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The effect of ions on the permittivity and dielectric relaxation of an uncrystallizable heptanol

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Abstract

Solvation of ions in a liquid tends to reduce the extent of intermolecular hydrogen bonding. This changes the effective dipolar orientation correlation factor, g, in most alcohols and in water, and hence the equilibrium permittivity ε_s, but not the relaxation time, τ. An increase in temperature has a similar effect on ε_s, but the relaxation time also decreases. Here we study the dielectric relaxation spectra of two concentrations of $LiClO_4$ solutions in 5-methyl-2-hexanol, and compare the findings against those for the pure liquid. We also compare the effect of the ions against that observed in a similar study of 1-propanol (Power *et al* 2002 *J. Chem. Phys.* **116** 4192). ε_s decreases by $\sim$7% on adding 1 mol% $LiClO_4$ at 173 K but increases by $\sim$12% at 223 K, and there is similar change in the strength of the Debye relaxation process. This may occur partly as a result of the changing ion–ion pair equilibrium with temperature. Initial addition of $LiClO_4$ (0.5 mol% solution) increases the dc conductivity, σ_{dc}, far more than further addition. The addition of electrolyte also causes the slowest relaxation to depart from the Debye process, but its characteristic relaxation rate does not change. Variation in σ_{dc} with τ does not follow the Debye–Stokes–Einstein relation for either the pure liquid or the $LiClO_4$ solutions, which indicates that diffusion of ions does not follow the Brownian diffusion of molecules.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In hydrogen-bonded liquids and solids, the equilibrium permittivity, ε_s, and dielectric relaxation features are determined by the short-range orientational correlation of dipoles. This is described

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quantitatively in terms of an empirical orientational correlation factor g in the Onsager–
Kirkwood–Fröhlich treatment [1–3]. When ε_s is much greater than the value expected on
the basis of the molecular dipole moment, as occurs in water [4–7], ices [7, 8], and many
alcohols [9, 10] and amides [11–13], $g > 1$. In some alcohols (certain octanols [9, 10, 14],
pentanols [15] and heptanols [16]) and liquid nitriles [17], when the effective dipole moment
decreases, ε_s approaches the value of a nonpolar liquid and in this case $g < 1$. The typical
molecular interpretation of these findings is that an increase in g above 1 is the result of
the formation of non-permanent linear chain-like structures due to intermolecular hydrogen
bonding. $g < 1$ corresponds to the formation in the liquid of predominantly ring-dimer
motifs [9, 10, 16] of low effective dipole moment. When neither of these two types of structures
form, or both structures are present and the effects cancel, $g = 1$.

Hydrogen-bonded materials also show a variety of features in their dielectric relaxation
spectra. A strong single relaxation time (Debye lineshape) process and a weaker and
broader relaxation process at higher frequencies have been observed in several monohydroxy
alcohols [10, 16, 18–22] and amides [12, 13], in hexagonal and cubic ices [8], and ices III, V,
VI and VII. More than 95% of the orientation polarization in these substances decays by the
slower Debye relaxation. In contrast, a number of monohydroxy [10, 23] and multihydroxy
alcohols [24] and almost all non-hydrogen-bonded liquids have shown a distribution of
relaxation times in their ultraviscous state. The Debye relaxation ($\beta_K = 1$, where β_K is
the Kohlrausch parameter quantifying broadness of the relaxation) of pure alcohols becomes
non-Debye (i.e. $0 < \beta_K < 1$) for dilute solutions of the alcohol in a nonpolar solvent [25].
According to an empirical correlation [26] of the parameter m (sometimes referred to as
fragility) of the Oldekop plots [27] with β, m should be minimum for a liquid showing the
Debye relaxation. Also, according to the dynamic heterogeneity view for a liquid's structure,
β should be less than 1. However the monohydroxy alcohols and amides showing Debye
relaxations are actually quite 'fragile' [26] (i.e. m is large). Thus, the results for some alcohols
and amides are found to conflict with the general concept of a correlation between heterogeneity
and glass formation.

It has been suggested [19] that the Debye relaxation in some alcohols and amides is
not related to the viscosity-determining structural relaxation. Instead, the immediately faster
non-Debye type dielectric relaxation is associated with viscous flow and hence structural
relaxation that involved Brownian diffusion, even though the Debye–Stokes–Einstein [28]
relation between the dielectric relaxation time and viscosity is generally not obeyed. Since
the faster relaxation is non-Debye, this would remove the anomaly of liquids with a large m
possessing a Debye structural relaxation. The suggestion is also made on the basis that the
Debye dielectric relaxation time is much slower than the liquid's structural relaxation time
obtained from other experimental techniques (see sections 4 and 5).

However, it is now recognized that light scattering, calorimetric, dilatometric, mechanical
and dielectric relaxation studies all probe different aspects and extents of structural fluctuations.
Therefore the features observed from such studies differ, and they do not yield the same
relaxation times. Dielectric relaxation is not observed if a molecule reorients along its dipolar
(twofold symmetry) axis and/or diffuses without a change in that axis, while other relaxations
are observed. This is because those particular molecular processes do not give rise to a
fluctuation of the dipole moment with the electric field.

In addition, the faster process relaxes less than $\sim$3% of the total orientational polarization
in alcohols [21]. It becomes doubtful that it alone can be responsible for the viscous flow
since according to the Onsager–Kirkwood–Fröhlich equation [1–3], this would mean that fewer
than 3% of the total number of molecules contributes to the viscosity-determining α-relaxation
process. Alternatively, all molecules contribute but they are oriented in an antiparallel manner

such as to reduce ε_s far below the value that would be expected from the –OH group's known dipole moment of ∼1.68 Debye. It should also be noted that for less than 2 mol% of 1-propanol, 1-butanol, 1-pentanol and 1-methyl-1-propanol in dilute benzene solutions, g has been found to be about 1 [29]. This indicates that these molecules either do not form hydrogen-bonded multimers with either $g < 1$ or $g > 1$, i.e., they persist as monomers in benzene solution, or else there is a mutual cancellation of the effects of formation of linear chains with $g > 1$ and ring dimers with $g < 1$.

The idea that the Debye process in the dielectric spectra of alcohols is not related to the structural relaxation has also been put into question by a study of the dielectric behaviour of 5-methyl-2-hexanol [21], a secondary alcohol, which like 1-propanol, also showed a prominent Debye relaxation and ∼3% contribution to ε_s from faster relaxations. A similar behaviour has also been observed for ethanol [30]. Since ions decrease the population of hydrogen bonds, this view was examined by adding an electrolyte to 1-propanol [31] containing 1 mol% LiClO$_4$. This salt has a good solubility in alcohols, while the Li$^+$ ions have a high surface charge density.

The study showed that although ions decrease the contribution to permittivity from relaxation processes I and II, they do not affect the relaxation rate of process I and they decrease the relaxation rate of process II. Unlike 1-propanol and ethanol, 5-methyl-2-hexanol contains an asymmetric carbon atom at site 2, namely CH$_3$–C*H(OH)–C$_4$H$_{11}$, and exists in optically isomeric form. Thus, in addition to steric hindrance to H bonding in its structure, the presence of *levo* and *dextro* forms of 5-methyl-2-hexanol in a racemic sample would also prevent extensive hydrogen bond formation. Here we report a dielectric study of two ionic solutions of LiClO$_4$ in 5-methyl-2-hexanol.

2. Experimental methods

5-methyl-2-hexanol and LiClO$_4$ were samples from earlier studies [21]. The dielectric cell used was a silver-plated stainless steel miniature capacitor with 24 plates, and a nominal capacitance of 27 pF in air. This commercially available capacitor has an inconsequential amount of stray capacitance and seems superior to the two parallel plates separated by spacers used successfully up to 1 MHz by several groups. Its empty capacitance was accurately measured prior to each experiment. Solutions of LiClO$_4$ in 5-methyl-2-hexanol were prepared by weighing in a volumetric flask, kept in a sealed container and stored in a refrigerator at 278 K until their study. These were in two concentrations, one of 0.5 mol% (i.e., 0.5 mol LiClO$_4$ in 100 mol of the LiClO$_4$ + 5-methyl-2-hexanol solution) and a second of 1.03 mol%. The capacitor was inserted in a 10 mm diameter, 33 mm long glass vial holding the liquid at 298 K. Care was taken to ensure that no air bubbles were trapped in the capacitor plates. A 100 Ω platinum resistance temperature sensor was also inserted into the cell and it rested above the capacitor but still in the liquid.

The sample temperature was maintained to within ±0.1 K for several hours required for a single measurement at millihertz frequencies. A new capacitor was used for each solution concentration. Dielectric measurements of complex permittivity, $\varepsilon^* = \varepsilon' - j\varepsilon''$, were made using a Solartron FRA1255A frequency response analyser connected to a Chelsea Dielectric Interface. Details of the procedure have appeared previously [21].

3. Results and analysis

The dielectric permittivity and loss, ε' and ε'', spectra of the 0.5 mol% solution of LiClO$_4$ in 5-methyl-2-hexanol were measured over a temperature range of 116.6–229.5 K, and that of the 1.03 mol% solution (referred to here as 1 mol% for convenience) over a temperature
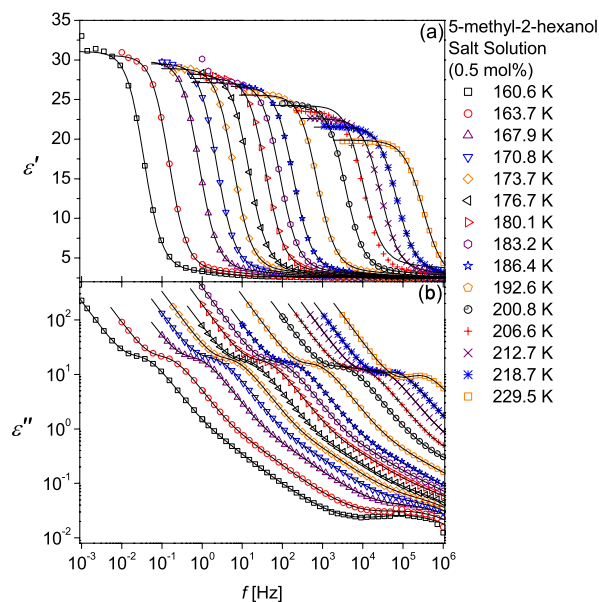
Figure 1. The (a) permittivity and (b) loss spectra of 5-methyl-2-hexanol containing 0.5 mol% LiClO$_4$ at selected temperatures (colour online).
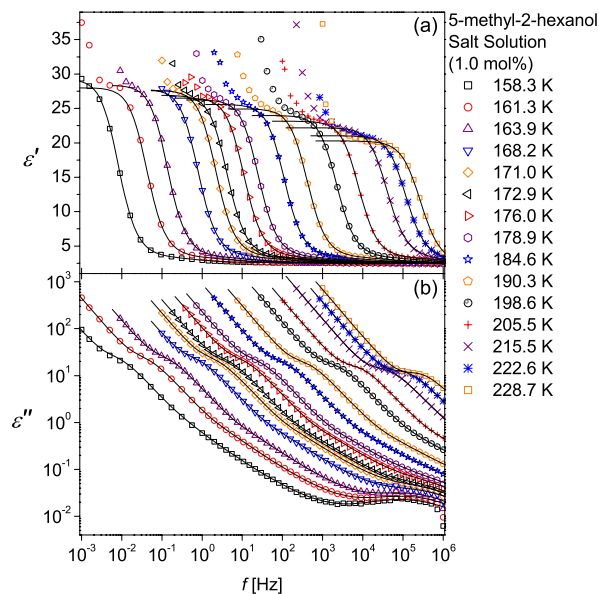

Figure 2. The (a) permittivity and (b) loss spectra of 5-methyl-2-hexanol containing 1.0 mol% LiClO$_4$ at selected temperatures (colour online).

range of 114.1–231.7 K. Several ε' and ε'' spectra for the 0.5 mol% solution are shown in figures 1(a) and (b) respectively, illustrating the evolution of the slowest relaxation with temperature. Similar spectra for the 1 mol% solution are shown in figures 2(a) and (b). The spectra for low temperatures, in the glassy state of the solution where the highest frequency
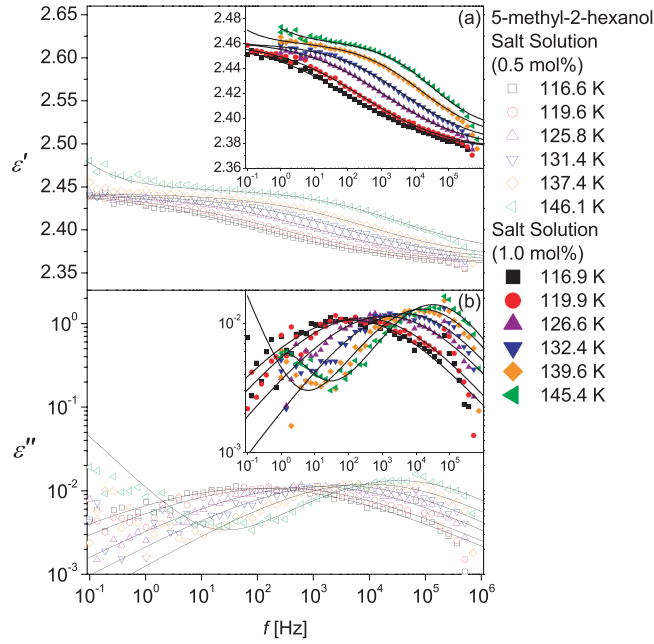
Figure 3. (a) Permittivity spectra of 0.5 mol% LiClO$_4$ in 5-methyl-2-hexanol measured at selected temperatures below and near T_g, as indicated. The permittivity spectra for the 1.0 mol% LiClO$_4$ solution at several temperatures are shown in the inset. (b) The corresponding loss spectra of 0.5 mol% LiClO$_4$ in 5-methyl-2-hexanol. Loss spectra for the 1.0 mol% LiClO$_4$ solution are shown in the inset here. The relaxation peak of the fastest process (process III) is visible in both cases despite the scatter in the data. The solid lines in both panels are the fits of equation (1) to the data (colour online).

relaxation is most apparent, are shown for the 0.5 mol% solution in figures 3(a) and (b) and for the 1 mol% solution in the insets of the same figure, with the temperature indicated in the figures.

The ε'' spectra of the two solutions in figures 1(b) and 2(b) show a large contribution from the dc conductivity, σ_{dc}, due to the mobile Li$^+$ and ClO$_4^-$ ions, as well as impurities in 5-methyl-2-hexanol itself. This renders the ε'' peak of the lowest frequency relaxation indiscernible. The consequent electrode polarization appears in the ε' spectra of the solutions causing a large ε' at low frequencies, particularly in figure 2(a). A shoulder at higher frequencies in the ε'' spectra indicates the presence of a second relaxation peak. Lastly, both the ε'' and ε' spectra in figure 3 show another relaxation process. In order of the increasing frequency of their appearance, we refer to these relaxations as I, II and III, and analyse the measured ε' and ε'' spectra as a sum of these relaxations and the contribution from σ_{dc} to ε'', by using the relation for the complex permittivity [32],

$$\varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \sum_{i=I}^{III} \frac{\Delta\varepsilon_i}{(1 + (j\omega\tau_{HNi})^{\alpha_i})^{\beta_i}} - \frac{j\sigma_{dc}}{\varepsilon_0\omega}, \tag{1}$$

where $\omega = 2\pi f$ is the angular frequency and ε_0 is the permittivity of free space. The subscript i denotes the ith relaxation process. $\Delta\varepsilon_i = \varepsilon_{si} - \varepsilon_{\infty i}$ is the dielectric relaxation strength of this process, τ_{HNi} is the Havriliak–Negami dielectric relaxation time for the ith process (i = I, II, or III); α_i and β_i are respectively the symmetric and asymmetric broadening parameters also for the ith process. The term $\frac{-j\sigma_{dc}}{\varepsilon_0\omega}$ takes account of the σ_{dc} contribution to ε'', and ε_∞ is the
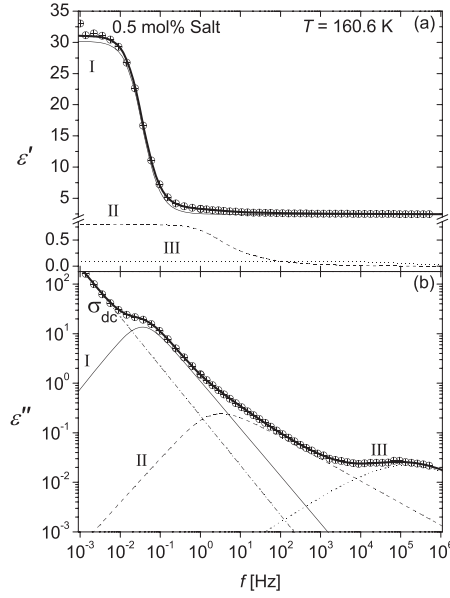
Figure 4. Resolution of the (a) permittivity and (b) loss spectra of 5-methyl-2-hexanol containing 0.5 mol% LiClO$_4$ at 160.6 K. The spectra are resolved into three components I, II and III and dc conductivity. The parameters used are $\Delta\varepsilon_I = 27.8$, $\tau_{HNI} = 4.59$ s, $\alpha_I = 1.00$, $\beta_I = 0.957$, $\Delta\varepsilon_{II} = 0.795$, $\tau_{HNII} = 92.7$ ms, $\alpha_{II} = 0.894$, $\beta_{II} = 0.499$, $\Delta\varepsilon_{III} = 0.102$, $\tau_{HNIII} = 1.07$ μs, $\alpha_{III} = 0.524$, $\beta_{III} = 1.00$, $\varepsilon_\infty = 2.41$, and $\sigma_{dc} = 1.22 \times 10^{-11}$ S m^{-1}.

sum of the permittivity contributions from vibrational, ionic and electronic polarizations. The imaginary part of equation (1) was fitted to the loss spectra using the WinFit dielectric fitting program purchased from Novocontrol.

Solid lines in figures 1 and 2 show the fitted curves. There is significant scatter in the spectra of process III in figure 3 because the ε'' here is approaching the measurement limits. Figures 4(a) and (b) show the ε' and ε'' spectra for the 0.5 mol% solution at 160.6 K (crossed circles). The heavy lines show the ε' and ε'' fit curves calculated with the parameters: $\Delta\varepsilon_I = 27.8$, $\tau_{HNI} = 4.59$ s, $\alpha_I = 1.00$, $\beta_I = 0.957$, $\Delta\varepsilon_{II} = 0.795$, $\tau_{HNII} = 92.7$ ms, $\alpha_{II} = 0.894$, $\beta_{II} = 0.499$, $\Delta\varepsilon_{III} = 0.102$, $\tau_{HNIII} = 1.07$ μs, $\alpha_{III} = 0.524$, $\beta_{III} = 1.00$, $\sigma_{dc} = 1.22 \times 10^{-11}$ S m^{-1} and $\varepsilon_\infty = 2.41$. The individual contributions from σ_{dc} and relaxations I, II and III in the overall fit are also shown. Figures 5(a) and (b) show the corresponding analysis for the 1.0 mol% salt solution at 158.3 K. The heavy line is for the sum of the three processes with $\Delta\varepsilon_I = 26.0$, $\tau_{HNI} = 20.8$ s, $\alpha_I = 1.00$, $\beta_I = 0.91$, $\Delta\varepsilon_{II} = 0.724$, $\tau_{HNII} = 0.429$ s, $\alpha_{II} = 0.920$, $\beta_{II} = 0.472$, $\Delta\varepsilon_{III} = 0.101$, $\tau_{HNIII} = 1.36$ μs, $\alpha_{III} = 0.500$, $\beta_{III} = 1.00$, $\sigma_{dc} = 5.00 \times 10^{-12}$ S m^{-1} and $\varepsilon_\infty = 2.41$. The overall fit is also resolved into the contribution from each term, as in figure 4. In the presence of interfacial contributions to the low frequency plateau of the ε' spectra, ε_s was determined from the fit parameters ($\varepsilon_s = \varepsilon_\infty + \sum_{i=I}^{III} \Delta\varepsilon_i$). Figures 6(a)–(c) show plots of ε_s, $\Delta\varepsilon_I$, and $\Delta\varepsilon_{II}$ and $\Delta\varepsilon_{III}$ against the temperature for the two solutions, with the data for pure 5-methyl-2-hexanol [21] included. The frequency of maximum loss of the ε'' peak, f_m, for the ith relaxation process was determined from the fit parameters [19, 21] and $f_{m,I}$, $f_{m,II}$, and $f_{m,III}$ for the two solutions are plotted on a logarithmic scale against $1000/T$ in figure 7. The fits of the Vogel–Fulcher–Tammann (VFT) equation [33–35],

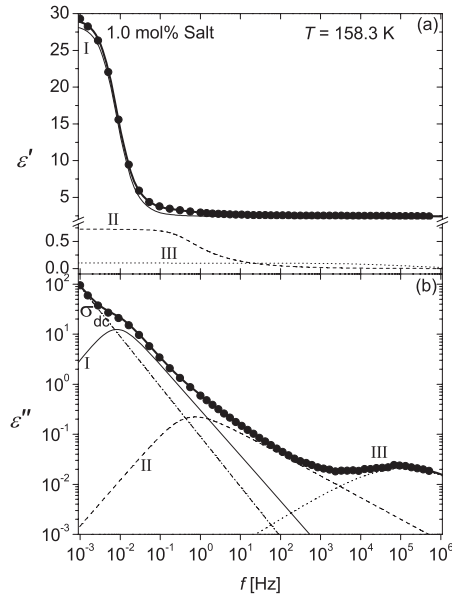$$f_m = A_{VFT} \exp[-B_{VFT}/(T - T_0)] \qquad (2)$$

Figure 5. Resolution of the (a) permittivity and (b) loss spectra of 5-methyl-2-hexanol containing 1.0 mol% LiClO$_4$ at 158.3 K. The spectra are resolved into three components I, II and III and dc conductivity. The parameters used are $\Delta\varepsilon_{\mathrm{I}} = 26.0$, $\tau_{\mathrm{HNI}} = 20.8$ s, $\alpha_{\mathrm{I}} = 1.00$, $\beta_{\mathrm{I}} = 0.91$, $\Delta\varepsilon_{\mathrm{II}} = 0.724$, $\tau_{\mathrm{HNII}} = 0.429$ s, $\alpha_{\mathrm{II}} = 0.920$, $\beta_{\mathrm{II}} = 0.472$, $\Delta\varepsilon_{\mathrm{III}} = 0.101$, $\tau_{\mathrm{HNIII}} = 1.36$ μs, $\alpha_{\mathrm{III}} = 0.500$, $\beta_{\mathrm{III}} = 1.00$, $\varepsilon_{\infty} = 2.41$, and $\sigma_{\mathrm{dc}} = 5.00 \times 10^{-12}$ S m^{-1}.
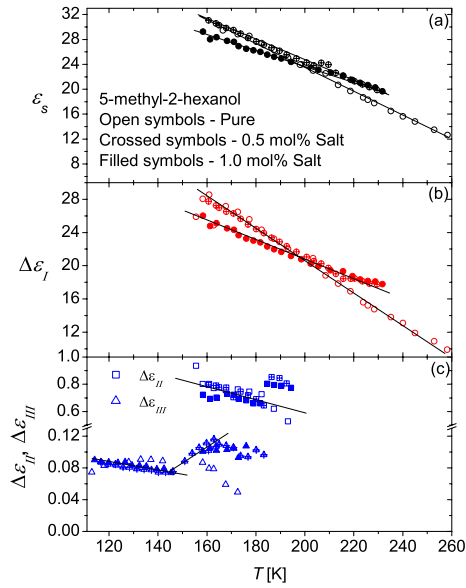
Figure 6. Plots of (a) ε_{s}, (b) $\Delta\varepsilon_{\mathrm{I}}$, and (c) $\Delta\varepsilon_{\mathrm{II}}$ and $\Delta\varepsilon_{\mathrm{III}}$ against the temperature for pure 5-methyl-2-hexanol (O) [21], 0.5 mol% LiClO$_4$ in 5-methyl-2-hexanol (⊕), and 1.0 mol% LiClO$_4$ in 5-methyl-2-hexanol (●). Lines are a guide to the eye only (colour online).

to $f_{m,\mathrm{I}}$ for the pure alcohol and solutions are shown by the lines. A_{VFT} is the relaxation frequency for $T - T_0 \to \infty$ and B_{VFT} is the activation energy. T_0 is the transition temperature
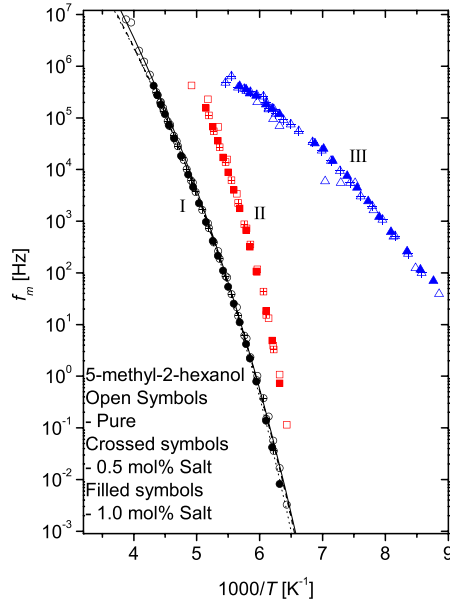
Figure 7. Arrhenius plots of $f_{m,\mathrm{I}}$, $f_{m,\mathrm{II}}$, and $f_{m,\mathrm{III}}$ (marked I, II, III in the figure) for pure 5-methyl-2-hexanol [21] (O), 0.5 mol% LiClO$_4$ ($\oplus$), and 1.0 mol% in 5-methyl-2-hexanol ($\bullet$). The lines are generated from the fits of the VFT equation to the $f_{m,\mathrm{I}}$ data of the pure alcohol (——), the 0.5 mol% solution (– – –), 1.0 mol% solution ($\cdots\cdots$) respectively with fit parameters given in table 1. The relaxation time, τ, discussed in the text is equal to $1/2\pi f_m$ (colour online).

Table 1. The fitting parameters of the VFT (Vogel–Fulcher–Tammann) equation for the relaxation rates of processes I and II and the Arrhenius equation for process III ($T_0 = 0$ K), for 5-methyl-2-hexanol and 1-propanol and their LiClO$_4$ solutions. Data for process II are given in parentheses and those for process III are marked with an asterisk. The values of T_g (10^{-4} Hz) calculated from the VFT equation (3) are also given.

LiClO$_4$ (mol%)	A_{VFT} (Hz)	B_{VFT} (K)	T_0 (K)	T_g
		5-methyl-2-hexanol		
0	$10^{13.63}$, $(10^{12.40})$, $10^{12.81}*$	2775, (1325) 2874*	79.80, (112.25), 0*	148(147)
0.5	$10^{12.92}$, $(10^{11.31})$, $10^{12.52}*$	2494, (1119), 2744*	84.70, (115.48), 0*	149(147)
1.0	$10^{12.60}$, $(10^{11.63})$, $10^{12.79}*$	2309, (1198), 2831*	89.53, (113.93), 0*	150(147)
		1-propanol		
0	$10^{11.91}$, $(10^{11.74})$, $10^{15.01}*$	1734, (1146), 2901*	52.68, (64.59), 0*	100(96.2)
1.0	$10^{12.11}$, $(10^{12.43})$, $10^{15.05}*$	1755, (1314), 2942*	53.22, (63.00), 0*	101(97.7)

where the relaxation frequency tends to zero. $T_0 = 0$ reduces equation (2) to the Arrhenius equation. The subscript VFT to the various parameters here denotes that these correspond to the Vogel–Fulcher–Tammann equation. The fitted curves are $f_{m,\mathrm{I}} = 10^{13.63}\exp[-2775/(T - 79.8)]$ for the pure alcohol (solid line), $f_{m,\mathrm{I}} = 10^{12.92}\exp[-2494/(T - 84.70)]$ for the 0.5 mol% salt solution (dashed line), and $f_{m,\mathrm{I}} = 10^{12.60}\exp[-2309/(T - 89.53)]$ for the 1.0 mol% solution (dotted line). The parameters together with those for pure 1-propanol and its 1.0 mol% salt solution [31] are listed in table 1. The values of α_{I} and β_{I}, α_{II} and β_{II}, and α_{III} and β_{III} are plotted in figures 8(a)–(c), respectively. For a Debye relaxation $\alpha = \beta = 1$, for
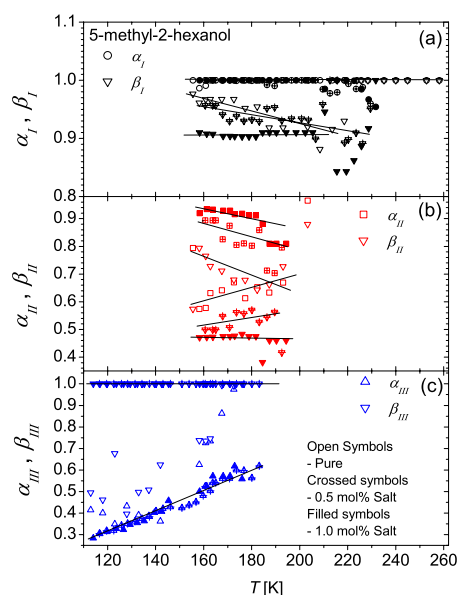
Figure 8. Plots of (a) α_I and β_I, (b) α_{II} and β_{II}, and (c) α_{III} and β_{III}, against the temperature for pure 5-methyl-2-hexanol [21] ($\circ$), 0.5 mol% ($\oplus$), and 1.0 mol% LiClO$_4$ in 5-methyl-2-hexanol ($\bullet$). Lines are guides for the eye (colour online).

a Davidson–Cole [36] distribution, $\alpha = 1$ and $\beta < 1$, while for a Cole–Cole [37] distribution $\alpha < 1$. For pure 5-methyl-2-hexanol, $\alpha_I = 1$ and $\beta_I \sim 0.96$, as for a Debye type relaxation [21], which is comparable with the values for the 0.5 mol% solution. $\alpha_I = 1$ and $\beta_I \sim 0.9$ in the 1.0 mol% solution. A similar reduction in β_I was found also in the 1.0 mol% solution of 1-propanol. The high σ_{dc} obscures the relaxation peak in the salt solutions and there is an uncertainty in the data analysis. In an earlier discussion of the solution's σ_{dc}, it was shown that it does not linearly vary with the relaxation rate, and does not follow the Debye–Stokes–Einstein equation for ion diffusion [38]. This was attributed to the changing structure of the alcohol in the presence of ions. The ionic equilibrium and temperature have a significant effect on σ_{dc}.

4. Discussion of the results

An earlier study of a LiClO$_4$ solution in 1-propanol has provided a general description of ion effects. Therefore, here we discuss comparatively the specific effects of ions on four dielectric features:

 (i) the limiting low and high frequency permittivities ε_s and ε_∞ respectively, and the total number of relaxation processes and their respective amplitudes,
 (ii) the relaxation time of the processes and their distribution parameters,
(iii) the temperature dependences of the relaxation time and
(iv) the dc conductivity.

As mentioned here earlier, 5-methyl-2-hexanol is a secondary alcohol. It contains an asymmetric carbon atom and therefore exists as optical isomers. Despite this structural difference that restricts the extent of hydrogen bonding, it has shown dielectric relaxation

features similar to those found for 1-propanol. Therefore it might be expected that the dielectric features of its salt solutions would be similar to those of 1-propanol [31], and in many respects that is so. However, the effect of salt addition on the static permittivity, ε_s and relaxation strength of the Debye relaxation for 5-methyl-2-hexanol is different. Also, the presence of ions is expected to increase ε_∞ due to increased absorbance in the IR region. The ε_∞ estimated from the ε' spectra fits at 103.6 K is ∼2.61 for 1-propanol and 2.62 at 104.4 K in the presence of the ions [31]. At a temperature of 103.1 K $\varepsilon_\infty = 2.26$ for pure 5-methyl-2-hexanol calculated from the data of Kalinovskaya and Vij [21] and $\varepsilon_\infty = 2.37$ for its 0.5 and 1.0 mol% LiClO$_4$ solutions. Addition of 1.0 mol% LiClO$_4$ decreased ε_s of 1-propanol at 117.6 K by 40% over the entire temperature range of the supercooled liquid [31]. The addition of 1 mol% LiClO$_4$ to 5-methyl-2-hexanol decreases ε_s by only about 7% at 172.9 K, and increases it above 200 K, as seen in figure 6(a). The presence of ions in either alcohol does not alter the number of relaxation processes in the dielectric spectra.

As discussed earlier by Johari and Andersson [28], the Debye–Huckel [39, 40], Debye–Falkenhagen [41], and Hubbard and Onsager [42] theories suggest reasons as to why the solvent ε_s would either increase [41] or decrease [39, 40, 42] on addition of salt. The formation of ion pairs at higher salt concentrations and lower temperatures may also increase ε_s. These ionic effects may be present independently of whether a liquid has hydrogen bonding or not. In H-bonded liquids there would be additional effects as ions tend to break the hydrogen bonds and thus may alter the magnitude of the dipolar orientation correlation factor, g. According to the discussion given previously [31], ions would tend to decrease ε_s of 1-propanol by disrupting H-bonded chain structures. The crossover at ∼200 K in 5-methyl-2-hexanol suggests a competition of two or more mechanisms having opposite effects on ε_s. Possible processes contributing to an increase in ε_s are the reorientation of a small concentration of (dipolar) ion pairs in the solution and/or a dissociation of H-bonded structures where the dipoles had tended to align in an antiparallel manner, as in ring dimers. However, both the relatively small decrease in the dielectric relaxation strength of the Debye process, $\Delta\varepsilon_I$, in 1.0 mol% solution and the lack of change in the relaxation rates as seen in figure 6, indicate that ions have much less effect on H bonding in the 5-methyl-2-hexanol than in 1-propanol. In terms of molarity (moles of ions per unit volume) at 298 K, the 1.0 mol% 5-methyl-2-hexanol salt solution is a factor of three less concentrated than the 1.0 mol% 1-propanol one.

We now consider the effect of ions on the relaxation strength of the Debye and faster relaxation processes in detail. Here, the behaviour of 5-methyl-2-hexanol in figure 6(b) is more complex: For the 0.5 mol% solution, $\Delta\varepsilon_I$ does not change at $T < 200$ K but *increases* by ∼16% at ∼224 K. For the 1.0 mol% solution, $\Delta\varepsilon_I$ decreases by ∼11% at ∼173 K compared to the value for pure 5-methyl-2-hexanol. It increases by 18% at T of ∼223 K. In comparison, the addition of 1 mol% LiClO$_4$ to 1-propanol decreased $\Delta\varepsilon_I$ by 44% at 117.6 K [31]. The addition of LiClO$_4$ to 5-methyl-2-hexanol has little effect on $\Delta\varepsilon_{II}$ and $\Delta\varepsilon_{III}$, as seen in figure 6(c). On addition of LiClO$_4$ to 1-propanol, $\Delta\varepsilon_{II}$ had increased and $\Delta\varepsilon_{III}$ slightly decreased [31], but their sum which constitutes the remainder of the orientational polarization increases by 8% at 117.6 K.

As seen in figure 7, the dissolved LiClO$_4$ has no effect on the relaxation time of the three processes in 5-methyl-2-hexanol. The dissolved LiClO$_4$ also had no effect on τ_I of 1-propanol, but in contrast to 5-methyl-2-hexanol, τ_{II} increased. This is contrary to what may have been expected based on ionic disruption of H bonding. There was no effect on τ_{III}. It may be noted that the viscosity of 1-propanol solutions and their mechanical relaxation times have also been found to increase for higher concentrations of LiClO$_4$ than were used in our studies [43, 44].

Since features of process I are obscured by a large σ_{dc} in the salt solutions, and there is a large uncertainty in analysing the small contributions from processes II and III, conclusions

Table 2. The fitting parameters of the VFT conductivity equation for 5-methyl-2-hexanol and 1-propanol and their LiClO$_4$ solutions.

LiClO$_4$ (mol%)	$A_{VFT,\sigma}$ (Hz)	$B_{VFT,\sigma}$ (K)	T_0 (K)
	5-methyl-2-hexanol		
0	$10^{-3.351}$	913.1	124.32
0.5	$10^{0.4529}$	1490	103.29
1.0	$10^{0.6963}$	1457	105.35
	1-propanol		
0	$10^{-1.129}$	1285	62.65
1.0	$10^{2.338}$	1400	61.66

regarding the effects of dissolved LiClO$_4$ on the distribution parameters of the three relaxation processes are tentative. For the 1 mol% LiClO$_4$ solution in 5-methyl-2-hexanol β_I in figure 8(a) decreases to ~0.9. This is consistent with the findings for 1-propanol that the Debye relaxation is slightly broadened by the addition of 1.0 mol% LiClO$_4$. For 5-methyl-2-hexanol, α_{II} increases from ~0.6 to ~0.9 and β_{II} decreases from ~0.7 to ~0.5 on addition of ions (figure 8(b)). The overall broadness of process II, as indicated by the product of the two broadening parameters α and β, remains unchanged, and this is also found to be the case for 1-propanol and its LiClO$_4$ solution [31]. Distribution parameters of process III in 5-methyl-2-hexanol (figure 8(c)) seem to be relatively unaffected by the addition of the salt. Process III in 1-propanol changed from a Havriliak–Negami [32] to a Cole–Cole [37] distribution in the salt solution. Since process III accounts for <1% of the polarization in these alcohols, changes in the fitting parameters may contain large errors in the fitting of a small relaxation region.

Changes in temperature dependence of the relaxation rates on addition of ions can be seen in both the trends in the parameters of the VFT equation (see table 1) and the glass transition temperatures, T_g. T_g (for $f_{m,I}$ and $f_{m,II} = 10^{-4}$ Hz) can be estimated from the VFT fit parameters using:

$$T_g(10^{-4} \text{ Hz}) = T_0 + B_{VFT}/(9.21 + \ln A_{VFT}). \qquad (3)$$

For process I in 5-methyl-2-hexanol, the parameter A_{VFT} decreases with an increase in the LiClO$_4$ concentration, B_{VFT} decreases, and T_0 increases slightly. For process II, there does not appear to be any clear trend in the parameters. T_g ($f_{m,I} = 10^{-4}$ Hz) increases marginally with values ranging from 147 to 150 K with concentration. T_g for process I and II estimated from the dielectric data are quite similar but the latter does not increase with concentration. For process I in 1-propanol it is observed that A_{VFT}, B_{VFT} and T_0 all increase on addition of 1.0 mol% LiClO$_4$. The parameters A_{VFT}, and B_{VFT} of process II increase and T_0 decreases. T_g ($f_{m,I} = 10^{-4}$ Hz) increases marginally from 100.0 to 100.5 K as does T_g ($f_{m,II} = 10^{-4}$ Hz).

Figure 9 shows that σ_{dc} increases by 266-fold on addition of 0.5 mol% LiClO$_4$ to 5-methyl-2-hexanol at a temperature of 224 K. Roughly doubling the salt concentration to 1.0 mol% increased σ_{dc} by a further factor of 1.7. Addition of 1 mol% LiClO$_4$ to pure 1-propanol increased σ_{dc} by a factor of ~250 at 117.5 K and 1000 at 150.6 K. In both alcohols, it was found that a VFT [33–35] type equation of the form $\sigma_{dc} = A_{VFT,\sigma} \exp[-B_{VFT,\sigma}/(T - T_{0,\sigma})]$ could be fitted to σ_{dc}. The values obtained for the fitting parameters $B_{VFT,\sigma}$ and $T_{0,\sigma}$, of this equation match most closely the analogous parameters B_{VFT} and T_0 for the f_m data of relaxation process II (see tables 1 and 2).

We now consider the relation between the transport property of ions and diffusion of dipoles. This is usually given in terms of the so-called Debye–Stokes–Einstein (DSE) equation.
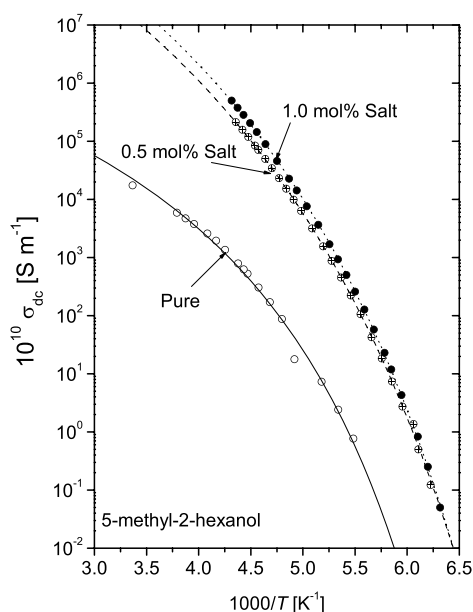
Figure 9. Arrhenius plots of σ_{dc} for pure 5-methyl-2-hexanol (O), 5-methyl-2-hexanol containing 0.5 mol% (⊕) and 1.0 mol% LiClO$_4$ (●). The lines through the datasets are obtained from fits of the conductivity form of the VFT equation to the data in each case. These fit parameters are given in table 2.

In this relation, σ_{dc} of the liquid is inversely proportional to the relaxation time, τ, or a plot of $\log_{10}(\sigma_{dc})$ against $\log_{10}(\tau)$ for a liquid obeying the DSE equation should be a straight line with a slope of -1. Johari and Andersson [28] have recently examined this relation and found it to be inconsistent with our current understanding that an ion–ion pair equilibrium exists in solutions and that this equilibrium changes as a liquid's structure changes with the temperature and pressure. Prior to the work [28], the term for the latter effect was not included in the DSE equation. To test the validity of the DSE equation we plot $\log_{10}(\sigma_{dc})$ against $\log_{10}(\tau)$ for 5-methyl-2-hexanol and its 0.5 and 1.0 mol% LiClO$_4$ solution in figure 10(a), and a straight line of slope -1 is drawn for comparison. The slope, $[d \log_{10}(\sigma_{dc})/d \log_{10}(\tau)]$, of the curves at each point of the three data sets is plotted against T in figure 10(b). This slope is close to -1 for low σ_{dc} and long τ, and at high temperatures (high σ_{dc} and short τ) it systematically deviates from -1. This seems to verify the validity of the development provided by Johari and Andersson [28]. The scatter in the slope is relatively high for 1-propanol, whose σ_{dc} becomes too low to be measured accurately.

Finally we discuss again the attribution of process II for such alcohols as the α-process and a mechanism for viscous flow [19] in place of process I, the pronounced Debye relaxation. It seems instructive to examine first the evidence presented for it, namely that the Debye relaxation does not seem to kinetically unfreeze at the calorimetric T_g when the glassy state of some of the alcohols is heated [45, 46]. Support for the view that the Debye relaxation differs from structural relaxation has been put forward by comparing the temperature at which τ of a Debye type dielectric relaxation is $\sim$100 s against the calorimetric T_g measured by heating at a certain rate. For example, it was argued that [46], 'More specifically, a detailed DSC study of 1-propanol resulted in $T_g = 96.2$ K [47], while the kinetic T_g's are 101.9 K for the Debye process and 97.0 K for the smaller α-process.' This analysis is misleading because the calorimetric T_g
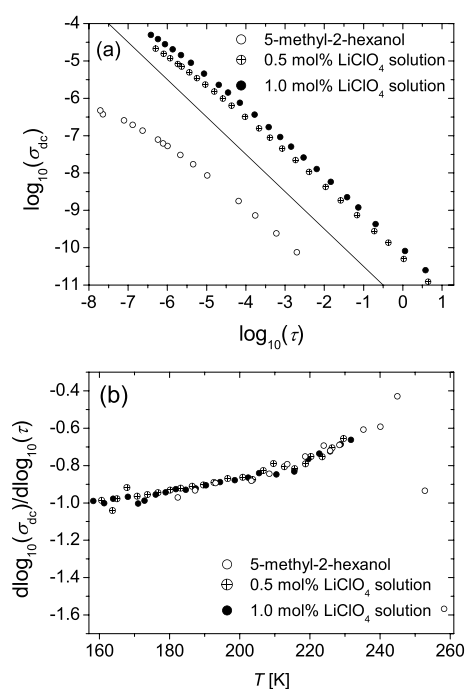
Figure 10. Logarithmic plots of (a) σ_{dc} of pure 5-methyl-2-hexanol ($\bigcirc$) and the 0.5 mol% ($\oplus$) and 1.0 mol% $LiClO_4$ ($\bullet$) solutions against the relaxation time, τ, of the Debye process. The corresponding plot of (b) $[d \log_{10}(\sigma_{dc})/d \log_{10}(\tau)]$ against temperature is also shown. τ is in seconds and σ_{dc} in units of S m^{-1}. The rapid decrease in the slope at high temperatures for the pure alcohol is an artefact.

of 1-propanol taken from Takahara *et al*'s study [47] is not based on the DSC measurements. It derives from an adiabatic calorimetry study where the cooling rate in the T_g range was 0.2–0.4 K min^{-1} and the heating rate, which corresponds to the adiabatic calorimetry, was much slower than that. It is well recognized that the T_g measured on heating is reduced when the heating rate is lower. In adiabatic calorimetry or in another method using slow heating rates, T_g appears at a relaxation time much longer than 100 s. Moreover, calorimetric and dielectric relaxation times for liquids generally do not agree, as excellently reviewed by McKenna [48] and is now known in the field of supercooled liquids. Calorimetric relaxation also has a much broader distribution of times or greater non-exponentiality than dielectric relaxation in general. This raises the issue of different dynamic heterogeneities for the same liquid inferred from the two methods.

Similar difficulties of analysis appear in another comparison using data for 2-ethyl-1-hexanol [46]. In this study, the temperatures at the extrapolated relaxation time of 100 s in figure 2 yields T_g-kinetic-α for the non-Debye relaxation as $\sim$142 K, T_g-kinetic-D for the Debye relaxation as $\sim$153 K and T_g from the onset temperature of 20 K min^{-1} heating DSC scan $\sim$147 K and from its mid-point temperature as $\sim$149 K. The τ data determined from fixed, high frequency dynamic heat capacity scans were taken to agree with the dielectric τ data for the non-Debye relaxation, but the two sets of data do not follow the same fitting equation and would not lead to the same extrapolated value of T for 100 s at T_g-kinetic-α. Moreover, dielectric and dynamic heat capacity scans [49] of polymers have already shown that dielectric and calorimetric T_g differ (see figure 2 in [49]).

It was also originally suggested that micelle type structures might be present in these pure supercooled alcohols [44, 45]. However, it has been pointed out that the Debye relaxation in pure monohydroxy alcohols cannot be attributed *a priori* to the formation of micelles in their liquid's structure [50]. We further point out that the presence of micelles in a liquid would cause it to show a non-Newtonian flow, which has not been observed. Also some of the long chain alcohols, such as a variety of isomeric octanols, which are expected to show a greater ability to form micelles, have shown a non-Debye behaviour of their slowest relaxation process [10]. Still, it may seem tempting to suggest the possibility of micelle formation by agglomeration of the hydrogen-bonded molecules, and then to suggest the possibility of difference between the proton conduction within the micelle and in the bulk. This would produce an interfacial polarization at the micelle–liquid interface, and there has been no evidence for presence of such micelles from light scattering techniques or simple optical observations.

In this context, it is remarkable that a Debye relaxation has now been observed for the slowest dielectric relaxation process in the ultraviscous state of a dilute solution of di-*n*-butyl ether in 3-methylpentane, and its total relaxation spectra has also been resolved into three relaxation regions [51], as was done for 1-propanol [19]. This demonstrates that hydrogen bonding in a liquid is unnecessary for the occurrence of a Debye relaxation process. Since its τ also shows a VFT [33–35] type temperature dependence over a wide temperature range down to a temperature approaching T_g, its features also conflict with the above mentioned view on the dynamic heterogeneity in an ultraviscous liquid's structure [52, 53] and the apparent correlation between the non-exponentiality and non-Arrhenius behaviour [25]. The data for di-*n*-butyl ether was interpreted in terms of the Anderson–Ullman [54] model for environmental fluctuation, as was originally done for monohydroxy alcohols [10].

More recently, a different explanation has been given: 'the Debye process corresponds to a transition among states which differ in energy only in the case of an electrical field,' i.e., 'a polarization process that involves states which differ in energy level only if an external field is applied' [46]. We point out that this is true in general for the dielectric and mechanical relaxation processes in all materials, in which an applied electrical or mechanical stress produces energetically different states in terms of electrical and elastic dipole orientations. Removal of the stress subsequently returns the system to its random orientation or energy state, a process seen as relaxation. It may also be pointed out that this is the basis of the potential barrier model for the dielectric relaxation process, where the probability for the orientation of the dipole in the direction of the electric field is higher (lower energy minima) than against it (higher energy minima), as first suggested by Debye [56] and detailed by Fröhlich [3].

5. Comments on finding T_g using dielectric relaxation data and its connection with the internal field

This comment is appropriately made in view of the fact that T_g values obtained from dielectric measurements for different relaxation processes are being compared with those found using DSC in order to decide which process gives rise to the structural relaxation in a viscous liquid and determine the extent of its heterogeneity. The relaxation time determined from dielectric experiments for a particular mechanism is a macroscopic parameter, the physical significance of which is that its inverse is the angular frequency where the energy dissipated per unit volume per cycle of the alternating field in a system is a maximum. If we need to interpret the molecular process in question, i.e., corresponding to an ensemble of molecules, we must not neglect the effect of all other dipoles except that of the reference dipolar molecule on the internal field, i.e., the field acting on the reference molecule (for details, see [55]). This field is different from the applied field. Debye [56] used the simple Lorentz expression for internal field, and found that

the microscopic (molecular) relaxation time, τ_{mol}, is related to the macroscopic relaxation time, τ, as follows:

$$\tau_{mol} = \frac{\varepsilon_\infty + 2}{\varepsilon_s + 2}\tau. \tag{4}$$

Here ε_s and ε_∞ are the static permittivity and the permittivity at a frequency where the permanent dipoles cease to contribute to the polarization, respectively. Powles [57] applied the Onsager model [1] to the dynamic case and instead obtained the following expression:

$$\tau_{mol} = \frac{2\varepsilon_s + \varepsilon_\infty}{3\varepsilon_s}\tau. \tag{5}$$

Although τ_{mol} and τ are of the same order of magnitudes especially in equation (5), their relationship is temperature dependent through different dependences of ε_s and ε_∞. In this case, ε_s and ε_∞ also depend on the relaxation process under consideration (see section 3). For process I, ε_s would be much greater than for process II. Applying the correction of either equation (4) or (5) and using τ_{mol} as the relaxation time would alter the value of T_g obtained from the dielectric measurements. This should further emphasize that comparison of T_g values measured using different techniques requires extreme caution.

Using the orientation susceptibility and the Lorentz expression for internal field we have shown [58]

$$\tau_\alpha = \frac{3}{\varepsilon_s + 2}\tau_\chi. \tag{6}$$

Here τ_α is the relaxation time of the polarizability of a sphere of unit molar volume and τ_χ is the relaxation time of the orientational polarization. Equation (6) is similar to equation (4). For $\varepsilon_\infty = 1$ we find as expected $\tau_\alpha = \tau_{mol}$ and $\tau_\chi = \tau$.

It is for this reason and for the reasons already advanced in this paper that a comparison of the value of T_g from either of the two relaxation processes to those found from the DSC for a system involving more than one relaxation process is meaningless. Dielectric spectroscopy is a useful and powerful technique for investigating a system where the fluctuation of the dipole moment is involved. However, a deduction at the molecular level requires an exact calculation of the internal field and because this field is model dependent and in reality unknown, it has been neglected in the recent literature for the quantitative deductions from the dielectric data. The experimental results reflect that all molecules participate in the structural relaxation: a large majority of the molecules, more than 95%, are involved in hydrogen bonding and these give rise to relaxation process I and $\sim$3% are relatively free and these give rise to process II. It is quite likely that the motion of the molecules involved in process I is arrested at a slightly higher temperature by 1 to $\sim$3 K than those involved in process II due to their different surroundings and consequently on account of these involved in different types of intermolecular interactions. However it would be incorrect to state that the value of T_g found from process II corresponds to T_g found by DSC or is the T_g of the structural relaxation and the heterogeneity of relaxation process II corresponds to the hetereogeneity of the entire system as claimed by Huth *et al* [46]. The kinetic T_g for the alcohol studied in any case is within $\sim$3 K of each other. The fact that the primary process becomes non-Debye with the addition of an electrolyte and its relaxation rate is unaltered can imply that this process should not be ignored from it primarily accounting for the structural relaxation of the system.

6. Conclusions

The addition of Li^+ and ClO_4^- ions decreases the equilibrium permittivity of 5-methyl-2-hexanol (a secondary alcohol with optical isomers) by $\sim$7% below 200 K and increases it

by 11% above 200 K. There is no change in the relaxation rate and only a small change in the distribution parameters of its principal relaxation. The dc conductivity increases, much more initially and then less so on further addition of ions. The distribution of relaxation times becomes slightly broader for the Debye process, and is unchanged for processes II and III. The decrease and then increase in the permittivity suggests an interplay between ionic mechanisms that raise and lower the permittivity of the solution and change in relative importance as the temperature is increased. A decrease in orientation correlation of molecules as H bonding is disrupted by the presence of ions is expected to decrease the viscosity of the solution and thereby increase the dipolar relaxation rate. As no increase was found in the relaxation rate of any of the three relaxation processes, either the relaxation rate is not related to the viscosity or the ion–dipole interaction in the solvation shell decreases this rate to compensate for the expected increase. The effect of ions on the dielectric relaxation of 5-methyl-2-hexanol is qualitatively similar to that observed for that of 1-propanol. This is despite the large differences in the steric hindrance to hydrogen bonds in the two alcohols. The findings show that the Debye process that relaxes ∼95% of the orientation polarization in both alcohols is the α-relaxation process that determines the transport properties. It may be considered in terms of the earlier models of structural fluctuations that involved the sequence of H bond breaking–dipolar reorientation–H bond reforming. We can visualize the alcohols and amides as heterogeneous systems too that involve clusters of slow moving molecules (hydrogen-bonded regions) inter-dispersed with fast moving molecules (non-hydrogen-bonded regions) but in our view this heterogeneity cannot be determined from a particular relaxation process.

Variation in the dc conductivity with the dielectric relaxation time does not follow the Debye–Stokes–Einstein relation for either the pure liquid or the $LiClO_4$ solutions. This suggests the need for extending this equation by including the liquid's structure-dependent electrostatic effects on the electrolytic dissociation constant. Evidently, translational diffusion of ions does not follow a liquid's configurational fluctuations due to Brownian diffusion, which involves both the rotational and translational motion of molecules.

Acknowledgments

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