sup> to explain a distribution of relaxation times. In the sense of local detail of the structures that may be in a dynamic equilibrium, it comes closer to the Anderson and Ullman’s mechanism for the distribution of times.<sup>6</sup> However, despite the expected dynamic heterogeneity in a binary solution, ultra-viscous 1 wt% solution of di-*n*-butyl ether in 3-methylpentane,<sup>11</sup> in which intermolecular H-bonds do not form, has also shown a Debye process. A review of various studies and issues arising from interpretation of the Debye-type relaxation have appeared in the context of dielectric features of 5-methyl-2-hexanol solution in isoamylbromide.<sup>12</sup> Since then, several groups have attempted to interpret the Debye process observed for another alcohol, 2-ethyl-1-hexanol, by comparing its dielectric features against the features observed by calorimetry,<sup>13</sup> mechanical spectroscopy<sup>14</sup> and also by studying the effects of high pressure on dielectric properties.<sup>15,16</sup> This comparison has led to a controversial interpretation. Fragiadakis *et al.*<sup>15</sup> have provided a brief and updated review of this controversy.

Dilution of an alcohol by a nonpolar solvent tends to break the extensive intermolecular H-bonded structure by steric hindrance. This changes the dielectric relaxation

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strength,  $\Delta\epsilon$ . In the absence of any solute–solvent interaction,  $\Delta\epsilon$  scaled by the mole fraction of the components would agree with the measured value. But if one component is intermolecularly H-bonded and scaling still gives a value comparable to that measured, the finding would suggest that the H-bond interactions in the solution do not change significantly. But if the scaled  $\Delta\epsilon$  is found to differ from that measured, the H-bond interactions would have changed and that would change the characteristics of the dielectric relaxation.

It is expected that as the extent of H-bonding decreases, or else the H-bond strength decreases, structural fluctuation would become less constrained, and the state of a liquid would explore a larger number of configurations at a given temperature. This would increase the configurational entropy and accordingly decrease the structural relaxation time according to the configurational entropy theory. (Neither this theory takes into account the distribution of relaxation times nor the free volume theory). Therefore, a partially H-bonded structure would have a shorter relaxation time than a fully H-bonded structure. The distribution of relaxation time for structural relaxation however may not be the same as that for dielectric relaxation because the first requires configurational fluctuations which do not require change in the dipole vector and the second requires only a change in the dipole vector, irrespective of the state of H-bonded molecules or their cluster sizes. Thus structural fluctuations may be distinguished from H-bond fluctuations in some cases. Here we used these concepts as a premise, and performed a detailed dielectric investigation of ultraviscous solutions of 5-methyl-2-hexanol in a nonpolar solvent, 2-methylpentane of three concentrations that correspond to the molar ratios of 2:1, 0.67:1, and 0.25:1 of the alcohol to solvent. Our investigations show that, (i) the Debye-type relaxation persists in the solution, (ii) the relaxation time is much less than that of the pure alcohol at low temperatures than at high temperatures, and (iii) the relaxation times of the solution and of the pure alcohol become closer as  $T$  is increased. We interpret these findings in terms of the presence of intermolecularly H-bonded clusters of alcohol molecules in the solutions, or aggregation at a nanoscale.

The general premise of our interpretation is that if a feature of pure liquid persists on dilution, it would indicate an unchanging mechanism of polarization with changing structure in the solution. We consider it necessary to use the dielectric relaxation alone and thus avoid the uncertainty arising from comparison of the structural relaxation-related, mechanistically different calorimetric, and mechanical responses. It is hoped that studies of solutions in nonpolar solvents in general would be used in the future for resolving whether or not calorimetric and mechanical relaxations admit to the same phenomenology as dielectric polarization.

## II. EXPERIMENTAL METHODS

For preparing the 2:1 molar ratio solution, we used the 5-methyl-2-hexanol and 2-methylpentane samples left over from our earlier studies.<sup>12,17,18</sup> For the 0.67:1 and 0.25:1 solutions, 5-methyl-2-hexanol was purchased from Sigma–Aldrich and distilled in vacuum. The technique for measurements is the same as before.<sup>12,17,18</sup> Briefly, the dielectric

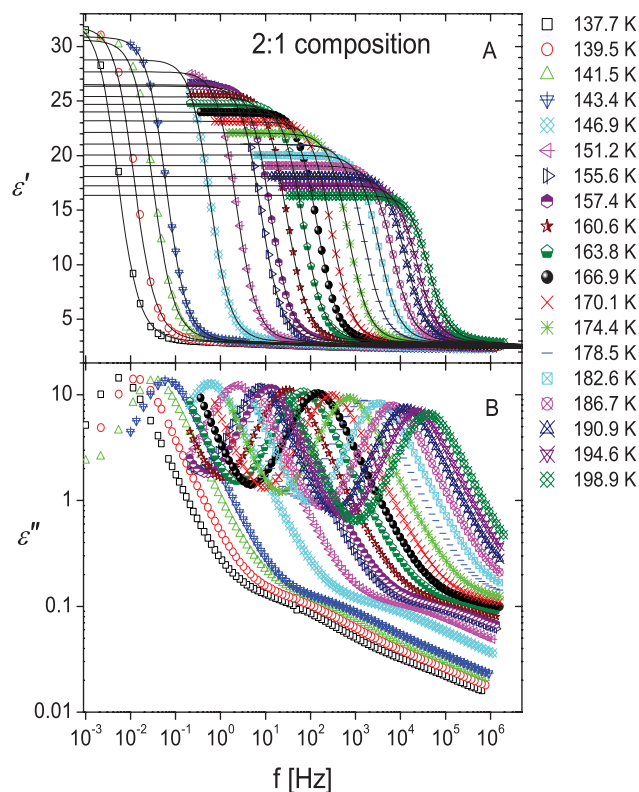


FIG. 1. (A) The dielectric permittivity and (B) loss spectra of 2:1 solution at selected temperatures. The solid lines in panel (A) are the composite fits to Eq. (1). Symbols denote experimental data points.

cell used was a silver-plated stainless steel miniature capacitor with 24 plates, and a nominal capacitance of 27 pF in air, which was accurately measured prior to each experiment and whose empty cell capacitance showed no change over the temperature range 100–300 K. The capacitor has an inconsequential amount of stray capacitance which was independent of the dielectric permittivity of the liquid. Solutions of 5-methyl-2-hexanol in 2-methylpentane were prepared by weighing in small glass bottles, which were sealed and stored in a refrigerator at 278 K until their dielectric study. The capacitor was inserted in a 10 mm diameter and 33 mm long glass vial holding the liquid at 298 K. Care was taken to ensure that no air bubbles were trapped between the capacitor plates. A 100  $\Omega$  platinum resistance temperature sensor was also inserted into the cell and it rested above the capacitor but still in the liquid.

The temperature of the sample was maintained to within  $\pm 0.1$  K for several hours, as required for a single measurement at megahertz frequencies, by using a specially designed Oxford Instruments cryostat for the purpose. The dielectric permittivity and loss,  $\epsilon'$  and  $\epsilon''$  spectra were measured by using an Alpha-A analyzer and ZG4 dielectric interface purchased from Novocontrol.

## III. RESULTS AND DATA ANALYSIS

The  $\epsilon'$  and  $\epsilon''$  spectra of 5-methyl-2-hexanol in 2-methylpentane solutions were measured over a temperature range of 104–199 K. Typical spectra for the 2:1 (mol:mol) composition solution, which are provided in Figs. 1(A)

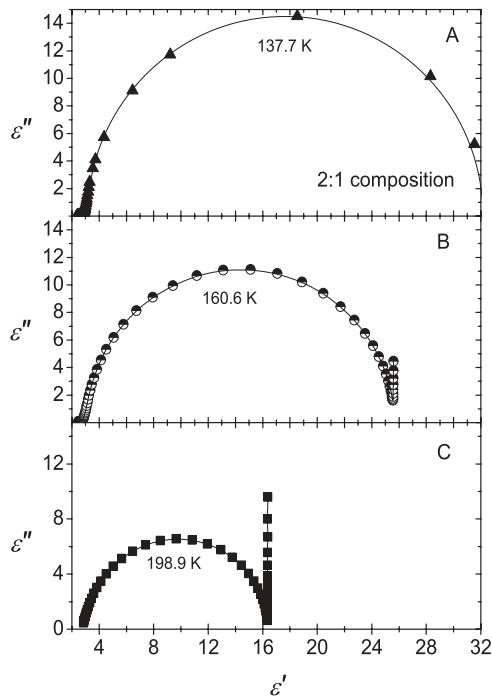


FIG. 2. The Cole–Cole plots for 2:1 solution at (A) 137.7, (B) 160.6, and (C) 198.9 K.

and 1(B), show the evolution of the relaxation processes with change in the temperature,  $T$ . The spectra of  $\epsilon''$  in Fig. 1(B) show also the contribution from the dc conductivity,  $\sigma_{dc}$ , which may be due to the diffusion of impurity ions in the solution, but it is small and causes no significant electrode polarization, and its effect on  $\epsilon'$  is too small to be observed. A shoulder in the  $\epsilon'$  spectra at higher frequencies indicates a further relaxation (process II), whose  $\epsilon''$  peak is overwhelmed by the large contributions from the spectra of the slower process I. The four  $\epsilon'$  and  $\epsilon''$  spectra at  $T < 145$  K in Fig. 1 indicate a further (inverted) sigmoid-shape decrease in  $\epsilon''$  in the  $10^4 - 10^5$  Hz frequency range, indicating the presence of a yet faster relaxation process which is overwhelmed by contribution to  $\epsilon''$  from processes I and II. In order to examine these features qualitatively, Cole–Cole plots at 137.7, 160.6, and 198.9 K are shown in Fig. 2. Here the effect of  $\sigma_{dc}$  is seen as a vertical rise of the plot on the right hand side at the lowest frequencies. Process II and a further relaxation together constitute the foot of the plot before  $\epsilon'$  decreases to 2.3.

Since the magnitude of the fastest relaxation process is extremely small, it was neglected and the  $\epsilon'$  and  $\epsilon''$  spectra were analyzed to resolve  $\sigma_{dc}$  and only processes I and II. The relation for the complex permittivity used is,<sup>19</sup>

$$\epsilon^*(\omega) = \epsilon' - j\epsilon'' = \epsilon_\infty + \sum_{i=I}^{II} \frac{\Delta\epsilon_i}{(1 + (j\omega\tau_{HNI})^{\alpha_i})^{\beta_i}} - \frac{j\sigma_{dc}}{\epsilon_0\omega}, \quad (1)$$

where  $\omega = 2\pi f$  ( $f$  being the frequency in Hz), and  $\epsilon_0$  is the permittivity of free space. The subscript  $i$  denotes the  $i$ th relaxation process,  $\Delta\epsilon_i = \epsilon_{si} - \epsilon_{\infty i}$  is the dielectric relaxation strength of this process,  $\tau_{HNI}$  is the characteristic (Havriliak–Negami<sup>19</sup>) relaxation time,  $\alpha_i$  and  $\beta_i$  are

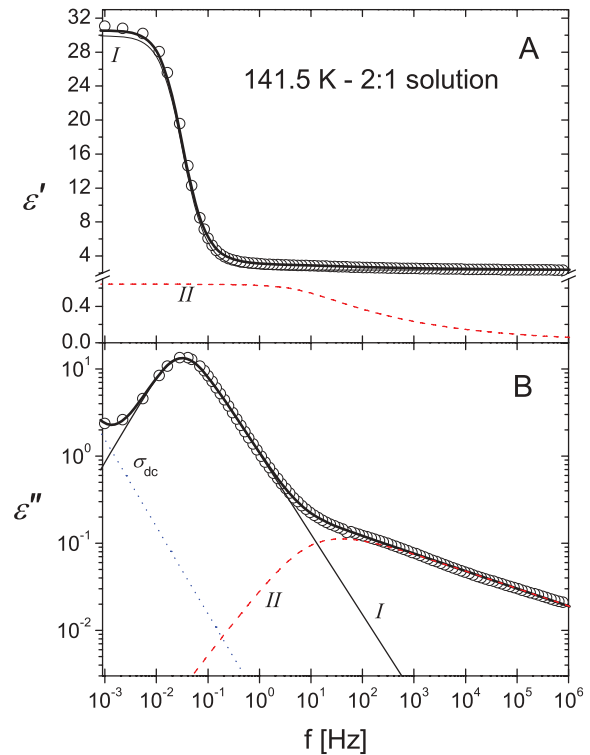


FIG. 3. The resolution of the (A)  $\epsilon'$  and (B) spectrum of 2:1 solution measured at 141.5 K. The fit of Eq. (1) to the  $\epsilon'$  and  $\epsilon''$  data is shown by thick solid lines. Symbols denote experimental data points. The contributions of process I and II, and the dc conductivity loss term to the fit are shown by the thin solid, dashed, and dotted lines, respectively. The fit parameter values are  $\Delta\epsilon_I = 27.6$ ,  $\tau_{HNI} = 5.29$  s,  $\alpha_I = 1.00$ ,  $\beta_I = 0.925$ ,  $\Delta\epsilon_{II} = 0.642$ ,  $\tau_{HNI} = 19.6$  ms,  $\alpha_{II} = 0.772$ ,  $\beta_{II} = 0.259$ ,  $\epsilon_\infty = 2.33$ , and  $\sigma_{dc} = 8.60 \times 10^{-14}$  S m<sup>-1</sup>.

respectively the symmetric and asymmetric broadening parameters. The term— $j\sigma_{dc}/\epsilon_\infty\omega$  takes into account the  $\sigma_{dc}$  contribution, and  $\epsilon_\infty$  is the sum of the permittivity contributions from vibrational, ionic, and electronic polarizations. The imaginary part of Eq. (1) was fitted to the loss spectra by using the WinFit dielectric fitting program purchased from Novocontrol, and the various parameters in Eq. (1) were determined. Fitting to the real part of the permittivity was also carried out for some of the solutions to further refine the fitted parameters.

The continuous lines for  $\epsilon'$  in Fig. 1(A) are for the fitted curves. A typical fitting to two relaxation processes is shown for the spectra at 141.5 K in Fig. 3. The fit parameters are  $\Delta\epsilon_I = 27.6$ ,  $\tau_{HNI} = 5.29$  s,  $\alpha_I = 1.00$ ,  $\beta_I = 0.925$ ,  $\Delta\epsilon_{II} = 0.642$ ,  $\tau_{HNI} = 19.6$  ms,  $\alpha_{II} = 0.772$ ,  $\beta_{II} = 0.259$ ,  $\epsilon_\infty = 2.33$ , and  $\sigma_{dc} = 8.60 \times 10^{-14}$  S m<sup>-1</sup>. The individual contributions from processes I and II in the overall fit of the data are also shown in Fig. 3. Here,  $\epsilon_\infty$  is insignificantly different from the limiting high-frequency permittivity of process II. The contribution to permittivity from dipolar orientation,  $\Delta\epsilon$  was obtained from the difference between the static permittivity,  $\epsilon_s$ , at a temperature  $T$  and  $\epsilon_\infty$  estimated from spectra measured at  $T \ll T_g$ .<sup>12,18</sup> Dielectric spectra obtained for the 0.67:1 and 0.25:1 solutions were similarly analyzed and the plots were found to be qualitatively similar to those shown in Figs. 1–3. For the sake of brevity, these plots are excluded. Values of  $\alpha_I$  and  $\beta_I$  are listed in Table I.

TABLE I. The distribution of relaxation times parameters  $\alpha_I$  and  $\beta_I$  and the fit parameters for the Vogel–Fulcher–Tammann equations. Subscript I refers to the Debye process and II to the next faster process.

Composition	$\alpha_I$ ( $\beta_I$ )	$-\log(A_I)$	$B_I$	$T_{0,I}$	$-\log(A_{II})$	$B_{II}$	$T_{0,II}$
1 : 0 (pure) <sup>a</sup>	1.00(0.95)	14.43	2775	79.8	13.20	1325	112.3
2 : 1	0.98(0.94)	11.38	1591	84.4	10.50	662.5	104.4
0.67 : 1 <sup>b</sup>	1.00(1.00)	10.02	799.68	86.78	10.96	490.59	94.3
0.25 : 1 <sup>c</sup>	1.00(1.00)	8.67	598	88.0	10.06	376.14	92.78

<sup>a</sup>From Ref. 20.

<sup>b</sup> $T$ -range 133–190 K.

<sup>c</sup> $T$ -range 120–155 K.

The plots of  $\Delta\varepsilon$ ,  $\Delta\varepsilon_I$ , and  $\Delta\varepsilon_{II}$  for the 2:1 solution are shown in Fig. 4 and those of  $\Delta\varepsilon_I$  and  $\Delta\varepsilon_{II}$  against  $T$  for the 0.67:1 and 0.25:1 mol:mol solutions are shown in Figs. 5 and 6, respectively. For comparison, the corresponding values for pure 5-methyl-2-hexanol from previous studies<sup>20</sup> are included in Fig. 4.

Parameters  $\alpha$  and  $\beta$  characterize the shape of the relaxation spectra. For a Debye relaxation  $\alpha = \beta = 1$ ; for a Davidson–Cole distribution,<sup>19</sup>  $\alpha = 1$  and  $\beta < 1$ ; and for a Cole–Cole distribution,<sup>19</sup>  $\alpha < 1$ , and  $\beta = 1$ . The value of  $\alpha_I$  and  $\beta_I$  (Table I) show Debye relaxation at all  $T$ . The  $\alpha_{II}$  and  $\beta_{II}$  varied with  $T$ . For the pure alcohol,  $\alpha_{II} = 0.57 \pm 0.09$ , and  $\beta_{II} = 0.79 \pm 0.05$  (160–190 K) from previous studies.<sup>20</sup> For

the 2:1 solution,  $\alpha_{II} = 0.6$  to 0.2, and  $\beta_{II} = 0.3$  to 1.0 (140–170 K) and for the 0.67:1 solution  $\alpha_{II} = 0.38$  to 0.59, and  $\beta_{II} = 1.0$  to 0.7 (133–154 K). Lastly, for 0.25:1 solution,  $\alpha_{II} = 0.6$  to 1.0, and  $\beta_{II} = 0.28$  to 0.12 (126–143 K).

The  $\varepsilon''$  peak frequency observed in an isothermal spectra for processes I and II was converted to the relaxation times  $\tau_I$  and  $\tau_{II}$  and these values are plotted logarithmically against  $T$  in Fig. 7, where data for the pure 5-methyl-2-hexanol taken from an earlier study<sup>20</sup> are included. The Vogel–Fulcher–Tammann equation,<sup>21–23</sup>

$$\tau = A \exp \left[ \frac{B}{(T - T_0)} \right], \quad (2)$$

was fitted to the data in Fig. 7 and the fit is shown by the lines. Values of the fit parameters  $A$ ,  $B$ , and  $T_0$  for processes I and II are listed in Table I. (Note that the data for process II are approximate because of the errors in resolving it from the prominent spectra of process I).

It is of interest to consider how the temperature effect may be quantitatively related to the dilution effect. For this analysis, the net change in  $\tau_I$  resulting from change in  $T$  and

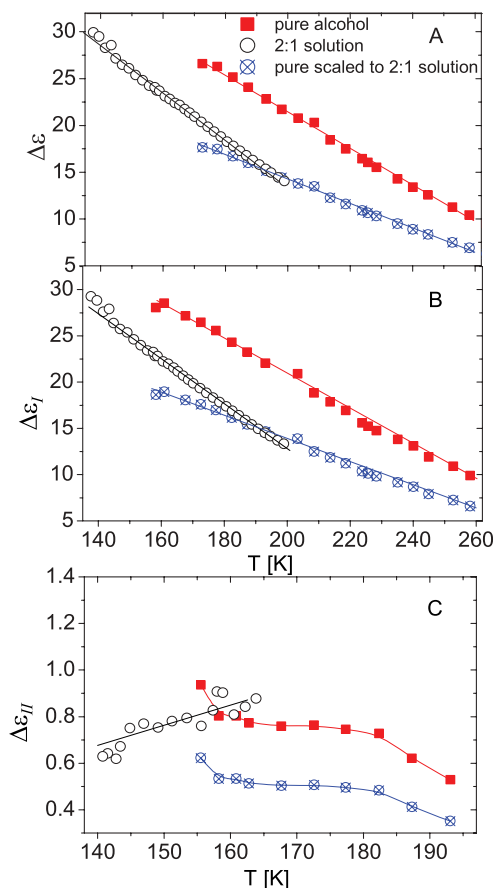


FIG. 4. Plots of (A)  $\Delta\varepsilon$ , (B)  $\Delta\varepsilon_I$ , and (C)  $\Delta\varepsilon_{II}$  2:1 solution against the temperature. Filled data points are for the pure alcohol, open data points are for the solution, and crossed data points are for the alcohol scaled to the solution composition. The lines are meant as a guide to the eye.

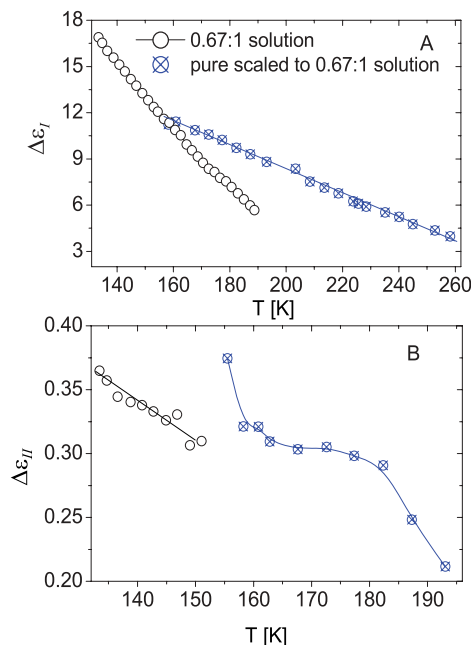


FIG. 5. Plots of (A)  $\Delta\varepsilon_I$  and (B)  $\Delta\varepsilon_{II}$  0.67:1 solution against the temperature. Open data points are for the solution and crossed data points are for the alcohol scaled to the solution composition. The lines are meant as a guide to the eye.



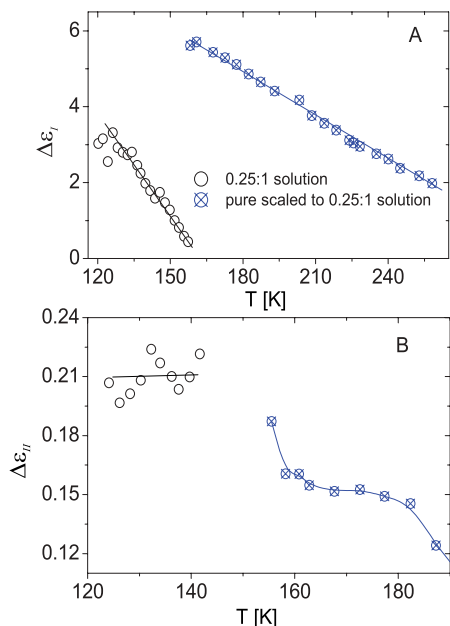


FIG. 6. Plots of (A)  $\Delta\epsilon_I$  and (B)  $\Delta\epsilon_{II}$  0.25:1 solution against the temperature. Open data points are for the solution and crossed data points are for the alcohol scaled to the solution composition. The lines are meant as a guide to the eye.

in the solution's composition may be written as,  $d\tau_I = (\partial\tau_I/\partial T)_x dT + (\partial\tau_I/\partial x)_T dx$ , where  $x$  is the mole% of the alcohol. Since  $(\partial\tau_I/\partial T)_x$  is negative and  $(\partial\tau_I/\partial x)_T$  is positive, the temperature equivalence of dilution may be calculated. For example, if the temperature of the pure alcohol is decreased from 207.5 to 190.8 K,  $\tau_I$  increases from 10 to 287  $\mu\text{s}$  according to the plots in Fig. 7. Thereafter, when the pure alcohol at 190.8 K is diluted to 66.5 mol%,  $\tau_I$  decreases and its value is restored to 10  $\mu\text{s}$ . Similar analyses may be done for other temperatures and dilution and for other  $\tau_I$  or  $\tau_{II}$  values.

Also, if there were no change in the H-bond interactions on dilution and if such interaction varied with  $T$  for the pure

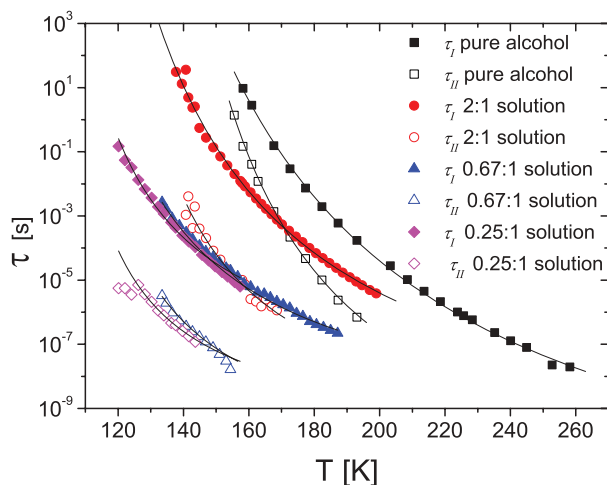


FIG. 7. Plots of  $\tau_I$  (filled symbols) and of  $\tau_{II}$  (open symbols) (shown on a logarithmic scale) for pure and 2:1, 0.67:1, 0.25:1 solutions against the temperature. The solid lines are the fits of Eq. (2) to the pure 5-methyl-2-hexanol and solutions. The fit parameters are listed in Table I.

and dissolved states of alcohol identically, the net change in  $\Delta\epsilon_I$  would also be the sum of two contributions,  $d\Delta\epsilon_I = (\partial\Delta\epsilon_I/\partial T)_x dT + (\partial\Delta\epsilon_I/\partial x)_T dx$ . Since the term  $(\partial\Delta\epsilon_I/\partial T)_x$  is negative and  $(\partial\Delta\epsilon_I/\partial x)_T$  is positive, one may be able to estimate the temperature equivalence of dilution.

## IV. DISCUSSION

### A. Relaxation strength and hydrogen bonding

Figure 4(A) shows that  $\Delta\epsilon$  of the 2:1 solution is less than that of the 5-methyl-2-hexanol. If the extent and mechanism of the dielectric fluctuations did not change on dilution, it would be equal to the scaled value,  $x\Delta\epsilon_{\text{alcohol}}$ , where  $x$  refers to the mole fraction and  $\Delta\epsilon_{\text{alcohol}}$  to  $\Delta\epsilon$  of the pure alcohol. The measured  $\Delta\epsilon$  is higher at  $T < 175$  K, and it may appear that it crosses over the scaled value at  $T$  of  $\sim 200$  K, but their shape shows that the measured  $\Delta\epsilon$  may extrapolate to the scaled values at  $T > 195$  K. Since  $\Delta\epsilon_I$  is only slightly less than  $\Delta\epsilon$ , the corresponding plots in Fig. 4(B) show similarity.

For the 0.67:1 solution, the measured and the scaled  $\Delta\epsilon_I$  seem to cross at  $T$  of  $\sim 160$  K in Fig. 5. At 190 K, the measured  $\Delta\epsilon_I$  is 38.1% less than the scaled value. This suggests that  $\Delta\epsilon_I$  in this solution would originate in a local structure whose polarization (per mole of the alcohol) has decreased from the corresponding polarization in 2:1 solution and in the pure alcohol. The plots in Fig. 6 show that for the 0.25:1 solution at 157 K the difference in  $\Delta\epsilon_I$  increases to 92% and at 148 K the (extrapolated) difference is 76%. It may appear that further dilution of the 2:1 solution shifts the crossover to a lower temperature, and while it can be seen for the 0.67:1 solution at  $\sim 160$  K, it is not seen for the 0.25:1 solution because of lack of data at  $T < 129$  K.

To compare these findings against those for solution in a polar solvent, (i)  $\Delta\epsilon$  of the 0.25:1 molar solution of 5-methyl-2-hexanol in isoamylbromide measured at 156 K was  $\sim 35\%$  of the correspondingly scaled  $\Delta\epsilon$ ,<sup>18</sup> and (ii)  $\Delta\epsilon$  of the 0.25:1 molar solution of *n*-propanol in isoamylbromide measured at 120 K<sup>18</sup> was also  $\sim 35\%$  of the scaled value of the pure *n*-propanol. Therefore, even though both the nonpolar and polar solvents disrupt intermolecular H-bonding, the consequences of the disruption for equilibrium dielectric properties differ.

Both the relatively weak short-range correlations due to intermolecular H-bonds and stronger dipole-dipole interactions have an effect on  $\Delta\epsilon$ . These interactions are included in the statistical theory of dielectric polarization given by Onsager,<sup>24</sup> Kirkwood,<sup>25</sup> and Fröhlich.<sup>26</sup> It expresses the interactions quantitatively in terms of a dipolar (orientational) correlation factor  $g$  which is a measure of the change in the effective dipole moment from its vapor phase value. Its inclusion yields the effective dipole moment that reorients when a molecule in a condensed phase reorients. The expressions<sup>24-26</sup> contain the effect of changing dipole population per unit volume independently of  $T$ . In our study, dilution decreases this population and thus serves to lower  $\Delta\epsilon$ . Moreover, any decrease in  $g$  toward one resulting from disruption of H-bonds further lowers  $\Delta\epsilon$ . On that basis, if extrapolation of the measured  $\Delta\epsilon$  for the 2:1 solution agreed with the scaled  $\Delta\epsilon$  at  $T > 190$  K, it would indicate that  $g$  does not change in this

solution. But if there were a crossover of the two curves, it would indicate that at  $T < 190$  K,  $g$  is higher for the solution than for the pure alcohol and at  $T > 190$  K, it is lower. The crossover of the plots for the 0.67:1 solution indicates that at  $T < 160$  K,  $g$  is higher for the solution than for the pure alcohol and at  $T > 160$  K, it is lower and for the 0.25:1 solution  $g$  is lower over the entire temperature range of our study.

It is also worth comparing how dilution of an alcohol by a nonpolar as well as a dipolar solvent effects the dielectric relaxation features through changes in intermolecular H-bonding, as for example in solutions of, (i) *n*-propanol with 2-methylpentane,<sup>27</sup> (ii) 1-phenyl-2-propanol with 2-methylpentane,<sup>17</sup> (iii) isoamylbromide with 2-methylpentane,<sup>28</sup> (iv) *n*-propanol with isoamylbromide,<sup>18</sup> (v) 5-methyl-2-hexanol with isoamylbromide,<sup>12</sup> and (vi) *n*-butanol with *n*-butyl bromide.<sup>29</sup> Denny<sup>27</sup> originally discussed some of these studies in terms of clustering of the alcohol molecules as was evident from the two relaxation spectra he observed for solutions in polar solvents and a similar discussion has appeared more recently.<sup>12,18</sup> It was found that for concentrations greater than 50 mol% *n*-propanol in 2-methylpentane, the Debye relaxation persisted. For lower concentrations, the spectra changed to a skewed arc shape of the Davidson–Cole formalism, and a further small relaxation polarization was found before  $\epsilon'$  decreased to  $\epsilon_\infty$  value,<sup>30</sup> but the origin of this polarization remained uncertain. Denny and Ring's data for *n*-propanol solution in 2-methylpentane<sup>30</sup> yield  $\Delta\epsilon_I$  as 27.8 at 150.4 K for the 2:1 solution, and  $\Delta\epsilon_I$  as 51.8 at 150 K for pure *n*-propanol. Scaling of  $\Delta\epsilon_I$  of *n*-propanol to the solution concentration yields 34.5. This would be the value of  $\Delta\epsilon_I$  if the extent and type of intermolecular H-bonding remained unchanged from pure alcohol to the solution state. The measured  $\Delta\epsilon_I$  of 27.8 is  $\sim 21\%$  less than the scaled value, which indicates a significant decrease in both  $g$  on dilution and the internal field effect, the latter being determined by the term  $[\epsilon_s/(2\epsilon_s + \epsilon_\infty)][(\epsilon_\infty + 2)/3]^2$  for a spherical dipole surrounded by other dipoles.<sup>24</sup> For solutions, the magnitude of this term decreases as  $\epsilon_s$  decreases and it approaches unity at infinite dilution. (Note that this decrease allows one to determine the dipole moment of an isolated molecule by measuring  $\epsilon_s$  of dilute solutions.<sup>31</sup>)

Effects of change in the alcohol clustering and in the internal field on dilution are relevant to our interpretation. If alcohol molecules were to form H-bonded clusters, the number of near neighbors shielding a molecule would not change from that in the pure liquid. Therefore, there would be no change in  $\Delta\epsilon$  due to the internal field effects. In that case only the change in  $g$  that results from change in the extent of H-bonding would be observable. (Even if the 2:1 solution were homogeneous at a nanoscale, the molar ratio seems high enough to maintain some intermolecular H-bonds). It is also worth noting that the relative effects of the decrease in the internal field and in H-bonding of a variety of alcohols in benzene solutions at 298 K (Ref. 32) had shown that H-bonds form even at concentrations as low as 0.04:1 molar ratio solutions. This seems tantamount to H-bond cluster formation. Moreover, Schwerdtfeger *et al.*<sup>33</sup> have shown that for higher concentrations of homologous alcohols in *n*-alkanes at 298 K, the most prominent relaxation is Debye-like, but at lower

concentrations it changes to the Cole–Davidson skewed arc type. They discussed the relaxation time and the shape of the spectra observed for the solutions in terms of “wait and switch” model of relaxation by considering the effect of nonpolar hydrocarbon groups on the activation enthalpy of the relaxation process, and concluded that the concentration of H-bond partners has a dominant role in the dielectric relaxation. From our previous studies,  $\Delta\epsilon_I$  of 0.67:1 solution of 1-phenyl-2-propanol in 2-methylpentane at 210 K is  $\sim 8$  and for pure 1-phenyl-2-propanol  $\Delta\epsilon_I$  is  $\sim 19.2$ , whereas scaling yields a value of 9.6.<sup>17</sup> The measured value for the solution is  $\sim 20\%$  less than the scaled value, which indicates that in this case also there is a significant decrease in the H-bond induced orientation correlation on dilution.

In contrast,  $\Delta\epsilon$  is 5.51 for the 1:1 solution of isoamylbromide in 2-methylpentane and 13.06 ( $= 12.84 + 0.22$ ) for pure isoamylbromide at 110.1 K,<sup>28</sup> which gives the scaled value as 6.5. The measured value of 5.51 is  $\sim 18\%$  less than the scaled value. Since there is no H-bonding in isoamylbromide, this must indicate the effect of decrease in the internal field, density or other changes. Since both the change in the internal field effects and loss of intermolecular H-bonds on dilution tend to decrease  $\epsilon_s$ , the agreement between the scaled and measured values for  $\Delta\epsilon_I$  for the 2:1 solution here indicates that neither of the two changes have a significant effect on the origin of the Debye-type relaxation.

In summary, in its solution in isoamylbromide, 66.7 mol% *n*-propanol has shown two distinct relaxations,<sup>18</sup> corresponding to each component in the form of nanoscale aggregates. The same feature was found for the 66.7 mol% solution of 5-methyl-2-hexanol with isoamylbromide.<sup>12</sup> In both cases, the measured  $\Delta\epsilon_I$  of the solution is significantly less than the scaled  $\Delta\epsilon_I$  of the pure alcohol to the concentrations of the solutions. A recent study<sup>29</sup> of solutions of *n*-butanol and *n*-butyl bromide has also shown two relaxation regions indicating clustering of the alcohol molecules or liquid–liquid phase separation, but in this study  $\Delta\epsilon_I$  has been found to scale with the molar concentration of *n*-butanol. This is seen to confirm that H-bond induced orientational correlation does not change when *n*-butanol molecules aggregate to form clusters locally. Intercomparisons of the results for various solutions and the disagreement observed between the measured and scaled dielectric relaxation strengths show that despite the disruption of intermolecular H-bonding on addition of a second component, the two relaxations continue to persist and the predominant relaxation in these solutions is of Debye-type. Therefore, we argue that the values of  $\Delta\epsilon_I$  and  $\Delta\epsilon_{II}$  for pure 5-methyl-2-hexanol and for its solutions in 2-methylpentane correspond to the polarization of alcohol molecules in, most likely, nanometer-size clusters dispersed in the viscous liquids.

## B. Relaxation spectra and the relaxation times

The data in Table I obtained from the shape of the plots in Figs. 1 and 2 show that dilution of the alcohol does not change the  $\alpha_I$  and  $\beta_I$  parameters for process I, i.e.,  $\alpha_I = 1$  and  $\beta_I \sim 0.95$ , within experimental and analytical errors. There is

also no doubt that  $\sim 95\%$  of the polarization of pure 5-methyl-2-hexanol occurs by process I, which is Debye-type (single exponential) in the pure alcohol as well as of its solutions. Change in  $T$  has only a marginal effect on the values of these parameters for both the pure liquid and the solutions.

In Fig. 7,  $\tau_I$  for the 2:1 solution is about an order of magnitude less than that of pure alcohol at 205 K. The difference rapidly grows on cooling and there is a much greater, immeasurably high difference between their respective  $\tau_I$  at 140 K (pure 5-methyl-2-hexanol is vitrified at  $T$  near 149 K).<sup>12</sup>  $\tau_I$  of the solution and of the pure alcohol approach each other as their respective  $\tau_I$  decrease toward the nanosecond range on heating to 298 K. In contrast, for 5-methyl-2-hexanol in solution with a polar solvent, isoamylbromide, the difference between the  $\tau_I$  of the solution and the pure alcohol was several orders of magnitude, and their respective  $\tau_I$  did not show an approach toward comparable values at high temperatures (See Fig. 3, Ref. 12). Evidently, consequences of clustering on the relaxation time in solution with a polar liquid are distinguished from those in solution with a nonpolar liquid, even though the relaxation remains Debye-like in both types of solutions.

On the basis of the finding that Debye-type processes I and the usual process II persist in ultraviscous solutions of this study, we conclude that the H-bond induced nanometer scale-clustering of alcohol molecules has no effect on the mechanism of dipolar relaxation of processes I and II. In the dynamic heterogeneity conjecture,<sup>7-9</sup> this would mean that presence of 2-methylpentane in the ultraviscous solution does not add to the dynamic heterogeneity of the dielectric relaxation of the alcohol molecules in it. Clearly, the findings of the dilution effect here, together with the previous finding from solutions of alcohols in isoamylbromide, have consequences for our understanding of both, (i) the mechanism of the Debye relaxation and for the features of calorimetric relaxation, and (ii) the restricted Brownian diffusion of the H-bonded states of alcohol molecules in locally formed clusters.

Moreover, in terms of the variation of  $\tau_I$  and  $\tau_{II}$  with variations in  $T$  and dilution, it is evident that a decrease in  $T$  is equivalent to an increase in dilution. For example, increase in  $\tau_I$  on cooling the pure alcohol from 207.5 to 190.8 K would be annulled by diluting the alcohol to 2:1 molar ratio at 190.8 K, while the Debye relaxation persists. Similar conditions may be deduced for  $\Delta\varepsilon_I$  and  $\Delta\varepsilon_{II}$ , but the data available here are insufficient for doing so.

### C. Debye relaxation and calorimetric relaxation

The inference that the most prominent dielectric polarization (amounting to 97% of the total polarization in *n*-propanol) may not contribute to structural relaxation, was based on an analysis of *n*-propanol data whose process I seemed incompatible with its viscosity in terms of the Einstein–Debye equation, mechanical relaxation, and mainly the light scattering measurements.<sup>34</sup> Similar light scattering and other studies of another liquid with a similarly large Debye relaxation have not yet been performed to support the inference for a “nonstructural relaxation” mechanism for the Debye process. But dielectric studies had been performed to

examine the merits of this inference by adding LiClO<sub>4</sub> to *n*-propanol<sup>35</sup> and to 5-methyl-2-hexanol,<sup>36</sup> and also by studying their respective mixtures in isoamylbromide.<sup>12,18</sup> Addition of LiClO<sub>4</sub> was expected to eliminate the “nonstructural” mechanism of the Debye relaxation of process I, but it was not found to do so. A further study of the effect of steric hindrance<sup>17,37</sup> on H-bonding by using 1-phenyl and 2-phenyl propanols, in which the phenyl group in the molecule hinders the formation of H-bonds, also showed that the Debye relaxation persists. Moreover, crystallization kinetics study of D-sorbitol<sup>38</sup> supported the view that the Debye process is a structural relaxation process. In view of these studies, it seems difficult to explain the Debye-like dielectric features of the modified H-bonded state of alcohols without considering that alcohol-molecules form clusters in the solution and relaxation occurs by H-bond breaking and reforming within the clusters.

Dynamic and apparent specific heats,  $C_p^*$ , and  $C_{p,app}$ , of 5-methyl-2-hexanol measured during its cooling and heating through the liquid–glass range at the same slow rates of 2, 12, and 60 K/h,<sup>39</sup> have shown that, (i) the calorimetric relaxation time,  $\tau_{cal}$ , estimated at the onset temperature of the  $C_{p,app}$  endotherm is inconsistent with that determined from dynamic  $C_p^*$  measurements (Fig. 3, Ref. 39), and is also inconsistent with the dielectric relaxation times of both processes I and II, and (ii) the distribution of relaxation time parameter varies slightly with the heating rate, which was attributed to enthalpy change from the temperature-dependent hydrogen-bond population. Thus it seems that even for a pure alcohol, the Debye process may contribute to the enthalpy relaxation of its glassy state.

It is worth pointing out that there are materials whose Debye-type dielectric relaxation is known to contribute to the configurational entropy. The well-known example of such a case is the dielectric relaxation in hexagonal and cubic ices and in the high-pressure forms of ice. Here fluctuations of H-bonded structure in the crystal lattice of ice contribute to configurational thermodynamics<sup>40</sup> and the temperature derivative of the entropy shows up as the specific heat,  $C_p$ . Details are given in Ref. 41.

### D. Change in dielectric properties in molecular nanoaggregates

In Figs. 4–6,  $\Delta\varepsilon_I$  for the 2:1 solution at  $T < 190$  K is more than that expected on the basis of mixture rule, which indicates an increased  $g$ , and  $\Delta\varepsilon_{II}$  is also more than expected and its value is comparable to that in the pure alcohol. This would be the case if change in  $g$  had the same effect on both. This view is supported by the data for the 0.67:1 solution, whose expected values for both  $\Delta\varepsilon_I$  and  $\Delta\varepsilon_{II}$  are more than the extrapolated  $\Delta\varepsilon_I$  and  $\Delta\varepsilon_{II}$  to high temperatures. For the properties of 0.25:1 solution shown in Fig. 6,  $\Delta\varepsilon_{II}$  could not be accurately estimated because of its small magnitude and proximity of the spectra to that of process I, but within this uncertainty, the extrapolated value of  $\Delta\varepsilon_{II}$  to 140 K is higher than the estimated value, as is the case for  $\Delta\varepsilon_I$  in Fig. 7(A). This of course is weak evidence for a correlation between  $\Delta\varepsilon_I$  and  $\Delta\varepsilon_{II}$  and further studies may be able to examine it. Despite that, it should be noted that the H-bonded chains are



much shorter in the clustered domains in solutions than in pure alcohols, and process II would contribute to structural relaxation only if a change in the dipole vector in this process were to change the configurational state without changing the energy of the state.

It is debated whether or not molecular motions of the  $\alpha$ -process are faster in nanoconfined liquids and in free-standing, nanofilms of polymers than in the bulk state. Some studies indicate that the glass transition temperature decreases on nanoconfinement,<sup>42–44</sup> and others found that the dielectric relaxation time does not change.<sup>45</sup> The decrease in the relaxation time observed here are for conditions different from those of liquids confined to cavities, and it is free from the surface tension and interfacial effects in a free standing polymer film. It is possible that the faster dynamics of dielectric fluctuations resulting from breaking and reforming of weakened H-bonds within the clusters in an ultraviscous solvent indicate nanodomains of a type different from those studied so far.

In a recent modeling of the dielectric relaxation time of binary mixtures of alcohols and polymers, cluster-association and dissociation model has been used to fit the relaxation time data<sup>46</sup> by using the heat and volume of transformation between clusters and monomers. Some of these binary mixtures showed only one relaxation process and others showed two relaxation processes of the individual components.<sup>46</sup> While this configurational entropy based treatment is useful for liquids that in their pure state show only one relaxation process, it would be interesting to see if it is also useful when a liquid in solution shows two relaxation processes. It is also noteworthy that by using 1-octanol as model system for lipid molecules in biological membranes, MacCallum and Tieleman<sup>47</sup> have suggested a micellar aggregation with a polar core of up to 15 hydroxyl groups bonded together in mostly linear structures, and Fragiadakis *et al.*<sup>15</sup> have considered it as a model for intermolecular association in 2-ethyl-1-hexanol. It is not clear how such a model may be applicable to solutions of an alcohol with a hindered -OH group as in 5-methyl-2-hexanol dissolved in a hydrocarbon.

## V. CONCLUSION

The Debye-like relaxation of 5-methyl-2-hexanol is not altered by the presence of 2-methylpentane despite the anticipated disruption of H-bonds and their weakening. This indicates that 5-methyl-2-hexanol molecules remain H-bonded in the solution in such a manner that exponential kinetics for decay of polarization remains dielectrically indistinguishable from that of the pure alcohol. This may be interpreted as a consequence of nanometer-size clustering in solutions of alcohols or aggregates of folded H-bonded chains. Molecular motions of 5-methyl-2-hexanol in the 2:1 solution relative to that of the pure liquid becomes more faster at low temperatures than at high, differing by  $\sim 10^3$  at 160 K. The difference is reduced at higher temperatures. This would indicate that the H-bonded structure is more distorted in the nanometer size clusters than in the pure alcohol.

Electrical and elastic dipolar reorientations are more selective of reorienting vector than random configurational

fluctuations that include all orientations including ones in which the dipole or elastic vectors do not reorient. These fluctuations may not necessarily occur on the same time scale as dielectric relaxation. Therefore, comparative and correlative analyses of the calorimetric and mechanical relaxation data used for inferring the role of Debye relaxation may need to be re-examined. Our findings also bear upon our understanding of the relation between the shear modulus and the dielectric relaxation time of alcohol clusters in a solution.<sup>14</sup>

It is possible that both processes I and II contribute to structural fluctuations in proportion to the extent by which their respective underlying H-bond fluctuations produce a new configuration in the liquid's structure, but it is not certain how process I would be modified from a single relaxation time to a calorimetrically observed, apparent distribution of relaxation times. Dielectric and mechanical relaxation measurements of ultraviscous solutions of alcohols in nonpolar and polar solvents would be revealing of the role of such clusters as well as the relation between their respective time scales. Mechanical relaxation studies of the type performed for alcohols<sup>14</sup> but for ultraviscous 1 wt% solution of di-*n*-butyl ether in 3-methylpentane,<sup>11</sup> would also help to resolve why, despite the presumed dynamic heterogeneity, its dielectric relaxation is of the Debye-type.

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- <sup>41</sup>In an ice structure, each H<sub>2</sub>O molecule is tetrahedrally H-bonded to four other H<sub>2</sub>O molecules with no angular distortion, and each H<sub>2</sub>O molecule has six orientations of equal probability. This produces  $(3/2)^N$  configurations per mole, where  $N$  is the Avogadro number. [D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Clarendon, Oxford, 1969); J. B. Hasted, *Aqueous Dielectrics* (Chapman and Hall, London, 1973)]. When all configurations have the same energy, the molar configurational entropy is equal to  $R \ln(3/2)$ , where  $R$  is the gas constant, and this entropy does not vary with  $T$ . Thus, an ideal ice lattice would have no configurational contribution to its  $C_p$ . But structural and other defects inherent to ice cause the HO–H (hydrogen) bonds to slightly differ in energy and hence some orientations of a H<sub>2</sub>O molecule become slightly more probable than others. Consequently, a multiplicity of configurations of different energies would occur in an ice structure. An increase in  $T$  would therefore cause its state point to explore higher energy configurations, and hence it would have a configurational  $C_p$ . Adiabatic calorimetry measurements have shown that there is a minute increase in the  $C_p$  of ice at  $\sim 120$  K when, on heating, H<sub>2</sub>O molecules begin to reorient on an experiment's time scale, as occurs for a glass on heating through its  $C_g$ . [O. Yamamuro, M. Oguni, T. Matsuo, and H. Suga, *J. Phys. Chem. Solids* **48**, 935 (1987); *J. Phys. Chem. Solids* **49**, 425 (1988); G. P. Johari, *Chem. Phys.* **258**, 277 (2000)]. Also, these energetic differences are greater in the H-bonded structure of the ice clathrates, which show a larger change in  $C_p$  on kinetic freezing of its structure, based on the findings in the three preceding references, on which the following discussion is based. The  $C_p$ -increase occurs at  $T$  close to  $T$  at which  $\tau_{\text{diej}}$  is comparable to the measurement time in an adiabatic calorimetry experiment. Also, as for glasses, the  $C_p$ -increase is greater when the ice and ice clathrate samples have been annealed at a low temperature. Therefore, one anticipates that the H-bonded configurations in the structure of liquid alcohols would differ in energy by a much larger amount than the configurations in the ice and clathrate structures, and therefore such H-bonded liquids are anticipated to show a much large  $C_{p,\text{app}}$ -increase on kinetic unfreezing partly due to a decrease in the hydrogen-bond population on heating and partly due to the increase in the number of accessible configurations. When two relaxation processes are observed in the liquid state with different relaxation times, as for several pure monohydroxy alcohols and poly (propylene glycols), it is also difficult to envisage which relaxation time is controlled by the variation of the configurational entropy with  $T$ . In a solution, there is an added contribution to the entropy from the configurations of the solvent molecules and there is entropy of mixing.
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