Effects of ions on the dielectric permittivity and relaxation rate and the decoupling of ionic diffusion from dielectric relaxation in supercooled liquid and glassy 1-propanol

G. Power
Laboratory of Advanced Materials, Department of Electronic Engineering, Trinity College,
University of Dublin, Dublin 2, Ireland

G. P. Johari
Department of Materials Science and Engineering, McMaster University,
Hamilton, Ontario L8S 4L7, Canada

J. K. Vij[a)]
Laboratory of Advanced Materials, Department of Electronic Engineering, Trinity College,
University of Dublin, Dublin 2, Ireland

The effects of intermolecular H bonds on the equilibrium permittivity, ϵ_s, the relaxation rate, f_m, and changes in the dielectric relaxation spectra of 1-propanol were studied by adding a strongly dissociating electrolyte $LiClO_4$. The spectra of both 1 mol % $LiClO_4$ containing 1-propanol (1 molecule of $LiClO_4$ per 99 molecules of 1-propanol), and of pure 1-propanol were measured over a temperature range from $\sim$90–160 K in the frequency range 1 mHz–1 MHz. An analysis of the spectra showed that the three relaxation processes (I, II, and III in ascending rapidity), that occur in the pure alcohol persist in the presence of ions, the equilibrium permittivity, ϵ_s, decreases, the distribution characteristics of the processes changes, and the rate of relaxation, f_m, of processes I and III remains constant within analytical errors, while that of process II is reduced. The temperature dependencies of $f_{m,I}$ and $f_{m,II}$ are non-Arrhenius while that of $f_{m,III}$ is Arrhenius. The temperature dependence of the dc conductivity, σ_0 is also non-Arrhenius, but the parameters of the fit differ from those of $f_{m,I}$ and are closer to those of $f_{m,II}$. Its 1000-fold increase on adding 1 mol % $LiClO_4$ is due to the increase in ion concentration and a decrease in the viscosity as a result of the breaking of H bonds. However, as $f_{m,I}$ and $f_{m,III}$ remain constant on the addition of $LiClO_4$, and $f_{m,II}$ decreases slightly, an expected decrease in viscosity would seem to be unrelated to the relaxation rates of these processes. In that case, σ_0 is decoupled from these dipolar relaxation modes. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1448289]

I. INTRODUCTION

When dipolar molecules form intermolecular hydrogen bonds in a liquid or solid, their dielectric properties change. Such bonding may raise the equilibrium permittivity, ϵ_s, if it leads to an increase in the effective dipole moment of the complex that effectively reorients when an individual molecule reorients, and it may lower ϵ_s to a value close to that of a nonpolar liquid if it leads to a decrease in the dipole moment. This has been expressed in terms of a change in the orientational correlation factor, g[1], in the statistical-mechanical theory of dielectric polarization formulated by Kirkwood,[1] Onsager,[2] and Fröhlich.[3] Population of intermolecular H bonds and their rate of breaking and reforming also controls the dielectric relaxation rate, the distribution of relaxation rates, viscosity and self-diffusion coefficient. It is well recognized that at high temperatures where intermolecular association by H bonds is minimal, ϵ_s of a liquid is re-

duced to a value that agrees with the Onsager[2] theory. At these temperatures, the relaxation rate tends to be determined by the Arrhenius equation.

Several types of interactions can reduce the extent of H bonding in a liquid or a solid and thereby affect the dielectric behavior. These are (i) interaction with a nonpolar molecule, such that the viscosity does not change, (ii) adsorption on a crystal, glass, or another liquid surface which prevents extensive intermolecular H bonding when the surface to volume ratio is large, and (iii) formation of a solvation layer on ions, which decreases the extent of intermolecular H bonds by selectively aligning the molecular dipole vector. The first occurs in solutions, the second in thin films, and in liquids and solids confined to nanosize pores of another solid and in nanosize droplets in an emulsion, and the third in ionic solutions. In all cases, a decrease in the number of H bonds alters the orientational correlation of dipoles and the rate of H-bond breaking and reforming. This in turn suggests that the nature of the interactions that alter the H-bond populations may be studied by measuring the dielectric properties. Here we report a study of the effect of solvation on the extent of H bonding.

---
a)Author to whom correspondence should be addressed; electronic mail: jvij@tcd.ie

We chose 1-propanol for such a study. Its dielectric properties have been reported by several groups[4–7] since 1951, and the high magnitude of its ϵ_s has been interpreted in terms of the formation of H-bonded linear chains, which increases its dipolar orientational correlation factor. However, the mechanism of its dielectric relaxation has been a subject of debate recently.[7–13] The debate has resulted from recent studies[7,8] showing that the slowest dielectric relaxation process, which is responsible for ~95% of its polarization is associated with an unspecified mechanism that does not contribute to the viscosity and the density fluctuations in the light scattering measurements. Our study showed that 1-propanol can also dissolve a significant amount of ionic salts and, as its ϵ_s is relatively high, the ionic dissociation of the salts is significant. Also, since ionic diffusion in a liquid is determined by its viscosity, η, one expects that the dc conductivity, σ_0, of 1-propanol would change with temperature in the presence of ions only in as much as the viscosity changes. If the magnitude of orientational polarization also changes, then σ_0 would be determined additionally by the population of the ions as determined by the ion-association constant (K_A) which varies with ϵ_s as $K_A \propto \exp(-\epsilon_s)$. Thus both ϵ_s and σ_0 would depend upon the extent of intermolecular H bonding. The study here shows that ϵ_s decreases and σ_0 increases on adding LiClO$_4$ to 1-propanol. The relaxation rates of processes I and III remain relatively constant and the relaxation rate of process II decreases. These are discussed in terms of the mechanism of dielectric relaxation and decoupling of the ionic transport and the viscosity from the dielectric relaxation rate. In recognition of the possibility that purity of pure 1-propanol studied by various groups may differ and therefore the earlier data may not be used for comparison here, pure 1-propanol was also studied, so that comparison could be made with the data for solutions.

II. EXPERIMENTAL METHODS

1-propanol of purum grade and 99% pure lithium perchlorate (LiClO$_4$) were purchased from Fluka Chemicals. Both substances were used as such. LiClO$_4$ was chosen for its high solubility in alcohols,[14] including 1-propanol. The dielectric cell used was a miniature, tunable parallel plate condenser containing 18 plates, with an air capacitance of nominally 27 pF. (This capacitor seems superior to the parallel plates separated by spacers used successfully up to 1 MHz by several groups.) Its capacitance was accurately measured in air. The capacitor was immersed in the liquid sample contained in a glass vial, and its temperature was controlled by keeping it inside a cryostat, model Oxford Spectrodn 20 spectrostat, purchased from Oxford Instruments. The controller (model ITC502, also from Oxford Instruments) was set to maintain a given temperature, as referenced by a sensor inside the sample chamber of the cryostat. To improve accuracy, the sample temperature was measured independently with a 100 Ω platinum resistor situated inside the sample container itself. The temperature measured was recorded by a Keithley 195A digital multimeter. This setup allowed control of the sample temperature to within 0.1 K for ~4 h required for the collection of spectra at the lowest frequencies. The real and imaginary components, ϵ' and ϵ'', respec-
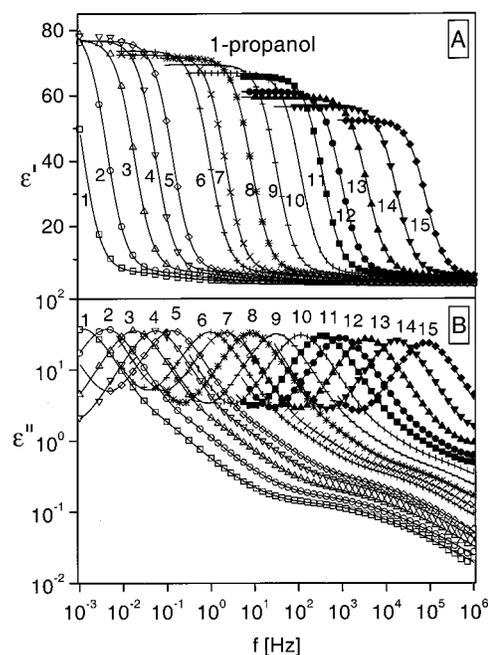

FIG. 1. The ϵ' (A) and ϵ'' (B) spectra of pure 1-propanol recorded at selected temperatures, labeled as follows: (1) 103.6 K, (2) 105.4 K, (3) 107.7 K, (4) 109.7 K, (5) 111.4 K, (6) 115.5 K, (7) 117.5 K, (8) 121.4 K, (9) 125.2 K, (10) 129.2 K, (11) 133.4 K, (12) 137.2 K, (13) 142.9 K, (14) 150.6 K, and (15) 160.2 K. Solid lines are the composite fits to Eq. (1), symbols denote the experimental data.

tively, of the complex permittivity were measured over the frequency range 1 mHz to 1 MHz using a Solartron FRA-1255A frequency response analyzer interfaced with a Chelsea dielectric interface.

III. RESULTS AND ANALYSIS

The ϵ' and ϵ'' spectra were obtained for 34 different temperatures for 1-propanol over the temperature range 89–160 K, and 32 different temperatures for 1-propanol containing 1 mol % LiClO$_4$ over the range 89–161 K. Figures 1(A) and 1(B) show the ϵ' and ϵ'' spectra, respectively, of pure 1-propanol at various temperatures. The ϵ' and ϵ'' spectra of the 1.0 mol % LiClO$_4$ solution at selected temperatures are plotted in Figs. 2(A) and 2(B). The evolution of the spectra, in particular the fastest relaxation, at low temperatures for both pure 1-propanol (main plots) and the solution (inset plots) are also shown in Fig. 3.

The dielectric spectra for pure 1-propanol were analyzed by assuming that each spectrum is the sum of several contributions from different relaxation processes, each one of which can be described by a term in the Havriliak–Negami[15] equation:

$$\epsilon^*(\omega) = \sum_{i=1}^{n} \frac{\epsilon_{s,i} - \epsilon_{\infty,i}}{[1 + (j\omega\tau_{\text{HN}i})^{\alpha_i}]^{\beta_i}} - \frac{j\sigma_0}{\epsilon_0\omega}, \qquad (1)$$

where α_i and β_i are the width parameters (symmetric and assymetric, respectively), $\epsilon_{s,i}$ and $\epsilon_{\infty,i}$ are the limiting low and high frequency values of the permittivity (and their difference is denoted $\Delta\epsilon_i$), and $\tau_{\text{HN}i}$ is the characteristic (in this case Havriliak–Negami) relaxation time, all for the ith pro-
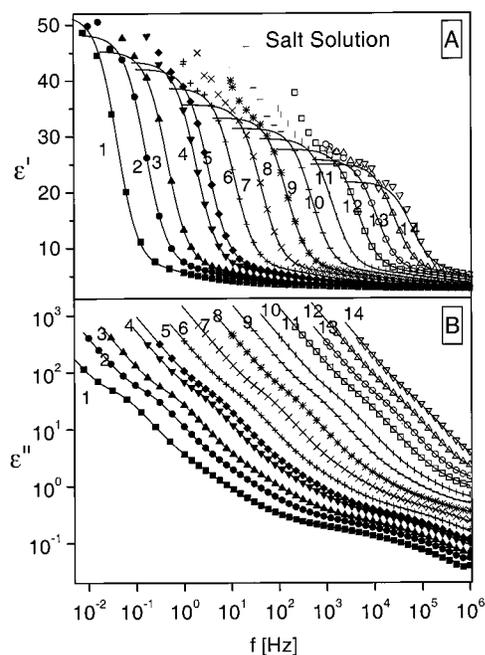
FIG. 2. The ϵ' (A) and ϵ'' (B) spectra of 1-propanol containing 1.0 mol % LiClO$_4$ recorded at selected temperatures and labeled as follows: (1) 107.0 K, (2) 109.7 K, (3) 112.2 K, (4) 114.4 K, (5) 117.6 K, (6) 118.9 K, (7) 122.2 K, (8) 126.0 K, (9) 130.0 K, (10) 134.2 K, (11) 138.1 K, (12) 143.2 K, (13) 147.5 K, (14) 152.5 K, and (15) 157.7 K. Solid lines are the composite fits to Eq. (1), symbols denote the experimental data. The discrepancy at low frequencies to ϵ' between the fits and the experimental data is due to the interfacial polarization at the electrodes (double layer effect) arising from the dc conductivity.

FIG. 3. The ϵ' (A) and ϵ'' (B) spectra of the fastest relaxation (process III) in pure 1-propanol (main plots) and 1-propanol containing 1.0 mol % LiClO$_4$ (insets), recorded at selected temperatures and labeled as follows: 1-propanol (main plots): (1) 88.6 K, (2) 91.7 K, (3) 93.9 K, (4) 95.9 K, (5) 97.8 K, (6) 99.5 K, and (7) 101.5 K. Salt solution (insets): (1) 92.1 K, (2) 94.3 K, (3) 97.4 K, (4) 99.7 K, (5) 102.5 K, (6) 104.4 K, (7) 107.4 K. Solid lines are the composite fits to Eq. (1), symbols denote the experimental data.

cess. The $(-j\sigma_0/\epsilon_0\omega)$ term accounts for loss at lower frequencies due to conduction by impurity or deliberately added ions. Equation (1) was fitted to the complex permittivity data using the WINFIT dielectric fitting program, as described earlier[9,16] and used by others.[7,17] It was found, in agreement with previous work, that three processes were required to fully represent the complex permittivity data for 1-propanol. The parameters of the Havriliak–Negami equation were extracted from the fits. The solid lines in Figs. 1–3 are the composite fits to Eq. (1), with three relaxation processes and the dc conductivity. In general the fits to the experimental data are excellent, except to ϵ' at low frequencies. The discrepancy at low frequencies between the fits and the experimental data of ϵ' is due to the interfacial polarization at the electrodes (double layer effect) arising from the relatively large dc conductivity. Fitting of process I of the solution data was consequently difficult as the low frequency side of the large loss peak is obscured by the ionic conductivity losses (the peak can still be seen as a shoulder). The fitting was made possible by assuming that this loss peak is approximately Debye-like, as in 1-propanol itself. As for the pure alcohol, three Havriliak–Negami terms were required to describe the spectra.

As an example, the resolution of the spectra of 1-propanol at 123.3 K and the solution at 124.0 K into several relaxation regions is shown in Figs. 4 and 5, respectively. The continuous lines in Figs. 4(A) and 4(B) are the curves calculated with the parameters, $\sigma_0 = 4.04$
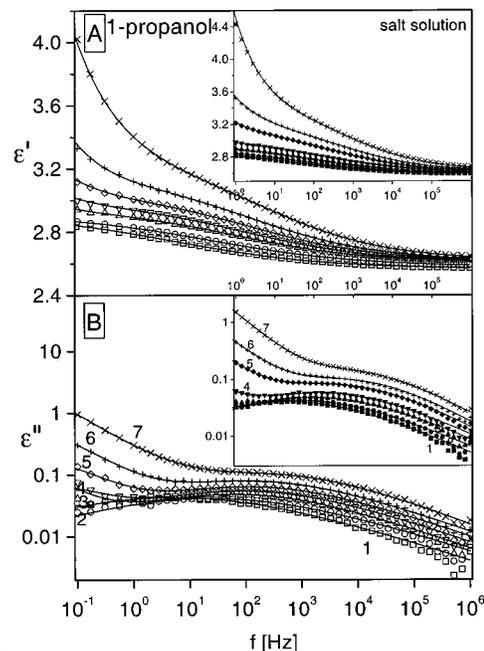
$\times 10^{-11}$ S m^{-1}, $\Delta\epsilon_I = 64.8$, $\alpha_I = 0.998$, $\beta_I = 0.999$, $\tau_I = 9.80$ ms, $\Delta\epsilon_{II} = 1.91$, $\alpha_{II} = 0.947$, $\beta_{II} = 0.502$, $\tau_{II} = 0.190$ ms, $\Delta\epsilon_{III} = 1.16$, $\alpha_{III} = 0.518$, $\beta_{III} = 0.851$, $\tau_{III} = 3.37$ μs for 1-propanol. Similarly, the continuous lines in Figs. 5(A) and 5(B) are the curves calculated with the parameters, $\sigma_0 = 3.84 \times 10^{-8}$ S m^{-1}, $\Delta\epsilon_I = 30.7$, $\alpha_I = 1.00$, $\beta_I = 0.970$, $\tau_I = 7.29$ ms, $\Delta\epsilon_{II} = 2.15$, $\alpha_{II} = 0.863$, $\beta_{II} = 0.581$, $\tau_{II} = 0.231$ ms, $\Delta\epsilon_{III} = 1.22$, $\alpha_{III} = 0.471$, $\beta_{III} = 1.00$, $\tau_{III} = 2.74$ μs for propanol containing 1.0 mol % LiClO$_4$.

Values of ϵ_s, of pure 1-propanol, and 1 mol % LiClO$_4$ containing 1-propanol were determined from the analysis of the spectra obtained at different temperatures. These are plotted against T in Fig. 6(A). The corresponding values of $\Delta\epsilon_I$ are plotted in Fig. 6(B), and similarly the corresponding values of $\Delta\epsilon_{II}$ and $\Delta\epsilon_{III}$ are plotted in Fig. 6(C). The quantity, $f_m (= 1/2\pi\tau_{max})$, i.e., the frequency of maximum dielectric loss, is used to examine the temperature dependence of dynamical processes. This was calculated using the usual equation:[7]

$$f_{m,I} = (2\pi\tau_{HNi})^{-1}\left[\sin\left(\frac{\alpha_i\pi}{2+2\beta_i}\right)\right]^{1/\alpha_i}\left[\sin\left(\frac{\alpha_i\beta_i\pi}{2+2\beta_i}\right)\right]^{-1/\alpha_i}.$$

(2)

We use it here as a measure of the average rate of dielectric relaxation. Its value for the three processes, I, II, and III for both pure 1-propanol; and 1 mol % LiClO$_4$ containing 1-propanol is plotted logarithmically against $1/T$ in Fig. 7. In this figure, lines are drawn for the Vogel–Fulcher–Tammann (VFT) equation according to $f_{m,I} = 10^{11.91}\exp[-1734/(T-52.68)]$ for 1-propanol, and $f_{m,I} = 10^{12.11}\exp[-1755/(T$
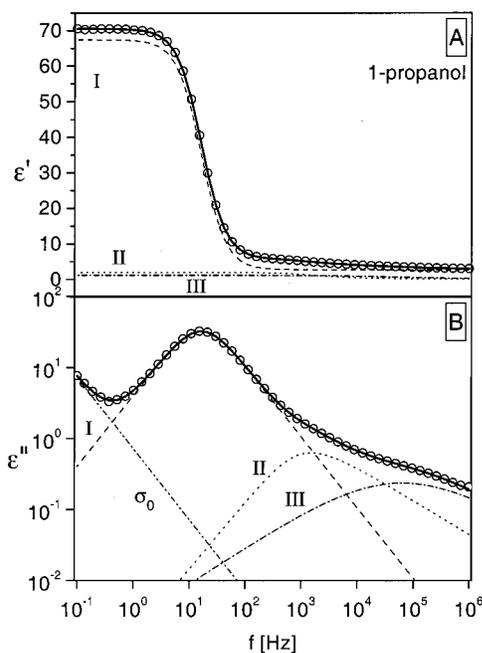
FIG. 4. Resolution of the ϵ' and ϵ'' spectra of 1-propanol at 123.3 K into their various components, as determined by nonlinear fitting to a three-term HN equation with dc conductivity included. The contributions from relaxation processes I, II, and III are shown together with contributions to ϵ'' arising from the dc conductivity. The thick lines are the sum of all components. The parameters used are: $\Delta\epsilon_I=64.8$, $\tau_I=9.80\times10^{-3}$ s, $\alpha_I=0.998$, $\beta_I=0.999$, $\Delta\epsilon_{II}=1.91$, $\tau_{II}=1.90\times10^{-4}$ s, $\alpha_{II}=0.947$, $\beta_{II}=0.502$, $\Delta\epsilon_{III}=1.52$, $\tau_{III}=3.37\times10^{-6}$ s, $\alpha_{III}=0.518$, $\beta_{III}=0.851$, $\sigma_0=4.04\times10^{-11}$ S m^{-1}. This is a demonstration of the fits at a given temperature for pure 1-propanol.

$-53.22)]$ for 1 mol % LiClO$_4$ containing 1-propanol. Because of the high sensitivity of $f_{m,I}$ to various terms in the above-given equations, the T values here and elsewhere are quoted to two decimal places.

Values of α_I and β_I for 1-propanol and for its solution are plotted against T in Fig. 8(A), those of α_{II} and β_{II} in Fig. 8(B), and those of α_{III} and β_{III} are plotted in Fig. 8(C). The Havriliak–Negami distribution parameter α refers to $(1-\alpha_{Cole–Cole})^{18}$ and β is the same as the Davidson–Cole skewed arc parameter, β.[4] This means here that in the limits when $\beta=1$ and $\alpha=1$, the relaxation process is of Debye-type,[19] when $\beta=1$ and $0<\alpha<1$, it is of the Cole–Cole[20] type, and when $\beta<1$ and $\alpha=1$, it is of the Davidson–Cole[4] type. For all values of $0<\beta<1$ and $0<\alpha<1$, the shape of the spectra is distorted from the shape of the above-given three types.

In Fig. 8(A), the parameters α_I and β_I remain constant at 1.0 for 1-propanol. For its 1 mol % LiClO$_4$ solution, α_I is still 1 and β_I is ~0.97. We conclude therefore that β_I for the LiClO$_4$ solution differs from 1.0 and hence the relaxation process I in the solution is of the Davidson–Cole[4] type. Since the values of α_{II} and β_{II} in Fig. 8(B) are on the average less than 1, these processes for both 1-propanol and its solutions have a combined distribution of the Cole–Cole[20] and Davidson–Cole[4] type, described by the Havriliak and Negami empirical equation.[15] α_{III} and β_{III}, shown in Fig. 8(C), also have a combined distribution in 1-propanol but generally follow a Cole–Cole[20] distribution in the solution.
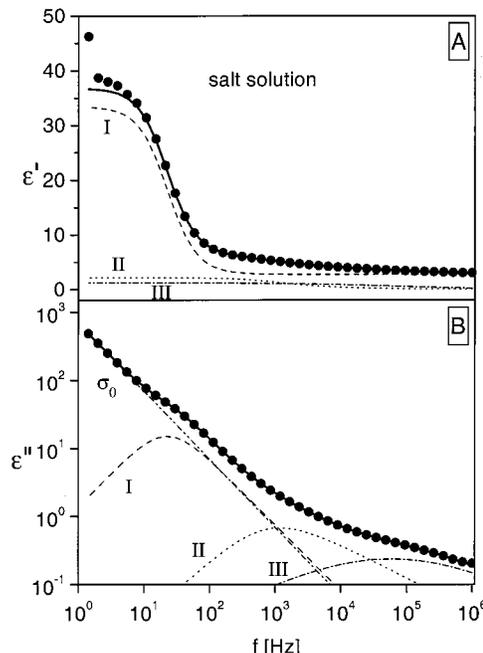

FIG. 5. Resolution of the ϵ' and ϵ'' spectra of 1-propanol containing 1.0 mol % LiClO$_4$ at 124.0 K into their components. This was performed in the same way as for pure 1-propanol (see Fig. 4). The parameters used are: $\Delta\epsilon_I=30.7$, $\tau_{II}=7.29\times10^{-3}$ s, $\alpha_I=1.00$, $\beta_I=0.970$, $\Delta\epsilon_{II}=2.15$, $\tau_{II}=2.31\times10^{-4}$ s, $\alpha_{II}=0.863$, $\beta_{II}=0.581$, $\Delta\epsilon_{III}=1.22$, $\tau_{III}=2.74\times10^{-6}$ s, $\alpha_{III}=0.471$, $\beta_{III}=1.00$, $\sigma_0=3.84\times10^{-8}$ S m^{-1}. This is a demonstration of the fits at a given temperature for the salt solutions.

IV. DISCUSSION

Our results for pure 1-propanol agree generally with those reported by Hansen et al.[7] The significance of its high equilibrium permittivity and of the individual contributions
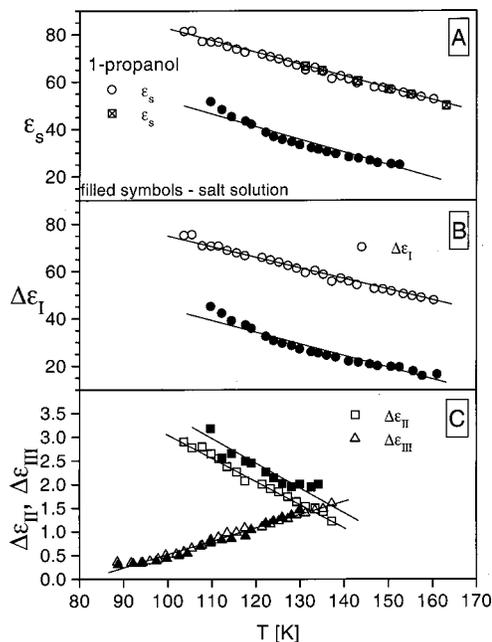

FIG. 6. Plots of ϵ_s (A), $\Delta\epsilon_I$ (B), and $\Delta\epsilon_{II}$ and $\Delta\epsilon_{III}$ (C) against the temperature for pure 1-propanol (open data points) and 1-propanol containing 1.0 mol % LiClO$_4$ (closed data points). Crossed squares are values of ϵ_s of 1-propanol at several temperatures from Denney and Ring (Ref. 5). Lines are a guide for the eye.
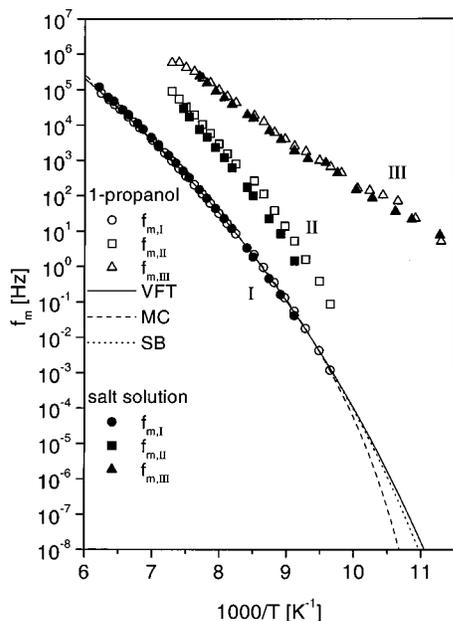
FIG. 7. Plots of $f_{m,I}$, $f_{m,II}$, and $f_{m,III}$ (on a logarithmic scale) against the inverse temperature in pure 1-propanol (open data points) and 1-propanol containing 1.0 mol % $LiClO_4$ (closed data points). To avoid confusion, the lines through the data points for $f_{m,I}$ only show the fits to the pure 1-propanol data according to the equations described in the text, as follows: solid line, Vogel–Fulcher–Tammann (VFT) [Eq. (6)], (– – –) mode-coupling (MC) [Eq. (8)], (···) Souletie–Bertrand (SB) [Eq. (9)]. Fits to the $f_{m,I}$ salt solution data have generally very similar parameters, as can be seen in Tables I and II.

to permittivity from the three relaxation processes has been discussed in an earlier study[10] where the effect of steric hindrance on ϵ_s was examined by replacing one H atom in the α-CH_2 group by the phenyl group. Therefore here only the
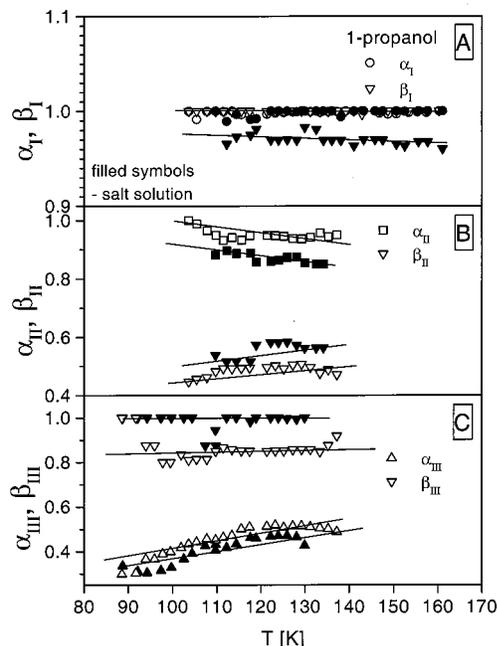

FIG. 8. Plots of α_I and β_I (A), of α_{II} and β_{II} (B) and of α_{III} and β_{III} (C) against the temperature for pure 1-propanol (open data points) and 1-propanol containing 1.0 mol % $LiClO_4$ (closed data points). Lines are guides for the eye.

ionic effects on ϵ_s will be examined. In Fig. 6, ϵ_s for 1-propanol is 72.4 at 117.5 K. In the presence of 1 mol % $LiClO_4$, its value decreases to 43.4 (at 117.6 K), i.e., it is reduced by ~40%. This reduction is a direct effect of the ions, which may form a complex with the OH group and/or break the intermolecular H bonds and thereby reduce ϵ_s. Here, $\Delta\epsilon_I$ decreases from 66.6 to 37.3 and $\Delta\epsilon_{II}$ and $\Delta\epsilon_{III}$ together increase by 0.2 units, the presence of ions decreases $\Delta\epsilon_I$ by 44% and increases the remaining orientational polarization by ~6%. This means that the dipolar orientational correlation factor, g, decreases by about ~44% at 117.5 K. Its magnitude is related to molecular dipole moment, density, and temperature by a statistical theory of dielectric polarization developed by Kirkwood,[1] Onsager,[2] and Fröhlich.[3] Accordingly,[21]

$$\Delta\epsilon = (\epsilon_s - \epsilon_\infty) = \left[\frac{3\epsilon_s}{2\epsilon_s + \epsilon_\infty}\right]\left(\frac{\epsilon_\infty + 2}{3}\right)^2 \frac{4\pi N_A \rho}{3k_B TM} g\mu_0^2, \quad (3)$$

where ϵ_∞ is the limiting high frequency permittivity of the orientation polarization associated with a certain relaxation process, N_A the Avogadro number, ρ is the density, M the molecular weight, k_B the Boltzmann constant, T the temperature, and μ_0 is the vapor phase dipole moment. The quantity g is equal to 1 when there is no intermolecular association and no correlation of dipole vectors. g is exactly defined as the sum of the dipole vectors of neighboring molecules.[1,3] When g is greater than unity, it indicates a predominantly parallel dipolar correlation. This occurs when the ROH molecules associate intermolecularly by H bonds and form linear chain structures. The significance of analysis in terms of g, albeit done in the form of a chemical equilibrium between H-bonded and non-H-bonded species, lies in both (i) the implication that (nonpermanent) linear chains of intermolecularly H-bonded structures may occur on the time average, and (ii) ring dimers form in the alcohol's structure leading to an ϵ_s value close to that of a nonpolar liquid at low temperatures. Both of these affect the relaxation characteristics of the liquid.

Equation (3) has been used earlier[4] to determine g of 1-propanol. For that purpose, the total value of $\Delta\epsilon(= \epsilon_s - \epsilon_\infty)$ in which ϵ_∞ had been taken as equal to $1.1n_D^2$, with n_D being the refractive index for the Na-D line (1.385) and the vapor phase dipole moment of 1.68 D was used for 1-propanol. It yielded $g = 4.3$ at 117.5 K. Addition of $LiClO_4$ alters the magnitude of the term ρ/M, and the value of ϵ_∞. It may increase ρ of 1-propanol by at most a few percent. It would also increase ϵ_∞ because the optical refractive index increases, and the infrared vibrational frequencies decrease. For 20 mol % $LiClO_4$ in glycerol, ϵ_∞ at 77 K has been found to increase from 2.77 to 4.21.[22] A similar increase would lower $\Delta\epsilon$ in the solution by at most ~2%. Thus the 40% decrease in ϵ_s on the addition of 1 mol % $LiClO_4$ is attributable to a decrease in g of 1-propanol. There is of course also an extrinsic effect of the ions, whose electric field alters the molecular arrangement near the ions.

The above-given analysis bears upon the conclusions regarding the mechanism of the first two relaxations, process I

and process II, in 1-propanol. It had appeared that its process I did not contribute to viscosity and structural relaxation, only its process II and possibly III did.[7] The latter two processes were attributed to the rotational–translational diffusion of unbonded molecules,[7] as in a molecular liquid with only the van der Waals type interactions, e.g., *ortho*-terphenyl, and these contributed to the transport property. In this study, these two processes are found to have total $\Delta\epsilon$ of 3.2 ($=2.1+1.1$) at 117.5 K, and addition of 1 mol % LiClO$_4$ increases it to 3.4 ($=2.5+0.9$). Now, if the $\Delta\epsilon$ value of 3.2 were due to the rotational diffusion of the unbonded 1-propanol molecules, then it is altered only marginally by the presence of ions, although $\Delta\epsilon_I$ decreases by ~44% and, as discussed previously, g decreases by 44%. The latter is an indication of the decrease in the extent of H-bond association. It has been concluded that process I in 1-propanol is not observable by Brillouin light scattering and photon correlation spectroscopy (see Ref. 7, p. 1090 for details), and therefore process I in 1-propanol may not be related to structural relaxation. But since this process has also been observed in LiClO$_4$ containing 1-propanol, where H-bond association is considerably decreased, and in 5-methyl-2-hexanol,[9] 1-phenyl-1-propanol,[10] and 1-phenyl-2-propanol,[11] Brillouin light scattering and photon correlation spectroscopy of these liquids would be required to test whether the behavior is typical of H-bonded alcohols.

A. The effects of ions on equilibrium permittivity

Dielectric behavior of ionic solutions is of some interest and needs to be discussed. In a continuum model of dielectrics, the presence of ions affects ϵ_s of a solvent. Also, the solubility of an electrolyte is more when the solvent's ϵ_s is high. There are exceptions, however, for certain electrolytes that dissolve readily in nonpolar solvents and remain as undissociated ion pairs. In turn, an electrolyte reduces ϵ_s of a dipolar solvent, even when there are no short-range intermolecular interactions that may alter the solvent's ϵ_s. As suggested by Debye and Hücker,[23] this may be seen as a positive deviation from Raoult's law. According to the Debye–Falkenhagen[24] dilute solution theory, ϵ_s of a solvent increases on the addition of ions. They provided a correction to ϵ_s of a solution. Hubbard and Onsager[25] have pointed out that the kinetic ion–solvent interaction affects the capacitive admittance in two closely related ways—first, as a result of polarization of molecules as an ion migrates, and second, the retardation in the development of an external electric field on an ion as a result of polarized molecules. This kinetic depolarization causes a decrease in ϵ_s of solution over that of the pure solvent by an amount that is proportional to the product of the dielectric relaxation time, τ_D, of the solvent and dc conductivity, σ_0, of the solution.[25] When the dielectric and viscosity relaxation times are comparable, the decrease in ϵ_s is most pronounced. The magnitude of this decrease is given by

$$\delta\epsilon_s = -2\pi(p+1)\left(\frac{\epsilon_s-\epsilon_\infty}{\epsilon_s}\right)\tau_D\sigma_0 - 4\pi\tau_{vis}\sigma_0, \qquad (4)$$

where $\delta\epsilon_s$ is the decrease in ϵ_s, τ_{vis} is the viscosity relaxation time, and the factor p depends upon the hydrodynamic

boundary conditions at the ion surface. The value of p is 1 for the sticking condition and 2/3 for the slip-condition. The theory is based on a continuum approximation for the solvent, and ignores any effects of ionic radius and chemical interaction between the ion and the solvent molecules. A revised version of the theory was provided by Hubbard *et al.*[26] and by Kusalik and Patey.[27] Winsor and Cole[28] have measured the decrease in permittivity of water on the addition of NaCl. They have found significant discrepancies between the calculated and measured values of ϵ_s. Our results here and elsewhere[14] show that the observed discrepancy in ϵ_s of water obtained by them may have been at least partly caused by the decrease in the value of g due to breaking of H bonds in water on the addition of ions.

B. The dielectric relaxation spectra

The slowest relaxation that contributes to the majority of orientational polarization in supercooled liquids[29–32] (and polymers[33]) is known as the α-relaxation process. This normally refers to the mechanism of translational and rotational diffusion of molecules, and their kinetic freezing on the time scale of an experiment causes a liquid's vitrification. The molecular motions involved in processes I, II, and III in 1-propanol have been discussed earlier,[4,7] as have the origins of similar processes observed in other alcohols.[9–11,34]

Hansen *et al.*[7] concluded that process II in 1-propanol, by virtue of its similarity in shape and temperature dependence to viscosity and light-scattering data, corresponds to the α process observed in other non-H-bonded liquids and is responsible for the structural relaxation. Process I was associated in some unclear way with rotational blocking of the breaking and reformation of H bonds and was not considered responsible for the structural relaxation. However, it may also be argued that the small dielectric strength of process II, and the small populations of molecules implied, makes it unlikely that it alone could be responsible for the structural relaxation.[9]

It is possible that process I in 1-propanol could correspond to the α-relaxation process observed in rigid molecular, non-H-bonded, supercooled liquids,[29–31] and this diffusion would contribute to its viscosity and its structural relaxation. The relaxation spectrum of this process in most liquids is broad, but here it is narrow, i.e., of the Debye type, and therefore seems anomalous and inconsistent with the usual models and theories of relaxation.[30,35–42] However, there is an alternative model by Anderson and Ullman,[43] which describes the conditions in which a Debye-type spectral shape or a Davidson–Cole or Cole–Cole type spectral shape may occur. In their fluctuating environment model, different conditions for the relative rates of structural relaxation and dipolar reorientation may produce either a single Debye-type process with a single relaxation time or a distribution of relaxation times. Briefly, if the dipole reorients slower than the surrounding relaxes, then the potential barriers are averaged and a single Debye type relaxation is observed. If the dipole reorients faster than the (molecular) environment of the dipole relaxes, i.e., the dielectric relaxation time is less than the structural relaxation time, the (dipolar) reorientation would physically occur in a potential energy

TABLE I. Values for the parameters obtained by fitting the four relaxation rate-temperature equations to the measured data for each of the three processes in 1-propanol. Data for process II are given in parentheses and those for process III are marked with an asterisk.

Model	Fitted function	A (Hz)	B (K), γ	T_0, T_c (K)
Arrhenius	$f_m = A_{ARR} \exp[-B/T]$	$10^{15.01}$*	2901*	$\cdots$
VFT	$f_m = A_{VFT} \exp[-B/(T-T_0)]$	$10^{11.91}$, ($10^{11.74}$)	1734, (1146)	52.68 (64.59)
Mode-coupling	$f_m = A_{mc}[(T-T_c)/T_c]^{\gamma}$	$10^{5.943}$	12.05	87.59
Souletie	$f_m = A_{SB}[(T-T_c)/T]^{\gamma}$	$10^{12.58}$	28.57	73.83

landscape which itself changes with the angular orientation of the dipole, without the need for cooperativity. Therefore, one would observe a distribution of relaxation times partly because of the angle-dependent barriers to reorientation and partly because different molecules would have different environments. This seems equivalent to the cage or free volume model for molecular relaxation, which is implicit in the Bueche[44] and the mode-coupling theory's[45] consideration of the problem, but only in terms of the structural relaxation. Its relevance here is that there is no unique shape for a liquid's dielectric spectra. Rather, it is determined by a set of conditions of environmental fluctuations and the dipolar reorientation.

If process I is in fact the α-relaxation, what then is process II? It is interesting to note that the relaxation rate of process II decreases (by 0.4 decades at 117.5 K) with the addition of the LiClO$_4$. It would seem that the presence of ions hinders this orientational process. This process has been identified with the rotation of the OR (where R is C$_3$H$_7$) group around the OH bond.[46] An argument in favor of this assignment, as opposed to the suggestion that it is a result of the orientation of unbonded propanol molecules, is that its relaxation amplitude, $\Delta\epsilon_{II}$, increases as the temperature is reduced [see Fig. 6(C)]. If this process were associated with the orientation of single unbonded molecules,[7] then it would be expected that $\Delta\epsilon_{II}$ would behave in the opposite manner and decrease as the temperature is reduced.

When its evolution at low temperatures is examined in Fig. 3, process III can be seen to be a separate broad peak or shoulder in the ϵ'' spectra of 1-propanol and the solution, and not a wing following a power law dependence. Process III increases in strength with temperature and the temperature dependence of its relaxation rate is Arrhenius. These are the characteristics of a relaxation associated with the localized motion of molecules, a Johari–Goldstein[29,30,47] β-relaxation process, as concluded previously for 1-propanol[7] and 5-methyl-2-hexanol.[9] The relaxation rate of process III is,

within experimental errors, unaffected by the addition of the LiClO$_4$. This may imply that the presence of ions does not alter the ''energy landscape'' picture in the supercooled liquid and glass, so as not to affect the dynamics of the Johari–Goldstein process.

C. Temperature-dependence of relaxation rates

As in the two earlier papers,[10,11] we consider three aspects of the temperature dependence of the relaxation dynamics, which continue to be a subject of debate[12,13] and are used to support one theory over the other. The detailed discussion has been given earlier,[10,11] and for that reason only a brief description and comparative analysis is needed here. First, the variation of f_m with T and its interpretation in terms of the configurational entropy theory[48] is written in the form

$$f_m = A_{AG} \exp(-z^* \Delta\mu / RT), \tag{5}$$

where z^* is the number of molecules forming a cooperatively re-arranging region, $\Delta\mu$, is ''... largely the energy barrier resisting the cooperative rearrangement per monomer segment,''[48] and R is the gas constant. The data in Fig. 7 can be described by the empirical Vogel–Fulcher–Tammann equation,[49–51]

$$f_m = A_{VFT} \exp[-B/(T-T_0)]. \tag{6}$$

As noted in Sec. III and Table I, $A_{VFT} = 10^{11.91}$ Hz, $B = 1734$ K, and $T_0 = 52.68$ K for pure 1-propanol. The corresponding values for its 1 mol % LiClO$_4$ solution are: $10^{12.11}$ Hz, 1755 K and 53.22 K (see Table II). As shown earlier,[52] the data may also be analyzed on the premise that the curved shape of the configurational entropy against T plot above T_g extrapolates to zero at T_0, where f_m also becomes formally zero, and that doing so does not imply that the configurational entropy of an equilibrium liquid in fact becomes zero at T_0. In this analysis, the preexponential term in Eq. (5) became identical to the preexponential term in Eq.

TABLE II. The relaxation rate-temperature fitting parameters for 1-propanol containing 1.0 mol % LiClO$_4$. As before the values are given according to process I, (process II), process III*.

Model	Fitted function	A (Hz)	B (K), γ	T_0, T_c (K)
Arrhenius	$f_m = A_{ARR} \exp[-B/T]$	$10^{15.05}$*	2942*	$\cdots$
VFT	$f_m = A_{VFT} \exp[-B/(T-T_0)]$	$10^{12.11}$, ($10^{12.43}$)	1755, (1314)	53.22 (63.00)
Mode-coupling	$f_m = A_{mc}[(T-T_c)/T_c]^{\gamma}$	$10^{6.314}$	11.55	90.36
Souletie	$f_m = A_{SB}[(T-T_c)/T]^{\gamma}$	$10^{12.73}$	28.15	75.15

J. Chem. Phys., Vol. 116, No. 10, 8 March 2002

Decoupling of ionic diffusion from dielectric relaxation   4199

(6). Without implying that the temperature T_0 has a thermodynamic significance, the identification of these terms[52] had led to: $\Delta\mu = 8.314B$ and $z^* = [T/(T - T_0)]$. By using the above-given values of B and T_0, we obtain, $\Delta\mu = 14.4$ kJ mol^{-1} and $z^*(T_g$ for $f_m = 10^{-4}$ Hz$) = 2.11$ for 1-propanol, and $\Delta\mu = 14.6$ kJ mol^{-1} and $z^*(T_g$ for $f_m = 10^{-4}$ Hz$) = 2.12$ for its 1 mol % LiClO$_4$ solution. These values may be compared against those for other alcohols as described in Ref. 10, which relies on the fact that a comparison between Eqs. (5) and (6) requires only the matching of the shapes of the plots of $\ln f_m$ against T at $T > T_g$ and that this matching has been done by using the available values of the parameters B and T_0. Therefore the estimates of z^* and $\Delta\mu$ depend sensitively on the values of B and T_0, which themselves in turn are obtained by using a relatively long extrapolation.

Dyre and co-workers[53,54] have preferred an alternative interpretation of the temperature dependence of relaxation rate in terms of a "shoving model."[54] Accordingly,

$$f_m = A_{\text{Dyre}} \exp(-G_\infty V_c / k_B T),\tag{7}$$

where G_∞ is the temperature-dependent shear modulus of a liquid and k_B the Boltzmann constant. A comparison of Eqs. (5) and (7) shows that $G_\infty V_c = z^* \Delta\mu$ when the quantities are represented in mole units. For 1-propanol at its T_g (or T for $f_m = 10^{-4}$ Hz), we calculated $z^*(T_g) = 2.11$ and $\Delta\mu = 14.4$ kJ mol^{-1} in the preceeding paragraph. This yields $G_\infty V_c = 30.4$ kJ mol^{-1}. Similarly, for its 1 mol % LiClO$_4$ solution, the values of $z^*(T_g) = 2.12$ and $\Delta\mu = 14.6$ kJ mol^{-1} calculated earlier here yield $G_\infty V_c = 31.0$ kJ mol^{-1}. The corresponding values calculated from recent data are 64.1 kJ mol^{-1} for 1-phenyl-1-propanol[10] and 50.6 kJ mol^{-1} for 5-methyl-2-hexanol.[9] These may be compared against the values for other liquids given earlier.[52]

Two more equations are currently used to fit the T dependence of f_m. The first is based on the mode-coupling theory,[55,56]

$$f_m = A_{\text{mc}}[(T - T_c)/T_c]^\gamma,\tag{8}$$

where A_{mc}, T_c, and γ are empirical parameters. The second is an empirical equation provided by Dissado and Hill,[57,58] namely, $f_m \sim (T - T_c)^\gamma$. These two equations admit to the same form, namely, that f_m varies as $(T - T_c)^\gamma$. But Souletie and Bertrand[59] have provided a somewhat different form,

$$f_m = A_{\text{SB}}[(T - T_c)/T]^\gamma,\tag{9}$$

where A_{SB}, T_c, and γ are also empirical constants. Equations (8) and (9) were fitted to the data for the relaxation rates, and the plots are shown in Fig. 5. For 1-propanol, the parameters used for the fitting are: $A_{\text{mc}} = 10^{5.943}$ Hz, $T_c = 87.59$ K, and $\gamma = 12.05$ for Eq. (8), and $A_{\text{SB}} = 10^{12.58}$ Hz, $T_c = 73.83$ K, and $\gamma = 28.57$ for Eq. (9). For its 1 mol % LiClO$_4$ solution, the parameters used for fitting are, $A_{\text{mc}} = 10^{6.314}$ Hz, $T_c = 90.36$ K, and $\gamma = 11.55$ for Eq. (8), and $A_{\text{SB}} = 10^{12.73}$ Hz, $T_c = 75.15$ K, and $\gamma = 28.15$ for Eq. (9). At first sight, the excellence of the fit seen in Fig. 7 would indicate that the theories on which Eqs. (8) and (9) are based are valid for 1-propanol and its 1 mol % LiClO$_4$ solution. However, according to these theories, the critical exponent γ
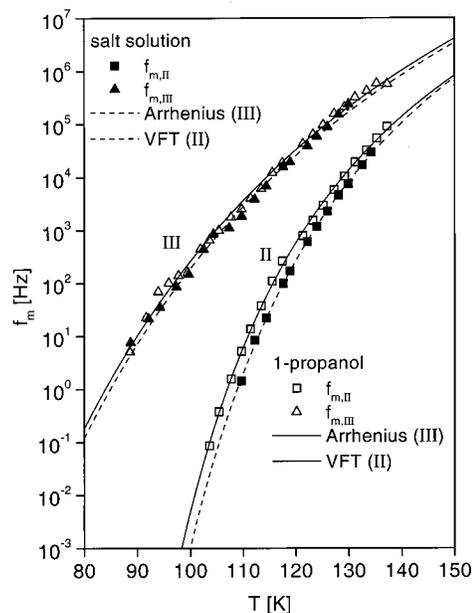

FIG. 9. Plots of $f_{m,\text{II}}$ and $f_{m,\text{III}}$ (on a logarithmic scale) against temperature in pure 1-propanol (open data points) and 1-propanol containing 1.0 mol % LiClO$_4$ (closed data points). Lines through the data points are fits of the Vogel–Fulcher–Tammann (VFT) equation (6) to process II and the Arrhenius equation to process III, as described in the text.

must be between 2 and 4, and usually the high temperature part of the curves is fitted to the mode-coupling theory and deviations occur at low temperatures. The values of γ observed here are evidently three to four times as high. It seems that in view of the requirement of the fits, no preference for one or other type of the power law equations can be made on the basis of the fits in Fig. 7.

This difference entails that the so-called energy landscape picture, which is currently being used for describing qualitatively the thermodynamics and molecular kinetics of supercooled liquids, would need to be revised. It also seems unsatisfactory to divide the entire temperature range in an *ad hoc* manner with the power laws obeying one range and the Vogel–Fulcher–Tammann equation the other.

The Vogel–Fulcher–Tammann equation (6) has also been fitted to process II, because although process II is not the α process, it is nevertheless governed by the vitrification process. The Arrhenius equation is fitted to process III. The fits to processes II and III are shown in Fig. 9. All of the parameters obtained for fitting of these equations to relaxation rate data for 1-propanol and its 1 mol % LiClO$_4$ solution are listed in Tables I and II, respectively, with the values for process II provided in brackets and those for process III marked with an asterisk.

D. Effects of ions on the relaxation time and the dc conductivity

We consider two more aspects of addition of ions on the relaxation kinetics of 1-propanol. Figure 7 has shown the effect of the ions on the relaxation rate. The similarity between the relaxation rate of 1-propanol and its 1 mol % LiClO$_4$ solution is remarkable in view of the fact that the
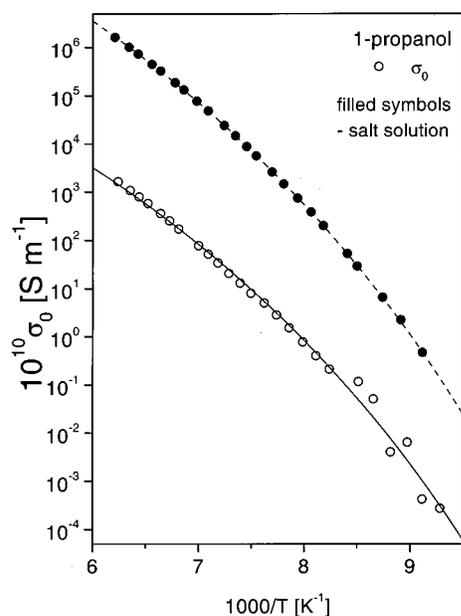
FIG. 10. Plots of the dc conductivity, σ_0 (on a logarithmic scale) against the inverse temperature for pure 1-propanol (open circles) and 1-propanol containing 1.0 mol % $LiClO_4$ (closed circles). The lines through the data points show the fit of the Vogel–Fulcher–Tammann equation (6) to both sets of conductivity data as described in the text.

extent of intermolecular H bonding that leads to a parallel correlation of dipoles in the former is reduced in the latter, as discussed earlier here. Figure 10 shows the effect on the dc conductivity, σ_0. It shows that σ_0 increases by about three orders of magnitude on the addition of 1 mol % $LiClO_4$. The values may be fitted to a Vogel–Fulcher–Tammann type equation for the dc conductivity in $S\,m^{-1}$: $\sigma_0(1-\text{propanol})$ $=10^{-1.129}\exp[-1285/(T-62.65)]$ and $\sigma_0(LiClO_4$ solution$)=10^{2.34}\exp[-1400/(T-61.66)]$. The dc conductivity, σ_0 is directly proportional to the population of the charge carriers and their mobility. In liquids, the mobility is inversely related to the viscosity according to the Stokes–Einstein equation. Thus, if no other effects were present, the ratio of σ_0 of 1-propanol to σ_0 of 1 mol % $LiClO_4$ solution would remain constant with changing temperature. The data in Fig. 8 show that this ratio increases with temperature (from ~250 at 117.5 K to ~1000 at 150.6 K). If the viscosity were to vary similarly in the two cases, this would imply that the number density of ions increases significantly with temperature. The relaxation rate itself is seen as proportional to the viscosity according to the Debye–Stokes–Einstein relation. But Rössler[60] has shown that this relation is inadequate for describing of the dynamics of supercooled liquids. However, discussion on the applicability of hydrodynamics has been continued by Hansen et al.,[61] who suggest that the dielectric relaxation time is proportional to the viscosity, η/T, and not proportional just to η, as suggested previously by Macedo and Litovitz.[62] Since T differs by usually no more than 50% in the extreme temperatures of measurements, the maximum difference arising from this revision would be a factor of 1.5. The Debye theory of dielectric relaxation and the Stokes–Einstein equation for hydrodynamics also of course relate the molecular volume, V_m, and η to its diffusivity, D_T or $f_{m,I}$ as follows: $D_T=kT/f\eta$ and $f_{m,I}$ $=kT/(2\pi V_m\eta)$ where f is a constant proportional to molecular size. Accordingly, the similarity of $f_{m,I}$ of 1-propanol and its 1 mol % $LiClO_4$ solution suggests that the ratio of the product, $V_m\eta$, of the two be equal to 1. Further it should remain so over the entire temperature range of the study, which it does. This would seem to be consistent with the relation provided by Hansen et al.[61] It also indicates that the glass-softening temperature, T_g, of 1-propanol and its 1 mol % solution are closely similar, if not identical.

V. CONCLUSION

Addition of Li^+ and ClO_4^- ions to 1-propanol causes no change in the relaxation rate and only a small change in the distribution parameters of its principal relaxation, although the dc conductivity increases ~1000-fold and ϵ_s decreases by ~56%, both at 150.6 K. The decrease in the permittivity is more than anticipated by the continuum theories[25–27] and is attributed to a decrease in the orientational correlation caused by intermolecular H bonds. This decrease is expected to decrease the viscosity of 1-propanol and thereby increase the dipolar relaxation rate. No increase was found in the relaxation rate of any of the three relaxation processes— indeed, that of process II decreased. Thus, either the relaxation rate is not related to the viscosity or the ion–dipole interaction in the solvation shell decreases the relaxation rate. The latter may be responsible for the observed decrease in the relaxation rate of process II. The spectra corresponding to the α-relaxation process contributes ~95% of the total polarization, and the spectra at different temperatures are superimposable. Process I is identified as the α-process and process II is assigned to the rotation of the $-OR$ group, where R in this case is C_3H_7. Both follow the Vogel–Fulcher– Tammann equation as both are intimately connected with the vitrification process. T_g at 10^{-4} Hz for process I is 100 K in pure 1-propanol and 100.5 K in the solution. It is 96.2 and 97.7 K for process II in the pure alcohol and solution, respectively. Process I is Debye and it is therefore concluded that a non-Debye process is not a prerequisite for the α-process. Process III can be separated, follows the Arrhenius equation, and persists below T_g. It is therefore assigned to the Johari–Goldstein process. We note however that assignments for the processes by Kudlik et al.[8] in pure 1-propanol are similar to those given by Hansen et al.[7]

A discussion in terms of the configurational entropy without implying an underlying thermodynamic transition in the equilibrium liquid below T_g led to a size of 2.11 molecules for the cooperatively rearranging region in 1-propanol at its T_g, and 14.4 $kJ\,mol^{-1}$ for the constant value of the potential energy barrier. In the solution, the cooperatively rearranging region size at T_g and the energy barrier were 2.12 molecules and 14.6 $kJ\,mol^{-1}$, respectively. The model[53–54] of Dyre et al. for a temperature-dependent Arrhenius energy leads to a set of parameters whose values can be estimated from the above-given values. However, uncertainty in the extrapolation of the parameters of the Vogel– Fulcher–Tammann equation may lead to an inconsistency in

the evaluated parameters. The power (or scaling) law based equations fit the data well, but the critical exponents for 1-propanol and its 1.0 mol % LiClO$_4$ solution were four times the value expected from these laws. This indicates that fitting of such power laws is ambiguous.

ACKNOWLEDGMENTS

[1] J. G. Kirkwood, J. Chem. Phys. **4**, 592 (1936).

[2] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

[3] H. Fröhlich, *Theory of Dielectrics*, 2nd ed. (Oxford University Press, Oxford, 1958).

[4] D. W. Davidson and R. H. Cole, J. Chem. Phys. **19**, 1484 (1951); **20**, 1389 (1952).

[5] D. J. Denney and J. W. Ring, J. Chem. Phys. **39**, 1268 (1963).

[6] S. K. Garg and C. P. Smyth, J. Phys. Chem. **69**, 1294 (1965).

[7] C. Hansen, F. Stickel, T. Berger, R. Richert, and E. W. Fischer, J. Chem. Phys. **107**, 1086 (1997).

[8] A. Kudlik, C. Tschirwitz, S. Benkhof, T. Blochowicz, and E. Rössler, Europhys. Lett. **40**, 649 (1997); J. Mol. Struct. (G.P. Johari special issue) **479**, 201 (1999).

[9] O. E. Kalinovskaya and J. K. Vij, J. Chem. Phys. **112**, 3262 (2000).

[10] G. P. Johari, O. E. Kalinovskaya, and J. K. Vij, J. Chem. Phys. **114**, 4634 (2001).

[11] O. E. Kalinovskaya, J. K. Vij, and G. P. Johari, J. Phys. Chem. A **105**, 5061 (2001).

[12] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, Contemp. Phys. **41**, 15 (2000).

[13] K. L. Ngai, J. Non-Cryst. Solids **275**, 7 (2000).

[14] K. Hofer and G. P. Johari, J. Chem. Phys. **95**, 2020 (1991).

[15] S. Havriliak, Jr. and S. Negami, Polymer **8**, 161 (1967); J. Polym. Sci., Part C: Polym. Symp. **14**, 89 (1966).

[16] O. E. Kalinovskaya and J. K. Vij, J. Chem. Phys. **111**, 10979 (1999).

[17] F. Stickel, E. W. Fischer, and R. Richert, J. Chem. Phys. **104**, 2043 (1996).

[18] U. Schneider, P. Lunkenheimer, R. Brand, and A. Loidl, J. Non-Cryst. Solids **235-237**, 173 (1998).

[19] P. Debye, *Polar Molecules* (Chemical Catalog, New York, 1929).

[20] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

[21] For a detailed analysis, see B. K. P. Scaife, *Principles of Dielectrics* (Clarendon, Oxford, 1998), p. 200.

[22] G. Astl, R. K. Chan, and G. P. Johari, J. Chem. Soc., Faraday Trans. **88**, 3053 (1992).

[23] P. Debye and E. Hückel, Phys. Z. **24**, 49 (1923); **24**, 185 (1923); **24**, 305 (1923).

[24] H. Falkenhagen, *Electrolytes* (Oxford University Press, London, 1934), Chap. IX.

[25] J. Hubbard and L. Onsager, J. Chem. Phys. **67**, 4850 (1977).

[26] J. B. Hubbard, P. Colonomos, and P. G. Wolynes, J. Chem. Phys. **71**, 2652 (1979).

[27] P. G. Kusalik and G. N. Patey, J. Chem. Phys. **79**, 4468 (1983).

[28] P. Winsor and R. H. Cole, J. Phys. Chem. **89**, 3775 (1985).

[29] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).

[30] G. P. Johari, J. Chem. Phys. **58**, 1766 (1973).

[31] C. J. Reid and J. K. Vij, J. Chem. Phys. **79**, 4624 (1983).

[32] G. P. Johari and W. Dannhauser, J. Chem. Phys. **50**, 1862 (1969).

[33] N. G. McCrum, B. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley, New York, 1967).

[34] F. X. Hassion and R. H. Cole, J. Chem. Phys. **23**, 1756 (1955).

[35] S. H. Glarum, J. Chem. Phys. **33**, 1371 (1960).

[36] S. Kahle, M. Schulz, and E. Donth, J. Non-Cryst. Solids **238**, 234 (1998).

[37] K. L. Ngai and R. W. Rendell, in *Supercooled Liquids, Advances and Novel Applications*, edited by J. T. Fourkas, D. Kivelson, U. Mohanty, and K. A. Nelson [ACS Symp. Ser. **676**, 45 (1997)].

[38] K. Schmidt-Rohr and H. W. Spiess, Phys. Rev. Lett. **66**, 3020 (1991).

[39] M. T. Cicerone, F. R. Blackburn, and M. D. Ediger, J. Chem. Phys. **102**, 471 (1995).

[40] C. K. Majumdar, Solid State Commun. **9**, 1087 (1971).

[41] J. T. Bendler and M. F. Schlesinger, Macromolecules **18**, 591 (1985).

[42] B. Scheiner, R. Böhmer, A. Loidl, and R. V. Chamberlin, Science **274**, 752 (1996).

[43] J. E. Anderson and R. Ullman, J. Chem. Phys. **47**, 2178 (1967).

[44] F. Bueche, J. Chem. Phys. **30**, 748 (1959).

[45] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).

[46] W. Dannhauser, J. Chem. Phys. **48**, 1918 (1968).

[47] U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, Phys. Rev. Lett. **84**, 5560 (2000).

[48] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).

[49] H. Vogel, Phys. Z. **22**, 645 (1921).

[50] G. S. Fulcher, J. Am. Ceram. Soc. **8**, 339 (1923).

[51] G. Tammann and W. Hesse, Z. Anorg. Allg. Chem. **156**, 245 (1926).

[52] G. P. Johari, J. Chem. Phys. **112**, 8958 (2000). [As mentioned in Refs. 10 and 11, the $\Delta\mu$ values for 2-methyltetrahydrofuran, *o*-terphenyl, *dextro-levo*, propylene carbonate, 3-bromopentane, *n*-propanol, and salol in Table II should be multiplied by 2.3026 in order to make them comparable with the form of the Vogel–Fulcher–Tammann equation as used here. The error occurred from notation *B* (in citations 9 and 27 in Table II—Ref. 48) which had been mistakenly obtained by using $\log_{10}$ instead of $\log_e$ in the Vogel–Fulcher–Tammann equation.]

[53] J. C. Dyre, N. B. Olsen, and T. Christensen, Phys. Rev. B **53**, 2171 (1996).

[54] J. C. Dyre, J. Non-Cryst. Solids **235-237**, 142 (1998).

[55] E. Leutheuser, Z. Phys. B: Condens. Matter **55**, 235 (1984); Phys. Rev. A **29**, 2765 (1984).

[56] U. Bengtzeleus, W. Götze, and A. Sjögren, J. Phys. C **17**, 5915 (1984).

[57] R. M. Hill and L. M. Dissado, J. Phys. C **15**, 5171 (1982).

[58] M. Shablakh, R. M. Hill, and L. M. Dissado, J. Chem. Soc., Faraday Trans. 2 **78**, 625 (1982); **78**, 639 (1982).

[59] J. Souletie and D. Bertrand, J. Phys. I **1**, 1627 (1991).

[60] E. Rössler, Phys. Rev. Lett. **65**, 1595 (1990).

[61] C. Hansen, F. Stickel, R. Richert, and E. W. Fischer, J. Chem. Phys. **108**, 6408 (1998).

[62] P. B. Macedo and T. A. Litovitz, J. Chem. Phys. **42**, 245 (1965).