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Mechanism of the Major Orientation Polarization in Alcohols, and the Effects of Steric Hindrance-, and Dilution-Induced Decrease on H-Bonding

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To gain insight into the effects of intermolecular H-bond association on the changes in permittivity and relaxation characteristics of supercooled alcohols, two techniques were used here: (i) introducing a C_6H_5 group in 2-propanol to obtain 1-phenyl-2-propanol, and thus increasing the steric hindrance to H-bonding, and (ii) dissolving the latter in 2-methylpentane and thus decreasing the extent of H-bonding by separating molecules in a nonpolar solvent. Broad-band dielectric spectroscopy studies of supercooled liquid 1-phenyl-2-propanol and its 1:1 (mol:mol) mixture in 2-methylpentane were performed over the 188−238 K range. These show that ∼94% of the total polarization decays according to the Davidson−Cole distribution of relaxation times and that the equilibrium permittivity decreases when phenyl group is substituted in 2-propanol. Analysis in terms of the statistical theories of dielectric behavior shows that the decrease is due to a decrease in the orientation correlation factor, and that this also occurs in the mixture with 2-methylpentane. The induced steric hindrance reduces the extent of intermolecular H-bonding in comparison with that of 2-propanol. The relaxation rate follows the non-Arrhenius temperature dependence. It has been examined qualitatively in terms of the Dyre theory which considers that the apparent Arrhenius energy itself is temperature-dependent, as in the classical interpretations, and quantitatively in terms of the cooperatively rearranging region's size, without implying that there is an underlying thermodynamic transition in its equilibrium liquid. The relaxation rate also fits the power law with the critical exponent of 14.52 for 1-phenyl-2-propanol and 12.9 for the mixture, instead of 2 to 4, usually required by the mode-coupling theory. This indicates the ambiguity of the power-law equations. The excess dielectric loss observed at high frequencies may indicate Nagle's "wing", or else a merged Johari−Goldstein relaxation.

Introduction

The exponential decay of orientation polarization by a single relaxation process in a supercooled liquid is regarded as incompatible with the mathematical models of molecular dynamics in supercooled liquids and their vitrification. This subject has been comprehensively and critically reviewed recently by Lunkenheimer et al.[1] and by Ngai.[2] They[1,2] have described the dielectric features of supercooled liquids, limitations of the interpretations of the data obtained in the different regions of the relaxation and resonance spectra and the data's significance itself for understanding the molecular dynamics of liquids in general. Yet, dielectric studies of certain aliphatic amides[3,4] and alcohols[5−11] and one secondary alcohol[12] have shown that a major fraction of their orientation polarization decays exponentially, in a Debye-type manner.[13] The temperature dependence of the relaxation rate in some cases remains Arrhenius over 4−6 decades,[3,4,9] although in most cases it has been found to be non-Arrhenius. To maintain consistency with the available models for a supercooled liquid's molecular dynamics,[1,2] the observed Debye-type relaxation has been seen as extrinsic to its vitrification. For example, it has been concluded that the Debye-type process in 1-propanol, which relaxes ∼95.5% of its orientational polarization at 119.7 K, is not likely to be associated with its structural relaxation.[10] This means that the molecular diffusion that contributes only ∼4.5% to its total polarization is able to control its viscosity-determining structural relaxation. This conclusion has been critically examined elsewhere, where the dielectric study of 5-methyl-2-hexanol,[12] also showed that the Debye-type relaxation contributes ∼97% to the static permittivity ϵ_s in remarkable similarity to the findings for 1-propanol. But, contrary to the interpretation of the Debye-type relaxation in 1-propanol,[10] the corresponding relaxation in 5-methyl-2-hexanol[12] was interpreted as a first-order rate process of H-bond breaking and reforming, which controlled the rate of orientation polarization. It had been further argued that if the Debye type relaxation did not contribute to the orientation polarization of 1-propanol and only less than 3% of the total number of molecules contributed to its structural-relaxation-determining α-relaxation process, then there is a difficulty in understanding how the orientational diffusion of this small population of molecules alone can be responsible for its supercooled liquid's structural relaxation and viscosity. This issue has been subsequently examined by a detailed dielectric relaxation study of supercooled liquid and glassy states of 1-phenyl-1-propanol,[14] $C_2H_5\,CH(C_6H_5)OH$, a molecule in which one H atom in the CH_2OH group of 1-propanol ($C_2H_5CH_2OH$) had been replaced by the phenyl group, thus converting it to a secondary alcohol. This introduced a steric hindrance to intermolecular H-bonding via the OH group without significantly affecting the net dipole moment. Moreover, 1-phenyl-1-propanol

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molecule contains an asymmetric carbon atom and therefore exists in the *dextro*-, and *levo*-forms, which also makes the formation of intermolecularly H-bonded chains between the two species difficult. Its dielectric relaxation spectra showed a Davidson−Cole type distribution of times,[5] rather than the Debye-type single relaxation time.[13]

Steric hindrance to H-bonding in 1-phenyl-1-propanol can be reduced by increasing the distance between the C_6H_5 group and the OH group within the molecule, which can increase the probability of intermolecular H-bonding. This would occur in 1-phenyl-2-propanol, where the OH group is attached to the second C atom and the C_6H_5 group remains at the first C atom, i.e., in this molecule the phenyl group substitutes an H atom on the terminal C atom of the 2-propanol molecule. As in 1-phenyl-1-propanol, *dextro*- and *levo*- forms may also exist for 1-phenyl-2-propanol, in which the second C atom (instead of the first in 1-phenyl-1-propanol) becomes asymmetric, and these may influence the intermolecular H-bonding. (It is worth noting that such designs of alcohol molecule isomers were used as a technique for studying the nature of intermolecular and intramolecular H-bonding during the 1960s[9,15−22] and 1970s,[23−28] albeit with limited frequency range for the dielectric measurements then possible with manually operated equipment.) Here we report on a detailed study of its dielectric spectra over a broad frequency and temperature range in both the supercooled liquid and vitrified states. Johari and Dannhauser[22] had performed a dielectric study of supercooled liquid 1-phenyl-2-propanol over a limited frequency and temperature range, and had analyzed its dielectric spectra in terms of both: (i) a sum of Debye-type process plus a small, unanalyzable relaxation and (ii) a Davidson−Cole relaxation process, or a skewed arc function.[5] Its ϵ_s was interpreted in terms of the formation of H-bonded linear chains which increased its dipolar orientational correlation factor g[29] from 1 to ∼1.4. They also studied the effects of hydrostatic pressure on its density and viscosity[30] at different temperatures.

When mixed with a nonpolar solvent, intermolecular H-bonding is considerably reduced if the alcohol molecules do not form clusters large enough to undergo phase-separation. If ϵ_s of the solution is found not to be in proportion to the alcohols concentration, then in the pure alcohol intermolecular H-bonding must have existed. If ϵ_s is less than that expected then a predominantly parallel correlation of the dipole vectors would have been present in the alcohol. But, if it is found to be more than that expected, a predominantly antiparallel correlation of the dipole vectors would have been present in the alcohols. Here we also use the solution study to investigate the state of H-bonding in 1-phenyl-2-propanol from measurements of its dielectric properties in a nonpolar solvent, 2-methylpentane.

Experimental Methods

1-Phenyl-2-propanol was purchased from Chemical Sample Company, Ohio, by W. Dannhauser in 1967 for dielectric relaxation[21,22] and viscosity studies under high pressures.[30] It was refluxed with CaH_2 in order to remove any moisture, and fractionally distilled in a vacuum. The middle fraction was collected for the dielectric and viscosity measurements. The left-over middle fraction sample, which had been stored in a hermetically sealed container for 22 years, was redistilled in a vacuum and studied here. (We are grateful to Professor Dannhauser (now retired) for donating to GPJ all samples of alcohols he and co-workers had studied in the 1960s and 1970s.) 2-Methylpentane of 99% +purity was purchased from Aldrich Chemicals, and was used as such. The solution of 1-phenyl-2-propanol in 2-methylpentane was prepared by weighing, kept in a sealed container, and studied immediately after its preparation. The dielectric cell used was a miniature, tunable parallel plate capacitor containing 18 plates, with an air capacitance of nominally 26.7 pF. (This commercially available capacitor has inconsequential amount of stray capacitance and seems superior to the two parallel plates separated by spacers used successfully up to 1 MHz frequency range by several groups. Its easy availability at low cost has been invaluable in studying dielectrically the growth of macromolecules in real time,[31−33] in which a capacitor cannot be reused.) 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 CF 1200, purchased from Oxford Instruments. Instead of preprogramming the cryostat, the temperature was controlled to within 50 mK at the desired value by its manual setting and up to a period of over 24 h needed for measurements at the lowest frequencies. The dielectric permittivity ϵ' and loss ϵ'' were measured over the frequency range, 1 mHz to 1 MHz by means of a Solartron FRA-1255A frequency response analyzer. The detailed procedure has been described earlier.[12,34]

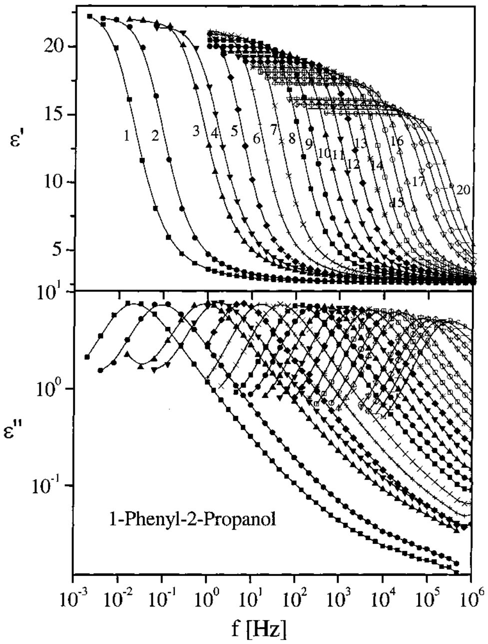

Figure 1. The ϵ' and ϵ'' spectra of supercooled liquid 1-phenyl-2-propanol at several temperatures. The curves are labeled as (1) 198.74 K, (2) 200.43 K, (3) 202.57 K, (4) 203.72 K, (5) 207.61 K, (6) 209.49 K, (7) 211.56 K, (8) 213.82 K, (9) 215.46 K, (10) 217.31 K, (11) 219.42 K, (12) 221.34 K and (13) 223.51 K, (14) 225.4 K, (15) 227.58 K, (16) 229.68 K, (17) 232.29 K, (18) 234.29 K, (19) 236.21 K, and (20) 238.23 K. Uncertainty in the temperature is 0.05 K.

Results and Analysis

Figure 1 shows the ϵ' and ϵ'' spectra of supercooled liquid 1-phenyl-2 propanol and Figure 2 those of its solution in 2-methylpentane at selected temperatures T. The ϵ'' spectra of both show no clear evolution of a shoulder on the high-frequency side of the ϵ'' peak which could be attributed to a second relaxation process. Therefore, at first sight it seemed that there is only one spectrally broad relaxation process in 1-phenyl-2 propanol and in its solution, as was initially assumed to be the case in glycerol[1] and propylene carbonate.[1] The dielectric spectra were analyzed by using the fitting algorithm as described earlier[12,34] and used by others.[10,35]

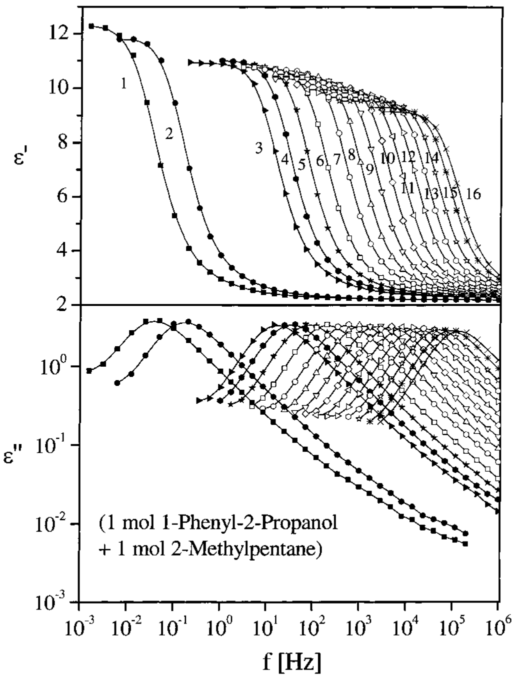

Figure 2. The ϵ' and ϵ'' spectra of supercooled liquid 1:1 (mol/mol) mixture of 1-phenyl-2-propanol and 2-methylpenatne at several temperatures. The curves are labeled as (1) 188.38 K, (2) 190.53 K, (3) 197.96 K, (4) 199.27 K, (5) 201.2 K, (6) 203.19 K, (7) 205.47 K, (8) 207.38 K, (9) 209.37 K, (10) 211.38 K, (11) 213.38 K, and (12) 215.41 K and (13) 217.38 K, (14) 219.38 K, (15) 221.72 K and (16) 223.49 K. Uncertainty in the temperature is 0.05 K.

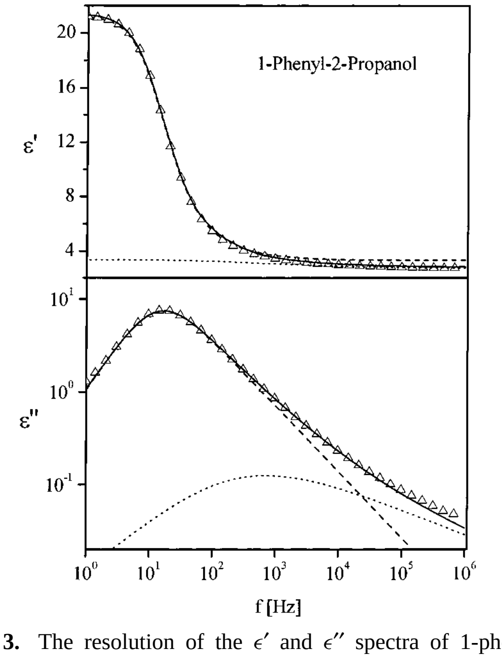

Figure 3. The resolution of the ϵ' and ϵ'' spectra of 1-phenyl-2-propanol at 209.49 K. The parameters used for the calculations are given in the text.

To elaborate how the relaxation spectra were resolved into several relaxation regions, the ϵ'' spectra of 1-phenyl-2-propanol at 209.5 K and of its 1:1 solution in 2-methylpentane at 199.3 K are shown in Figures 3 and 4, respectively. The continuous line in Figure 3 is the curve calculated with the parameters, $\Delta\epsilon_1 = 17.96$, $\alpha_1 = 0.986$, $\beta_1 = 0.723$, $\tau_{\mathrm{HN},1} = 12.63$ ms, $\Delta\epsilon_2 = 0.708$, $\alpha_2 = 0.57$, $\beta_2 = 0.48$, and $\tau_{\mathrm{HN},2} = 0.73$ ms for 1-phenyl-2-propanol and that in Figure 4 with the parameters, $\Delta\epsilon_1 = 8.6$, $\alpha_1 = 0.993$, $\beta_1 = 0.65$, $\tau_{\mathrm{HN},1} = 6.64$ ms, $\Delta\epsilon_2 = 0.15$, $\alpha_2 = 0.51$, $\beta_2 = 0.50$, and $\tau_{\mathrm{HN},2} = 0.0896$ ms for its mixture in 2-methylpentane. The highest frequency relaxation process could not be resolved owing to the exceedingly small values of its ϵ''contribution and the experimental errors. For brevity, the resolved spectra of ϵ' is partly shown here. The resolved shapes of the ϵ'-spectra are similar to the shapes described earlier.[14,34] Because of the low values of $\Delta\epsilon_2$ for both 1-phenyl-2-propanol and its solution, reliable values of $\Delta\epsilon_2$, α_2, β_2, and $\tau_{\mathrm{HN},2}$ could not be determined as a function of temperature. The situation was complicated by the fact that $\Delta\epsilon_2$ decreased rapidly with decreasing T. Therefore, values of these parameters are excluded from discussion here.

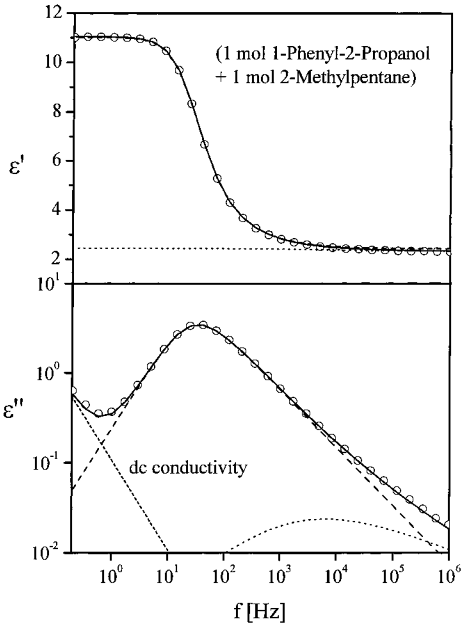

Figure 4. The resolution of the ϵ' and ϵ'' spectra of 1:1 mixture of 1-phenyl-2-propanol and 2-methylpentane at 199.27 K. The parameters used for the calculations are given in the text.

The values of the equilibrium permittivity, ϵ_s, of 1-phenyl-2-propanol, and of its 1:1 mixture with 2-methylpentane were obtained from an analysis of the spectra shown in Figures 1 and 2. These are plotted against T in Figure 5, where ϵ_s of 1-phenyl-1-propanol taken from our earlier study is also plotted for comparison. The ϵ_s of 1-phenyl-2-propanol is less than the value extrapolated from the data reported earlier[22] at low temperatures, but is consistent with the values at high temperatures.

The values of $\Delta\epsilon_1$, α_1, and β_1 for 1-phenyl-2-propanol and for its solution are plotted against T in Figure 6. It should be mentioned that the notations for the α in this computation refers to (1- $\alpha_{\mathrm{Cole-Cole}}$)[36] and β is the same as the Davidson−Cole skewed arc parameter, β.[5] This means that in the limits here when $\beta = 1$ and $\alpha = 1$, the relaxation is Debye-type, when $\beta = 1$ and $0 < \alpha < 1$, the relaxation is of the Cole−Cole type, and when $\beta < 1$ and $\alpha = 1$, it is the Davidson−Cole type.[5] 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 Figure 6, the quantity α_1 remains constant at 0.98 ± 0.01 for 1-phenyl-2-propanol, and at 0.995 for its solution. These values may be seen as close to 1, i.e., the distribution may be regarded as the Davidson−Cole type.[5] Nevertheless, it should also be pointed out that at the limiting low frequencies, the ϵ' and ϵ'' values often contain contributions from the dc conductivity, σ_{dc}, and interfacial polarization, as has been discussed in Appendix of ref 31. This tends to broaden the spectra at the low-frequency side enough to be fitted by the Havriliak and

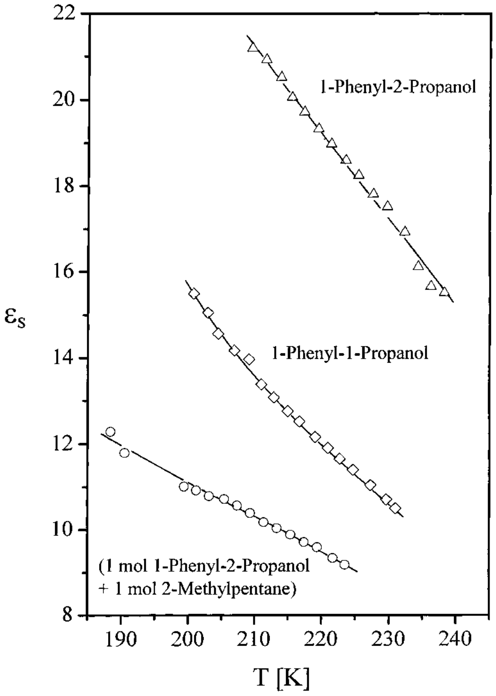

Figure 5. The equilibrium permittivity ϵ_s for 1-phenyl-2-propanol, 1:1 mixture of 1-phenyl-2-propanol and 2-methylpentane, and 1-phenyl-1-propanol[14] are plotted against the temperature.

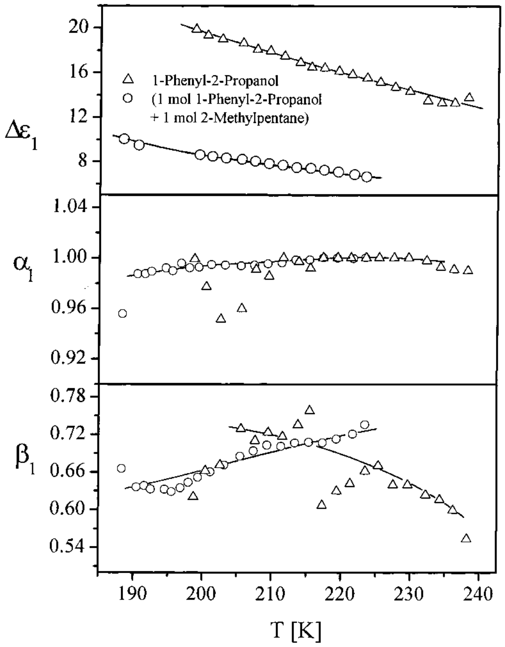

Figure 6. Top part: Plots of $\Delta\epsilon_1$ of 1-phenyl-2-propanol and of 1:1 mixture of 1-phenyl-2-propanol and 2-methylpentane against the temperature. Middle part: the corresponding plots of the parameter α_1. Bottom part: The corresponding plots of the parameters β_1.

Negami's[37] empirical combination of the Cole−Cole and the Davidson−Cole equations, which is an alternative to the original data analysis for polymers described in ref 38, as used here and in refs 10 and 35.

The shape of the measured ϵ' and ϵ'' spectra at the high-frequency side may become modified when the rates of the two relaxation processes are close to each other and/or when the contributions from the two processes are comparable. From a recent study of several supercooled liquids, Olsen et al.[39] have shown that when T is such that the α-relaxation and Johari−Goldstein relaxation[40,41] processes are widely separated, the normalized ϵ'' spectra, (i.e., after dividing the ϵ'' values by the ϵ'' peak height), superimpose satisfactorily well. That this is also the case here is indicated by the nearly constant values of the α_1 and β_1 for 1-phenyl-2-propanol and for its solution in 2-methylpentane as seen in Figure 6. A similar occurrence had been found earlier for some molecular liquids at 1 bar pressure.[40,41] Application of hydrostatic pressure has been found to broaden considerably the spectra for 1-phenyl-1-propanol[21] and glycerol.[42]

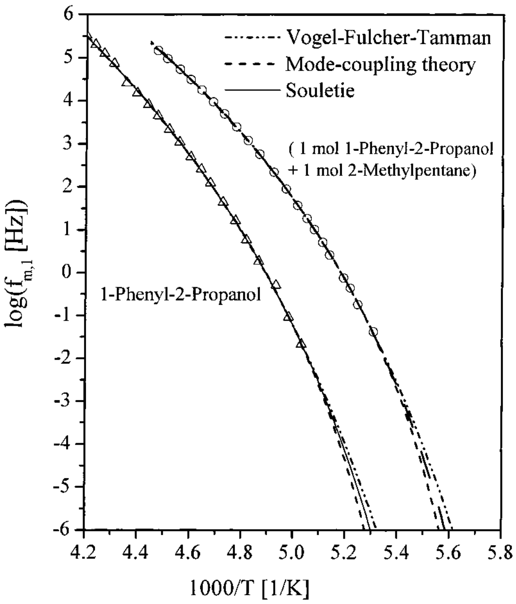

Figure 7. The ϵ'' peak frequency for 1-phenyl-2-propanol and 1:1 mixture of 1-phenyl-2-propanol and 2-methylpentane are plotted against the reciprocal temperature. The plots also show a comparison of the fits of the Vogel−Fulcher−Tamman equation, $f_m = 10^{14.88}\exp[-1984.54/(T - 146.55)]$; power law equation, $f_m = 10^{12.64}[(T - 180.11)/180.11]^{14.52}$; and the Souletie−Bertrand equation, $f_m = 10^{17.61}[(T - 173.97)/T]^{21.3}$ for 1-phenyl-2-propanol. The corresponding equations for the 1:1 mixture of 1-phenyl-2-propanol and 2-methylpentane are $f_m = 10^{13.27}\exp[-1458.95/(T - 145.21)]$; power law equation, $f_m = 10^{12.1}[(T - 172.96)/172.96]^{12.9}$; and the Souletie−Bertrand equation, $f_m = 10^{16.14}[(T - 168.53)/T]^{17.98}$

The quantity, f_m ($= {}^1/_{2\pi\tau_{\max}}$), has been deemed as suitable for delineating the temperature dependence of dynamical processes, and we use it here as a measure of the average rate of dielectric relaxation. Its value for the main relaxation processes in both 1-phenyl-2-propanol and its mixture with 2-methylpentane is plotted logarithmically against $1/T$ in Figure 7. The $f_{m,1}$ data for 1-phenyl-2-propanol are described satisfactorily by the equation, $f_{m,1} = 10^{14.88}\exp[-1984.54/(T - 146.55)]$, and that for its 2-methylpentane mixture by the equation, $f_{m,1} = 10^{13.27}\exp[-1458.95/(T - 145.21)]$. (Because of the high sensitivity of $f_{m,1}$ to various terms the values here and elsewhere are quoted to two decimal places.)

Discussion

Effect of Steric Hindrance on Equilibrium Permittivity. We first consider how change in the steric hindrance to OH group affects the orientation polarization of a monohydroxy alcohol, as determined from its equilibrium permittivity ϵ_s. In Figure 5, ϵ_s for 1-phenyl-2-propanol is 20.9 at 211.56 K, which is ~1.5 times the value of 13.4 for 1-phenyl-1-propanol at 210.96 K,[14] and 0.58 times the ϵ_s value of 36.0 for 1-propanol interpolated at 211.5 K.[43] Since the steric hindrance is highest for 1-phenyl-1-propanol, and lowest for 1-propanol, it follows that ϵ_s of the alcohols decreases when the steric hindrance to the −OH group is increased by changing the molecular constitution and ϵ_s (1-propanol) > ϵ_s (1-phenyl-2-propanol) > ϵ_s (1-phenyl-1-propanol).

The ϵ_s value of 1-phenyl-2-propanol may be compared also directly with that of 2-propanol. As calculated from the parameters provided by Hassion and Cole,[6] ϵ_s of 2-propanol is 36.1 at 211.6 K, which is comparable with the ϵ_s of ~36.0 for 1-propanol.[5] Thus, ϵ_s of 20.9 for 1-phenyl-2-propanol is again 0.58-times the value for 2-propanol. The magnitude of $\Delta\epsilon_1$ for the former is 17.5 and for the latter is 33.5. This seems to be a direct effect of an increase in the steric hindrance to the OH group on the equilibrium polarizability of an alcohol. It also implies a considerable decrease in the dipolar orientational correlation, owing to the formation of intermolecular H-bonds, in 1-phenyl-2-propanol over that in 2-propanol (and 1-propanol) and in 1-phenyl-1-propanol over that in 1-phenyl-2-propanol.

The extent of H-bonds and other interactions that tend to align the dipole vectors in a parallel or antiparallel manner may be determined from the magnitude of the contribution to permittivity $\Delta\epsilon$ from a relaxation process. This contribution is related to molecular dipole moment, density, and temperature by a statistical theory developed by Kirkwood,[29] Onsager,[44] and Fröhlich.[45] Accordingly, for liquids and solids,[46]

$$\Delta\epsilon = (\epsilon_s - \epsilon_\infty) = \left[\frac{\epsilon_s}{2\epsilon_s + \epsilon_\infty}\right]\left(\frac{\epsilon_\infty + 2}{3}\right)^2 \frac{4\pi N_A \rho}{3k_B T M} g {\mu_0}^2 \qquad (1)$$

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 known as the orientational correlation factor whose value is 1 when there is no intermolecular association leading to correlation of dipole vectors. Its definition is in terms of the summation of the dipole vectors of neighboring molecules (it is not empirical).[29,45] 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. This is a generally accepted molecular interpretation for the large values of ϵ_s which have been observed for H_2O,[47] amides[3,4] and alcohols[5−30] and for which g values have been found to be both greater than 1 and less than 1. 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 not only in the implication that (nonpermanent) linear chains of intermolecularly H-bonded structure may occur on the time average but also in that ring dimers form in the alcohol's structure leading to its ϵ_s value close to that of a nonpolar liquid at low temperatures.

A calculation from eq 1 based on 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, had led to value of g as ~3 for 1-phenyl-2-propanol at 219 K.[22] This in turn had indicated a significant extent of intermolecular H-bond association such that the dipole vectors were correlated in a parallel manner. Now since only the slowest relaxation process in 1-phenyl-2-propanol is being analyzed here, the limiting low-frequency permittivity of the faster relaxation process, $\epsilon_{s,2}$ (and not $1.1n_D^2$), needs to be taken as equal to $\epsilon_{\infty,1}$, the limiting high-frequency permittivity of the slow relaxation process. When this is done by using the data from Figure 1, $\Delta\epsilon_1$ ($= \epsilon_s - \epsilon_{\infty,1}$) is ~17.5 at 211.56 K. A recalculation with this value of $\Delta\epsilon_1$ from eq 1 yields the g value of ~2.3. In contrast, g was found to be ~1 for 1-phenyl-1-propanol,[14,22] which had indicated little intermolecular H-bonding in its supercooled liquid. In contrast, $g \approx 3.8$ for 2-propanol at 211 K from Table 4 in ref 6.

This indicates that there is a parallel correlation of dipole vectors that contributes to the slowest relaxation process in 1-phenyl-2-propanol, as it is in 2-propanol, and that the population of intermolecularly H-bonded chains is significant in 1-phenyl-2-propanol. Both 1-propanol[5,10,43] and 2-propanol[6] had shown a Debye-type relaxation process with a large $\Delta\epsilon$ contribution. Because this Debye-type process is absent in 1-phenyl-2-propanol, we conclude that the increased steric hindrance to H-bond association in 1-phenyl-2-propanol over that in 2-propanol has significantly reduced those dielectric relaxation effects of the linear-chain H-bond association, which had produced a Debye type relaxation in 1-propanol and 2-propanol. We recall that, in 1-phenyl-1-propanol, for which $g \approx 1$, this effect becomes undetectably small.[14]

Equation 1 may be further used to show how the $\Delta\epsilon$ value may be used to determine approximately whether extensive H-bonding occurs in a monohydroxy alcohol. The vapor phase dipole moment of a monohydroxy alcohols is 1.68 D. If intermolecular H-bond association were absent, i.e., g was equal to 1, then $T\Delta\epsilon$ for a relaxation process according to eq 3 would depend on the magnitude of the term ρ/M, and the value of ϵ_∞. Since ρ of liquid alcohols at a given low temperature differs by no more than 10−15%, and their ϵ_∞ varies between 2.6 and 3.0, i.e., within ~15%, one expects that at a given T, the $\Delta\epsilon$ value of liquid alcohols will be within 15−20% of each other's. Alternatively stated, $\Delta\epsilon$ for a molecular relaxation process in a mono-hydroxy alcohol at a given T should be inversely proportional to its molecular weight, within 10−20%.

The above arguments may be used to discuss a recent conclusions regarding the mechanism of the first two (slow) relaxations, process I and process II, in 1-propanol.[10] For that alcohol, it was concluded that its process I did not contribute to viscosity and structural relaxation, only its process II and possibly III did, which in turn were attributed to the rotational−translational diffusion of unbonded molecules, as in a molecular liquid with only the van der Waals type interactions, e.g., *ortho*-terphenyl. These two processes, which contributed to the transport property, had a total $\Delta\epsilon$ of 3.12 (= 2.45 + 0.67) at 119.7 K.[10] Now, if the $\Delta\epsilon$ value of 3.12 were due to the rotational diffusion of the H-bonds free state of 1-propanol molecules,[10] then it may be scaled with temperature according to eq 1, or according to the Curie law, to obtain the value for 1-phenyl-2-propanol at 211.56 K. This scaled value may then be compared against the measured value for 1-phenyl-2-propanol at 211.56 K. The value of $\Delta\epsilon_1$ thus obtained by scaling the 1-propanol data is ~1.80 (3.12 × 119.7/211.56) at 211.56 K, which should accordingly be expected for 1-phenyl-2-propanol. For comparison, the measured $\Delta\epsilon_1$ for the first (slowest) relaxation process that contributes to the viscosity and structural relaxation of 1-phenyl-2-propanol is ~17.5 at 211.56 K, as seen in Figure 6. Hence, the measured $\Delta\epsilon$ for 1-phenyl-2-propanol is ~10-times the value expected from an extension of the conclusions on 1-propanol[10] to 1-phenyl-2-propanol. On the contrary, if the conclusion in ref 10 was ignored and 2-propanol,[5,43] which also shows a Debye-type relaxation, was taken as reference, then the ratio is 0.52 (=17.5/33.5, i.e., the observed $\Delta\epsilon$ of 17.5 at 211.56 K for 1-phenyl-2-propanol divided by the observed total $\Delta\epsilon$ of 33.5 at 211.56 K for 2-propanol). This indicates lowering of g in 1-phenyl-2-propanol. This ratio seems consistent with the ratio of 0.60 (~3.8/2.3) of their respective g values determined earlier here.

Alternatively, the appropriateness of the proposed mechanisms for the relaxation processes in 1-propanol[10] may be discussed by considering the sum of $\Delta\epsilon$ of processes II and III in 1-propanol, which have been attributed to its H-bond free monomer reorientations, and scaling this sum with the molecular weight of 1-phenyl-2-propanol according to eq 3. This scaling yields $\Delta\epsilon$ of $\sim$0.83 ± 0.1 for 1-phenyl-2-propanol at 211.56 K (i.e., 1.80 × 60/136, where 60 is the molecular weight of 2-propanol and 136 is that for 1-phenyl-2-propanol, plus 0.3 is added to include the approximate differences arising from their different values of ρ and of ϵ_∞). Since the observed value of $\Delta\epsilon$ of $\sim$17.5 for 1-phenyl-2-propanol is 20-times this scaled value, it means that either the 1-phenyl-2-propanol molecules are H-bonded to form linear chains and thus increase $\Delta\epsilon$ by a factor of $\sim$20 or that the interpretation of $\Delta\epsilon$ in 1-propanol needs be revised. Since the already calculated value of g of $\sim$2.3 for 1-phenyl-2-propanol here has shown indication of relatively small extent of intermolecular association, it seems that the interpretation for the transport property contributing mechanism in 1-propanol may need further investigation. (A similar analysis done by following the attribution in ref 10 and therefore taking $\Delta\epsilon_2$ of 2-propanol[6] as 1.7 (= 3.8−2.1) at 211 K leads to a comparable discrepancy.) However, since process I could not be observed by Brillouin light scattering and photon correlation spectroscopy (see ref 10, p 1090 for details), there is a justification for the conclusion that process I in 1-propanol may not be related to structural relaxation. But now that process I is also observed in 5-methyl-2-hexanol, 1-phenyl-1-propanol, and 1-phenyl-2-propanol, the generality of that justification may be tested by Brillouin light scattering and photon correlation spectroscopy of these liquids.

The results of the analysis of the ϵ' and ϵ'' spectra of the 1-phenyl-2-propanol, 2-methylpentane mixture, which are shown in Figures 4 and 6, also demonstrate that the main spectra is of the Davidson−Cole type,[5] with the α_1 and β_1 parameters closely similar to those for pure 1-phenyl-2-propanol. For the mixture, ϵ_s is 10.2 at 211.4 K and $\Delta\epsilon_1$ is 7.7. The density of the solution is not known, but it should be less than that of 1-phenyl-2-propanol,[22] and the scaled molecular weight is 111 [= $^1/_2$ (86 + 136); 86 being the mol wt of 2-methylpentane and 136 that of 1-phenyl-2-propanol]. The value of ϵ_∞ for the process would also decrease in the mixture over its value for 1-phenyl-2-propanol. By ignoring the latter decrease, and scaling the g value on the basis of the number density of the dipoles alone, which is about half of that in the pure state, we obtain g as $\sim$1.1 in the mixture. This indicates that intermolecular H-bond association does not occur in the solution to raise its correlation factor by a significant amount.

Nature of Dielectric Relaxation Processes. The above-given arguments suggest that intermolecular H-bonded association does occur in 1-phenyl-2-propanol and not in its solution, and yet the additional Debye-type relaxation is absent in 1-phenyl-2-propanol and present in 1-propanol[5,10,43] and in 2-propanol.[6] Since dielectric relaxation occurring by the mechanism of rotation of the −OR group is found only when H-bonded chains are present,[5] it would be present in 1-phenyl-2-propanol and not in the mixture. It may be recalled that both processes occur in the extensively H-bonded structures in the liquid states of 1-propanol,[5,43] 2-propanol,[6] isomeric octanols,[9] and 5-methyl-2-hexanol.[12] Therefore, it seems that both features of 1-phenyl-2-propanol, namely, (i) the Davidson−Cole form[5] of the relaxation spectra and (ii) the non-Arrhenius variation of the f_m of its slow relaxation process, admit to the same underlying mechanisms that are responsible for the corresponding two features observed in the dihydroxy and trihydroxy alcohols, such as propylene glycol and its oligomers,[48,49] petanediols,[50] and glycerol.[1,4,51−53] In these alcohols, extensive intermolecular H-bonding does occur, and their g values are greater than 1 at low temperatures. But these two features of the spectra are also found in rigid molecular non-H-bonded liquids,[39−41,54] for which g is equal to 1 at all temperatures, and they are also found for amorphous polymers.[38] (Certain mono-hydroxy long chain alcohols have shown a similar behavior,[55] but the Arrhenius variation of their f_m with T was determined over a limited temperature range and the data were less accurate because their ϵ_s value decreases to a value approaching that of a nonpolar liquid at low temperatures. A restudy of these alcohols by the currently available techniques would help in determining the role of intermolecular H-bond association.)

The slowest relaxation that contributes to the majority of orientation polarization in supercooled liquids[39−41,54,55] (and polymers[38]) 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. In this sense, the slowest dielectric relaxation in 1-phenyl-2-propanol would correspond to the α-relaxation process observed in rigid molecular, non-H-bonded, supercooled liquids,[39−41,54] and this diffusion would contribute to its viscosity and its structural relaxation. The relaxation spectra of this process is usually broad. For certain alcohols in which it is narrow, i.e., of the Debye-type, it seems anomalous and inconsistent with the usual models and theories of relaxation,[41,56−63] a subject discussed earlier. But there is an alternative model by Anderson and Ullman,[64] 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. But, 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 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[65] and the mode-coupling theory's[66] consideration of the problem, but only in terms of the structural relaxation rate. 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.

Finally, the excess ϵ'' at high frequencies in Figures 3 and 4 appears as a deviation from a single power law above the peak frequency. This deviation may be resolved as a Nagle "wing" or a Johari-Goldstein relaxation process,[40,41,67] a subject reviewed recently.[1,2] Only further studies at high pressures[42] or measurements made after aging of the samples[67] may conclusively resolve this issue. In either case, the excess ϵ'' and the associated decrease in ϵ' on increasing frequency in this region indicates persistence of localized molecular motions.

Temperature Dependence of Relaxation Rates. We consider three aspects of the temperature dependence of the relaxation dynamics. These aspects continue to be a subject of debate,[1,2] and used to underscore support of one theory over the other. Since our discussion is analogous to that given elsewhere,[14] 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[68] is written in the form

$$f_m = A_{AG}\exp(-z^*\Delta\mu/RT) \tag{2}$$

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",[68] and R is the gas constant. The data in Figure 7 can be described by the empirical Vogel−Fulcher−Tamman equation,[69−71]

$$f_m = A_{VFT}\exp[-B/(T - T_0)] \tag{3}$$

As noted earlier here, and Figure 7, $A_{VFT} = 10^{14.88}$ Hz, $B = 1984.54$ K, and $T_0 = 146.55$ for 1-phenyl-2-propanol. The corresponding values are $10^{13.27}$, 1458.95, and 145.21 K for its 1:1 mixture with 2-methylpenatne. As shown earlier,[72] a further analysis of the data may be done 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 2 was seen as identical to the preexponential term in eq 3. Without implying that the temperature T_0 has a thermodynamic significance, the identification of these terms[72] had led to $\Delta\mu = 8.315B$ and $z^* = [T/(T - T_0)]$. By using the above-given values of B and T_0, we obtain $\Delta\mu = 16.4$ kJ/mol, $z^*(198.7\text{ K}) = 3.8$, and $z^*(T_g$ for $f_m = 10^{-4}$ Hz$) = 4.2$ for 1-phenyl-2-propanol, and $\Delta\mu = 12.1$ kJ/mol, $z^*(198.7\text{ K}) = 3.7$, and $z^*(T_g$ for $f_m = 10^{-4}$ Hz$) = 4.6$ for its 1:1 mixture with 2-methylpentane. The corresponding values for pure 1-phenyl-1-propanol are 12.7 kJ/mol, 3.8 and 5.05. These values may be compared against those for other alcohols as described in ref 14. It should, however, be stressed that a comparison between eqs 2 and 3, which has been used to estimate z^* and $\Delta\mu$, requires only the matching of the shapes of the plots of ln f_m against T at $T > T_g$ and 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 are in turn obtained by using a relatively long extrapolation.

Dyre et al.[73] and Dyre[74] have recently provided an alternative interpretation of the temperature dependence of relaxation rate in terms of a "shoving model".[74] Accordingly,

$$f_m = A_{Dyre}\exp(-G_\infty V_c/k_B T) \tag{4}$$

where G_∞ is the temperature-dependent shear modulus of a liquid and k_B the Boltzmann constant. Its relevance too has been discussed elsewhere.[14] Briefly, it leads to $G_\infty V_c = z^*\Delta\mu$ when the quantities are represented in mole units. For 1-phenyl-2-propanol at its T_g (or T for $f_m = 10^{-4}$ Hz), we calculate $G_\infty V_c = 68.9$ (or $z^*(T_g)\ \Delta\mu = 4.2 \times 16.4$) kJ/mol. For its mixture with 2-methylpentane, we calculate $G_\infty V_c = 55.7$ kJ/mol. The corresponding values calculated from the recent data is 55.7 kJ/mol for 1-phenyl-1-propanol[14] and 50.6 kJ/mol for 5-methyl-2-hexanol.[12] These values may be compared against the values for other liquids given earlier,[12] and further discussed, as before.

In the current literature, two more equations have been used to fit the T dependence of f_m. The first is an empirical equation provided by Dissado and Hill,[75,76] namely, $f_m \sim (T - T_c)^\gamma$, and the second by Nagel and co-workers,[77] $f_m \sim [(T - T_c)/T_c]^\gamma$. There is finally the equation based on the mode-coupling theory,[78,79]

$$f_m = A_{mc}[(T - T_c)/T_c]^\gamma \tag{5}$$

where A_{mc}, T_c, and γ are empirical parameters. These three equations admit to the same form, namely, that f_m varies as $(T - T_c)^\gamma$. Souletie and Bertrand[80] have provided a somewhat different equation,

$$f_m = A_{SB}[(T - T_c)/T]^\gamma \tag{6}$$

where A_{SB}, T_c, and γ are also empirical constants. Equations 5 and 6 were fitted to the data for the relaxation rates, and the plots are shown in Figure 7. For 1-phenyl-2-propanol, the parameters used for the fitting are $A_{mc} = 10^{12.64}$, $T_c = 180.11$, and $\gamma = 14.52$ for eq 5, and $A_{SB} = 10^{17.61}$, $T_c = 173.97$ K, and $\gamma = 21.3$ for eq 6. For its 1:1 mixture in 2-methylpentane, the parameters used for fitting are $A_{mc} = 10^{12.1}$, $T_c = 172.96$, and $\gamma = 12.9$ for eq 5, and $A_{SB} = 10^{16.14}$, $T_c = 168.53$ K, and $\gamma = 17.98$ for eq 6. Remarkably similar values of the parameters had been obtained for 1-phenyl-1-propanol[14] and 5-methyl-2-hexanol.[12]

At first sight, the excellence of the fit seen in Figure 7 would indicate that the theories on which eqs 5 and 6 are based are valid for 1-phenyl-2-propanol and its mixture, and for the two other alcohols.[12,34] However, according to these theories, the critical exponent γ 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 3−4 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 Figure 7.

It is necessary to point out that the shape of the ln f_m against $(1/T)$ plot expected from eq 3 fundamentally differs from the shape expected from eq 5.[81] The approach of f_m toward its high-temperature value in eq 3 is obtained by differentiating it with respect to $1/T$,

$$[\partial(\ln f_m)/\partial(1/T)] \approx -B \tag{7}$$

which implies that as $T \to \infty$, $\ln f_m \to \infty$. In contrast, by differentiating the power law equations or eq 5 with respect to $1/T$, one obtains

$$[\partial(\ln f_m)/\partial(1/T)] \approx -\gamma T \tag{8}$$

which implies that as $T \to \infty$, $\ln f_m \to \ln A$. Finally, according to the power law, a plot of ln f_m against $1/T$ would show a point of inflection at a temperature $T_x = 2T_c$, where $[\partial^2(\ln f_m)/\partial(1/T)^2] = 0$. This point of inflection has not been observed.[81]

The above-given characteristic shape of the plots suggests that the f_m data at high-temperatures should be able to discriminate between the fits of the Vogel−Fulcher−Tamman equation and the power-law equation. This discrimination has not been possible, nor has f_m been found to approach infinity as T increases toward the boiling point of the liquid. Moreover, according to the power law equations, the Oldekop plots[82] of $\log(\tau)$ against T/T_g would have a shape in which the high temperature limit would be undefined, producing thereby a plot

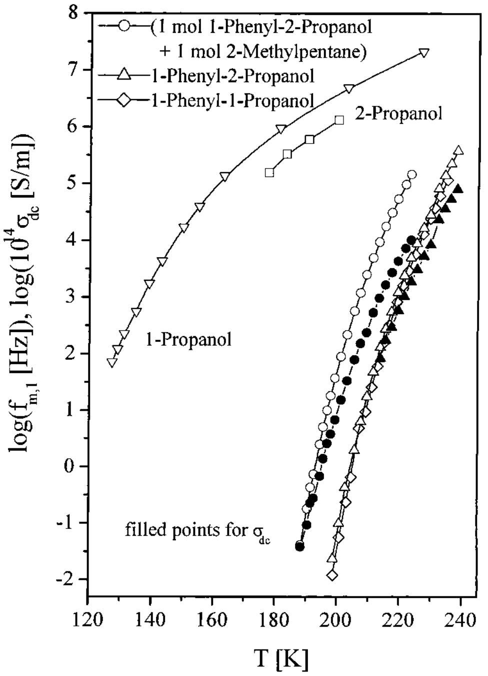

Figure 8. The ϵ'' peak frequency for 1-phenyl-2-propanol, 1:1 mixture of 1-phenyl-2-propanol and 2-methylpentane, 1-phenyl-1-propanol,[14] 1-propanol,[43] and 2-propanol[6] are plotted against the temperature. Also plotted is the dc conductivity multiplied by 10^{14}.

quite distinct from that generally observed for supercooled liquids. 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–Tamman equation the other. It is important here to refer to Richert's[83] conclusion that eq 3 is more appropriate for data fitting. In contrast, Colby[84] had found that a form of eq 5 fits the data for a majority of liquids.

Effects of Steric Hindrance and Dilution on Relaxation Time. We consider two more aspects of steric hindrance and dilution on the relaxation rate of the phenyl propanols. Figure 8 shows the plots of the relaxation rate against T for 1-phenyl-1-propanol, 1-phenyl-2-propanol, and of the latter's mixture with 2-methylpentane. Here the dc conductivity σ_{dc} of 1-phenyl-2-propanol and 1-phenyl-1-propanol multiplied by 10^{14} is also plotted for comparison against the relaxation rate data. The curves in Figure 8 show that the relaxation rates of 1-phenyl-2-propanol and 1-phenyl-1-propanol are similar in most of the temperature range. This similarity is remarkable in view of the fact that a certain extent of intermolecular H-bonding that leads to a parallel correlation of dipoles occurs in the former and not in the latter. Rössler[85] has shown that the Debye–Stokes–Einstein relation is inadequate for describing of the dynamics of supercooled liquids. But discussion on the applicability of hydrodynamics has been continued by Hansen et al.,[86] who suggest that the dielectric relaxation time is proportional to the viscosity η divided by T and not proportional just to η. Since T differs by usually no more than 50% in the extreme temperatures of measurements, the maximum difference arising from this revision would be by 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 or $f_{m,1}$. Accordingly, the similarity of $f_{m,1}$ of 1-phenyl-2-propanol and 1-phenyl-1-propanol suggests that the ratio of the product, $V_m\eta$, of 1-phenyl-2-propanol to that of 1-phenyl-1-propanol be equal to 1. Further it should remain so over the entire temperature range of the study. If this argument is extended to 2-propanol and 1-propanol, it would require that the corresponding ratio for these propanols be also equal to ~1. The relaxation rate of 2-propanol is 1.33 MHz at 200 K[43] and that of 1-propanol is 5 MHz at 202.9 K.[6] These values[6,43] are plotted against T also in Figure 8. The ratio of their respective $f_{m,1}$ shows that the ratio of their respective $V_m\eta$ values is ~4. In these latter two alcohols, intermolecular H-bonding is extensive, the g value is ~3, and the slowest relaxation process has a single relaxation time. On comparison with the corresponding values for the phenyl-propanols and their relative $f_{m,1}$, it seems that a decrease in the extent of H-bonding tends to bring the relaxation close to that expected from the hydrodynamic approaches. This would seem to be consistent with relation provided by Hansen et al.[86]

Finally, we consider the increase in the relaxation rate on dissolution of 1-phenyl-2-propanol in 2-methylpentane. At 205.47 K, $f_{m,1} = 1.8$ Hz for pure 1-phenyl-2-propanol, and 570 Hz for its 2-methylpentane mixture, i.e., there is ~300-fold increase in the relaxation rate. This difference is reduced to 43-fold increase at 221.5 K, as calculated from the data in Figure 8. This change is expected because at the limiting high temperature, $f_{m,1}$ for the two alcohols should approach approximately the same value in the THz frequency range. It also indicates that T_g of the mixture is lower than that of the pure alcohol. In terms of the hydrodynamic theory it means that the product $V_m\eta$ has increased in the 2-methylpentane mixture, and that the $V_m\eta$ ratio of the pure alcohol to that of its mixture increases progressively more on cooling from its expected value of ~1 in the high-temperature limit. Concurrently, the distribution of relaxation times becomes broader, a feature that is not considered in the hydrodynamic theories. From their exhaustive dielectric studies of various compositions of 1-propanol, 2-methylpentane mixtures, Denney and Ring[43] have described how the distribution of relaxation time changes, and how this distribution vanishes and becomes a single (relaxation time) Debye relaxation for 50 mol % composition. How the deviations from the hydrodynamic theories can be related to the distribution of relaxation times is an aspect of supercooled liquid yet to be considered.

Conclusion

The steric hindrance created by replacing one H atom by a phenyl group in 2-propanol molecule decreases the extent of intermolecular H-bonding, and hence the equilibrium permittiivity, and the Debye-type relaxation in the original 2-propanol, becomes Davidson–Cole type relaxation. This is similar to that observed for the effect of a similar substitution in 1-propanol. The dilution by a nonpolar solvent also decreases the intermolecular association via H-bonds. The dynamics of the dielectric relaxation in 1-phenyl-2-propanol is not clearly resolved into two processes. This may indicate the presence of a "wing" as suggested by Dixon, et al,[87] or a merged Johari–Goldstein process. Its characteristics could not be accurately determined owing to its small magnitude. The spectra corresponding to the α-relaxation process contributes ~94% of the total polarization, and the spectra at different temperatures is superimposable. The strength of the dielectric polarization is much larger than that observed for the presumed α-process in 1-propanol. For 1-phenyl-2-propanol, it is consistent with the conclusion that the α-relaxation involves reorientation of H-bonded molecules. 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 4.2 molecules for the cooperatively rearranging region at its T_g, and 16.4 kJ/mol for the constant value of the potential energy barrier. Dyre et al's model[73,74] 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−Tamman equation leads to an inconsistency in the parameters evaluated. The power (or scaling) law based equations fit the data well, but the critical exponent for 1-phenyl-2-propanol and its mixture with 2-methylpentane is 3−4 times the value expected from these laws. This indicates that fitting of such power-law is ambiguous.

The dielectric relaxation rates of 1-phenyl-2-propanol and 1-phenyl-1-propanol are remarkably similar over a broad temperature range, and those of 2-propanol and 1-propanol are close to each other. As the two molecules in each pair have identical volumes, this indicates that despite differences in the intermolecular H-bond association their hydrodynamic behaviors are similar. In mixture with 2-methylpentane, the relaxation rate is much faster, as the H-bond association and viscosity decrease.

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