

Effects of induced steric hindrance on the dielectric behavior and H bonding in the supercooled liquid and vitreous alcohol

G. P. Johari

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

O. E. Kalinovskaya and J. K. Vij^{a)}

Laboratory of Advanced Materials, Department of Electronic Engineering, Trinity College, Dublin 2, Ireland

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The extent of H bonding in alcohols may be reduced by sterically hindering its OH group. This technique is used here for investigating the reasons for the prominent Debye-type dielectric relaxation observed in monohydroxy alcohols [Kudlik *et al.*, *Europhys. Lett.* **40**, 549 (1997); Hansen *et al.*, *J. Chem. Phys.* **107**, 1086 (1997); Kalinovskaya and Vij, *ibid.* **112**, 3262 (2000)], and broadband dielectric spectroscopy of supercooled liquid and glassy states of 1-phenyl-1-propanol is performed over the 165–238 K range. In its molecule, the steric hindrance from the phenyl group and the existence of optical isomers reduce the extent of intermolecular H bonding. The equilibrium permittivity data show that H-bonded chains do not form in the supercooled liquid, and the total polarization decays by three discrete relaxation processes, of which only the slower two could be resolved. The first is described by the Cole–Davidson-type distribution of relaxation times and a Vogel–Fulcher–Tammann-type temperature dependence of its average rate, which are characteristics of the α -relaxation process as in molecular liquids. The second is described by a Havriliak–Negami-type equation, and an Arrhenius temperature dependence, which are the characteristics of the Johari–Goldstein process of localized molecular motions. The relaxation rate's non-Arrhenius temperature dependence 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 13.4, instead of 2–4, required by the mode-coupling theory, thereby indicating the ambiguity of the power-law equations. © 2001 American Institute of Physics. [DOI: 10.1063/1.1346635]

I. INTRODUCTION

Studies of dielectric relaxation in certain primary alcohols^{1–8} and aliphatic amides^{9,10} have shown that a major fraction of their orientation polarization decays exponentially, i.e., according to a single Debye-type relaxation. The temperature dependence of the relaxation rate, nevertheless, remains non-Arrhenius. Recently, Hansen *et al.*¹ concluded that the Debye-type process in 1-propanol, called process I, which relaxes ~95.5% of its orientational polarization at 119.7 K, is not associated with the supercooled liquid's structural relaxation and viscosity. This conclusion supported the prevailing view that the Debye-type relaxation process is incompatible with the non-Arrhenius temperature dependence of a supercooled liquid's transport properties. The remaining orientation polarization was resolved, in order of its increasing rate, into two processes, which were called processes II and III. Both had a broad distribution of relaxation times. Process II in 1-propanol contributed ~4.5% to its total polarization at 119.7 K, and process III ~1%. The average relaxation rate of both processes, I and II, were found to decrease with temperature in a non-Arrhenius manner, and

that of process III, according to the Arrhenius equation.¹ It was concluded that there was no contribution to the viscosity and structural relaxation from process I.

A more recent study of a secondary alcohol, 5-methyl-2-hexanol,³ also showed three relaxation regions similar to those observed for 1-propanol, and the relaxation rate of processes I and II approached each other on cooling toward the liquid's vitrification temperature. But contrary to the interpretation of processes I and II in 1-propanol,¹ process I in 5-methyl-2-hexanol was attributed to a relaxation mechanism of H-bond breaking and reforming and process II to the OR group motions within the H-bonded chains, as in the earlier interpretations of similar relaxations observed in monohydroxy alcohols.^{4–8}

The relatively broad, process II in both 1-propanol and 5-methyl-2-hexanol was identified as the well-known α -relaxation process,^{1,3} which is commonly observed in molecular liquids^{11,12} and amorphous polymers.¹³ Contributions to the permittivity from process II, $\Delta\epsilon_2$, decreased on heating, as expected from the Curie law, but its relatively small magnitudes, 2.45 for 1-propanol at 119.7 K¹ and 0.8 for 5-methyl-2-hexanol at 160.9 K,³ implied that in its interpretation, a very small fraction of molecules would contribute to

^{a)}Electronic mail: jvij@tcd.ie

the α -relaxation process. This created a difficulty in understanding how the orientational diffusion of a relatively small number of molecules that contribute only ~ 2.45 to the permittivity of 1-propanol can be seen as responsible for its supercooled liquid's viscosity and structural relaxation.

Here we examine these issues by a detailed study of a molecule, 1-phenyl-1-propanol [$(C_6H_5)HC(OH)-C_2H_5$], in which one H atom in the CH_2OH group of 1-propanol has been replaced by the phenyl group. This introduces a steric hindrance to H bonding without significantly affecting the net dipole moment. Moreover, the 1-phenyl-1-propanol molecule contains an asymmetric carbon atom, and therefore should exist in the *dextro*-, and *levo*-forms. Their presence may make it difficult to produce intermolecularly H-bonded chains, thereby keeping most of molecules in their non-bonded states. In an earlier study¹⁴ of its supercooled liquid performed over limited frequencies and temperatures, the dielectric spectra of 1-phenyl-1-propanol was analyzed in terms of both (i) a sum of Debye-type process plus a small, unanalyzable relaxation, and (ii) a Cole–Davidson relaxation process, or a skewed arc function.⁴ Its equilibrium permittivity was interpreted in terms of the formation of H-bonded linear chains which increased its dipolar orientational correlation factor, g ,¹⁵ from 1 to ~ 1.4 . Johari and Dannhauser^{16,17} also studied the effects of hydrostatic pressure on its density,¹⁶ viscosity,¹⁷ and dielectric behavior¹⁶ at different temperatures.

II. EXPERIMENTAL METHODS

1-phenyl-1-propanol was purchased from Chemical Sample Company, OH, by Dannhauser in 1967 for dielectric relaxation¹⁴ and viscosity¹⁷ studies under high pressures.^{16,17} It was refluxed with CaH_2 in order to remove any moisture, and fractionally distilled in vacuum. The middle fraction was collected for the dielectric and viscosity measurements. The left-over middle fraction sample was kept in a hermetically sealed container in storage for 22 years, redistilled in vacuum, and studied. The dielectric cell used was a miniature, tunable parallel plate condenser containing 18 plates, with an air capacitance of nominally 26.7 pF. (This conveniently available capacitor seems superior to the parallel plates separated by spacers used successfully up to 1 MHz frequency range by several groups.) The cell and the sample's temperature was controlled by keeping it inside a cryostat, model Oxford CF 1200, purchased from Oxford Instruments. Instead of preprogramming, the discrete temperature was set for isothermal control at the desired value by its manual setting. The temperature was controlled to within 50 mK over a period of up to 8 h, as was needed for measurements at the lowest temperature in the lowest frequency range. 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 and a Chelsea dielectric interface. This procedure has been described earlier.^{3,18}

III. RESULTS AND ANALYSIS

The ϵ' and ϵ'' spectra of supercooled liquid 1-phenyl-1-propanol at selected temperatures, T , are provided in Fig. 1.

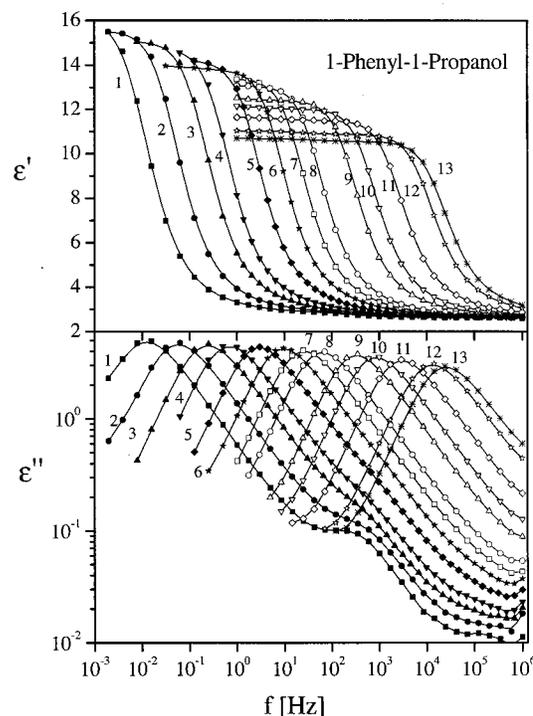


FIG. 1. The ϵ' and ϵ'' spectra of supercooled liquid 1-phenyl-1-propanol at several temperatures. The curves are labeled as: (1) 198.72 K, (2) 200.78 K, (3) 202.91 K, (4) 204.46 K, (5) 206.92 K, (6) 209.12 K, (7) 210.96 K, (8) 212.84 K, (9) 216.68 K, (10) 219.07 K, (11) 222.72 K, (12) 227.31 K, and (13) 229.65 K.

The ϵ'' spectra shows that a shoulder gradually develops on the high frequency side of the ϵ'' peak as the liquid is cooled below 205 K. Also, at $T < 209$ K and at frequencies higher than 10 kHz, ϵ'' approaches a plateau-like value. This indicates that a third very weak relaxation process may also be present, but its features cannot be analyzed mainly due to the limited frequency range of this study. Such a feature has been observed in other alcohols and molecular liquids, mainly in glycerol at $T < 204$ K.^{19,20} The ϵ' and ϵ'' spectra of glassy and highly viscous states of 1-phenyl-1-propanol at selected temperatures, T , are provided in Fig. 2.

Both the ϵ' and ϵ'' spectra were analyzed by using the WINFIT 2.7 program provided by Novocontrol, Hundsagen, Germany. An earlier version of the computational algorithm has generally been used in the dielectric data analysis by Fischer and co-workers,^{1,22} and the WINFIT 2.7 by two of us (O.E.K. and J.K.V.) in earlier studies.^{3,18} Briefly, the equation used is

$$\epsilon^*(\omega) = \epsilon_\infty + \sum_{i=1}^{i=n} \frac{\epsilon_{0,i} - \epsilon_{\infty,i}}{[1 + (i\omega\tau_i)^{\alpha_i}]^{\beta_i}}, \quad (1)$$

where the empirical parameters α_i and β_i determine the asymmetric shape of the spectra, $\epsilon_{0,i}$ and $\epsilon_{\infty,i}$ are the limiting, low-, and high-frequency permittivity values of the individual relaxation spectra, and τ_i its characteristic relaxation time. The frequency of the relaxation peak was calculated from

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

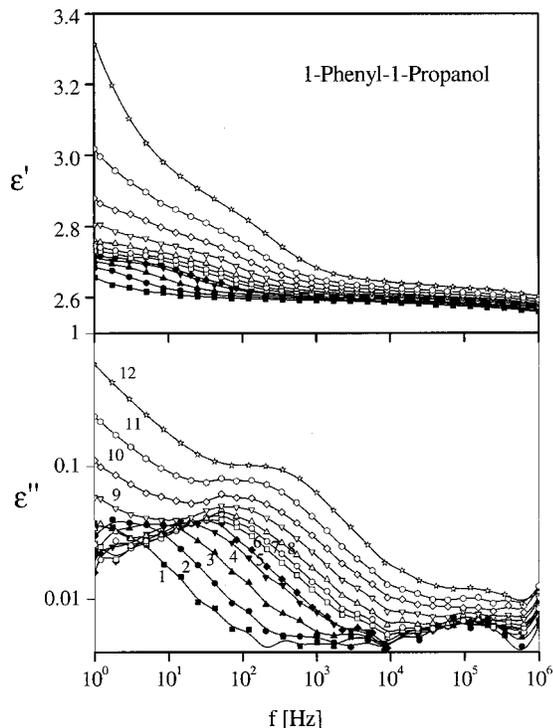


FIG. 2. The spectra of the faster relaxation observed in the highly viscous liquid, and vitrified states of 1-phenyl-1-propanol at different temperatures. The curves are labeled as: (1) 165.6 K, (2) 170.76 K, (3) 175.5 K, (4) 180.5 K, (5) 182.6 K, (6) 185.78 K, (7) 187.50 K, (8) 189.44 K, (9) 191.63 K, (10) 193.71 K, (11) 196.12, and (12) 198.72 K.

To elaborate how the relaxation spectra were resolved into several relaxation regions, the spectra of 1-phenyl-1-propanol at 206.92 K is shown in Fig. 3. The continuous line in Fig. 3 is the curve calculated with the parameters, $\Delta\epsilon_1 = 11.27$, $\alpha_1 = 0.974$, $\beta_1 = 0.64$, $\tau_{\text{HN},1} = 77.8$ ms, $\Delta\epsilon_2 = 0.247$, $\alpha_2 = 0.818$, $\beta_2 = 0.625$, $\tau_{\text{HN},2} = 0.504$ ms. The highest frequency relaxation process could not be resolved, which was mainly due to the exceedingly small values of its ϵ'' contribution and the experimental errors. Because α_1 remains constant at 0.98 ± 0.01 , which is within the uncertainty of the experimental data and the data analysis, its value may be seen as close to 1, i.e., the distribution is regarded as the Cole–Davidson type.⁴ It is worth noting that at the limiting low frequencies, the ϵ' and ϵ'' values often contain contributions from dc conductivity, σ_{dc} . As discussed in the Appendix of Ref. 19, this tends to broaden the spectra at the low-frequency side enough to be fitted by the Kohlrausch relaxation function (as in Refs. 2, 20, 21), or the Havriliak–Negami equation (as in Refs. 1 and 22), a subject. Therefore, no attempt was made to fit the data to the alternative Kohlrausch function as in Refs. 2, 20, and 21.

The quantity, f_m , ($= 1/2\pi\tau_{\text{max}}$), although arbitrary, has been deemed as suitable for delineating the temperature dependence of dynamical processes, and we use it as a measure of the average rate of dielectric relaxation. Its value for the two relaxation processes is plotted logarithmically against $1/T$ in Fig. 4, where σ_{dc} multiplied by a factor 10^{16} is also plotted for the purpose of comparing against the variation of f_m . The f_m data are described satisfactorily by the Vogel–Fulcher–Tammann empirical equation, $f_{m,1} = 10^{13.32}$

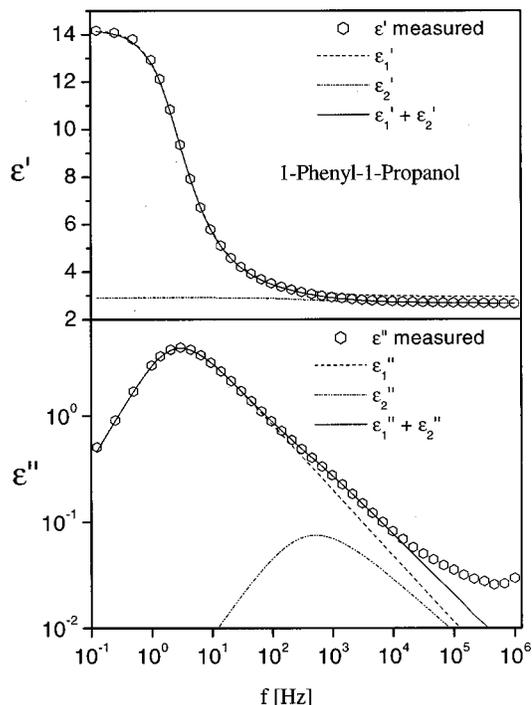


FIG. 3. The resolution of the α and the Johari–Goldstein processes in 1-phenyl-1-propanol at 206.92 K. The parameters used for the calculations are given in the text.

$\times \exp[-1529.3/(T - 155.1)]$, as is shown by the continuous line in Fig. 4. This fitting equation has also been used satisfactorily for describing the relaxation in supercooled liquids.^{1–8,12,13,18–21} The faster relaxation is described by the Arrhenius equation, $f_{m,2} = 10^{13.98} \exp(-10595.2/RT)$.

The magnitude of $\Delta\epsilon_1$, $\Delta\epsilon_2$ for the two relaxation processes is plotted against T in Fig. 5 (top panel). The values of

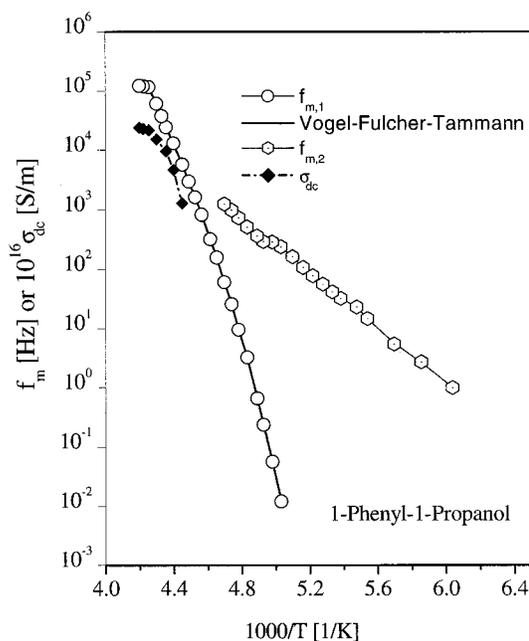


FIG. 4. Plots of $\log f_m$ for the α -relaxation and the Johari–Goldstein relaxation processes against the $1000/T$ for 1-phenyl-1-propanol. Also plotted logarithmically is the dc conductivity.

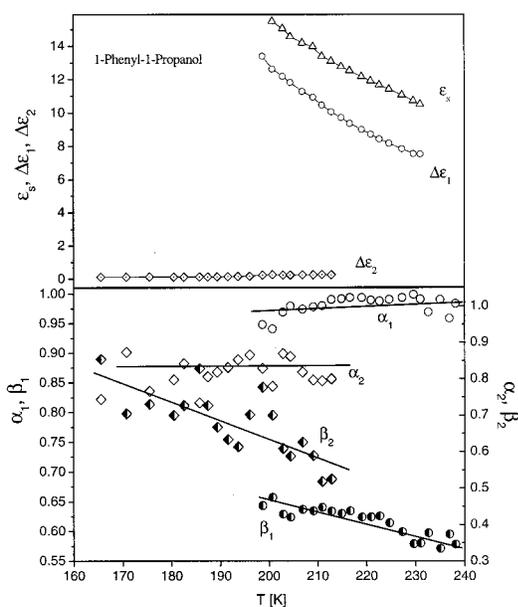


FIG. 5. Top frame: Plots of ϵ_s , $\Delta\epsilon_1$ and $\Delta\epsilon_2$ of 1-phenyl-1-propanol against the temperature. Bottom frame: The distribution parameters, α_1 and β_1 for the α relaxation and α_2 and β_2 for the Johari–Goldstein-relaxation spectra.

α_1 and β_1 and of α_2 and β_2 are plotted against T in Fig. 5 (bottom panel). From a recent study of several supercooled liquids, Olsen *et al.*²³ have shown that when T is such that the α -relaxation and Johari–Goldstein relaxation 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 may also be the case here is indicated by the nearly constant values of the α_1 and β_1 , as seen in Fig. 5 (bottom panel), particularly at high temperatures. The validity of this superposition may be directly seen from the plots of the normalized ϵ'' spectra provided in Fig. 6. Small differences in these parameters, as noted at different temperatures in Fig. 5 (bottom panel), do not seem to change the superposition significantly, as was found earlier for some molecular liquids,^{11,12} but hydrostatic pressure has been found to broaden the spectra for 1-phenyl-1-propanol considerably.¹⁶

Finally, Fig. 7 shows the relaxation spectra of a partially

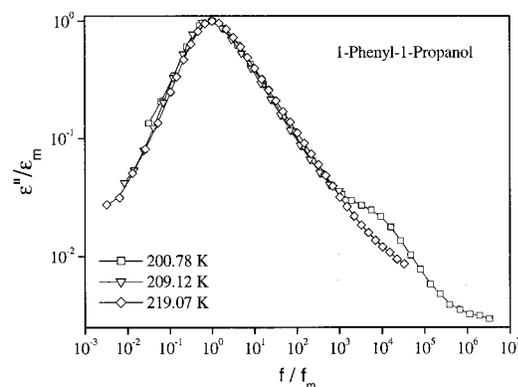


FIG. 6. The superposition of the dielectric loss spectra of 1-phenyl-1-propanol at three temperatures, as indicated.

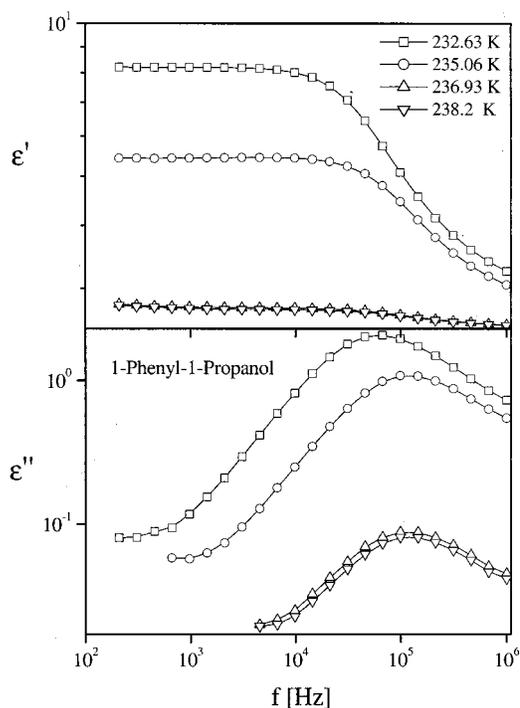


FIG. 7. The spectra of ϵ' and ϵ'' of partially crystallized sample of 1-phenyl-1-propanol at four temperatures showing the decrease in the ϵ_s and the insensitivity of the ϵ'' -peak frequency caused by the air gaps in the sample and the crystal/liquid interface effects on H bonding.

crystallized 1-phenyl-1-propanol sample at four temperatures. Here, the magnitudes of ϵ' and the height of the ϵ'' peak decrease on increasing T , as expected when an increasing fraction of the supercooled liquid slowly crystallizes. However, the peak frequency appears to become insensitive to increase in T partly due to the extrinsic effects of air gaps that form when the sample contracts on crystallization, and partly due to the change in H bonding caused by the crystal/liquid interface.

IV. DISCUSSION

A. The equilibrium permittivity

We first consider the effect of induced steric hindrance on the orientation polarization of a monohydric alcohol. The equilibrium permittivity, ϵ_s , of 1-phenyl-1-propanol as seen in Fig. 1, is 15.5 at 200.8 K, which is less than half the ϵ_s value of 38.5 for 1-propanol at 202.9 K.²⁴ This is a direct effect of the deliberately induced steric hindrance on the equilibrium dielectric property of an alcohol, and it indicates a considerable decrease in the dipolar alignment due to the intermolecular H-bond formation in 1-phenyl-1-propanol from that in 1-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,¹⁵ Onsager,²⁵ and Fröhlich.²⁶ Accordingly, for liquids and solids,²⁷

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

where ϵ_∞ is the limiting high frequency permittivity of the orientation polarization associated with a certain relaxation process, N_A is the Avogadro number, ρ is the density, M the molecular weight, k_B the Boltzmann constant, T the temperature, and μ_0 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 the correlation of dipole vectors. When g is greater than unity, it indicates a parallel dipolar correlation, which 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 ,²⁸ amides,^{9,10} and primary^{4–8} and secondary^{3,14,16} alcohols.

The quantity ϵ_s of 1-phenyl-1-propanol as seen in Fig. 1 is 15.5 at 200.8 K, which is consistent with the earlier reported values.¹⁴ A calculation from Eq. (3) based on the total value of $\Delta\epsilon (= \epsilon_s - \epsilon_\infty)$ in which ϵ_∞ was 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 ~ 1.6 at 213 K.¹⁴ This in turn had indicated a small 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-1-propanol is attributable to the long-range diffusion of molecules, $\epsilon_{s,2}$, the limiting low-frequency permittivity of the faster relaxation 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 Figs. 1 and 2, $\Delta\epsilon_1 (= \epsilon_s - \epsilon_{\infty,1})$ is ~ 12 at 198.7 K. A recalculation with this value of $\Delta\epsilon_1$ from Eq. (3) yields g as ~ 1 , within the uncertainty of the analysis. This indicates that any parallel correlation of dipole vectors does not contribute to the first relaxation process in 1-phenyl-1-propanol. Therefore, the population of intermolecularly H-bonded chains in 1-phenyl-1-propanol is negligible. Since 1-propanol has shown a large Debye-type relaxation as process I, and this process is absent in 1-phenyl-1-propanol, we conclude that the induced steric hindrance to H-bond association on replacing one H atom in the $-\text{CH}_2\text{OH}$ of 1-propanol by one phenyl group also causes the dielectric relaxation effects of linear H-bond association to vanish, or become undetectable.

We use Eq. (3) further to show how the $\Delta\epsilon$ value may be used to approximately determine whether or not extensive H bonding occurs in a monohydroxy alcohol. The vapor phase dipole moment of 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 the ρ values of liquid alcohols at a given low temperature differ by no more than 10%–15%, and their ϵ_∞ varies between 2.6 and 3.0, i.e., within $\sim 15\%$, one expects that at a given T , the $\Delta\epsilon$ value of liquid alcohols will be within 15%–20% of each other. Alternatively stated, $\Delta\epsilon$ for a molecular relaxation process in a monohydroxy alcohol at a given T should be inversely proportional to its molecular weight, within 10%–20%.

The above-given analysis has a bearing upon the recent conclusions regarding the mechanism of the first two relaxation processes in 1-propanol.¹ For that alcohol it was concluded that process I did not contribute to viscosity and structural relaxation; only process II and possibly III did. The relaxation processes that were attributed to the transport property (and structural relaxation) contributed a total $\Delta\epsilon$ of 3.12 ($=2.45+0.67$) at 119.7 K,¹ and were regarded as the dielectric polarization-contributing rotational–translational diffusion of unbonded molecules as in molecular liquids, e.g., *ortho*-terphenyl, in which only van der Waals type interactions are present. This is much less than $\Delta\epsilon$ of ~ 12 in Fig. 5, for the only process that contributes to the viscosity and structural relaxation in 1-phenyl-1-propanol at 198.7 K.

Moreover, since the g value of 1-phenyl-1-propanol calculated here has shown little indication of H-bond association, either process I observed in 1-propanol¹ is absent in 1-phenyl-1-propanol, or a suitable model that allows a mathematical relation between the population of molecules involved in structural relaxation in 1-propanol and in its dielectric relaxation processes II and III with $\Delta\epsilon$ of 3.12 needs to be developed. It is conceivable that the originally proposed mechanisms for the relaxation processes in 1-propanol⁵ and in other alcohols with extensive H-bond association⁸ is a more appropriate one. Nevertheless, a detailed analysis of the light scattering and other properties which were used to support the recent mechanism for relaxations in 1-propanol¹ is still required.

B. The nature of the dielectric relaxation processes

On the basis of the above-given analysis, intermolecular H-bonded association does not occur in 1-phenyl-1-propanol. This would explain why the additional Debye-type relaxation is absent in 1-phenyl-1-propanol, and present in 1-propanol. Since dielectric relaxation by the mechanism of rotation of the $-\text{OR}$ group occurs only when H-bonded chains are present,⁵ the latter will also be absent in 1-phenyl-1-propanol. It may be recalled that both processes occur in the extensively H-bonded structures in the liquid states of 1-propanol,^{5,29} isomeric octanols,⁸ and 5-methyl-2-hexanol.³ Therefore we conclude that as in rigid molecular, H-bond free liquids,^{11,12,23} both the Cole–Davidson form⁴ of relaxation spectra in 1-phenyl-1-propanol and its non-Arrhenius variation of $f_{m,1}$ of the slow relaxation process admit to the same underlying mechanisms that are responsible for the corresponding features observed in dihydroxy and trihydroxy alcohols, such as propylene glycol and its oligomers,^{30,31} pentane-diols,³² and glycerol,^{4,19,20,33–36} in which extensive intermolecular H-bonding does occur, and $g > 1$ at low temperatures. (Certain mono-hydroxy long chain alcohols have shown a similar behavior,³⁷ but it is uncertain whether the Arrhenius variation of their f_m with T was accurately determined for two reasons: (i) limited temperature range of measurements and (ii) a decrease in their ϵ_s to a value approaching that of a nonpolar liquid at low temperatures.)

The α -relaxation process, which is normally observed in supercooled liquids^{11,12} and polymers,¹³ has been attributed to translational–rotational molecular motions. Its freezing out on the time scale of one's experiment causes the liquid's

vitrification. In this sense, 1-phenyl-1-propanol shows the dielectric relaxation behavior of a typical, low-molecular weight, non-H-bonded supercooled liquid,^{11,12} and this orientational diffusion would contribute to its viscosity and its structural relaxation.³⁸

We now consider the reasons for the broad dielectric relaxation spectra observed in the studies of rigid molecular liquids, flexible molecular liquids with and without intermolecular H bonds, and in H-bonded alcohols. The distribution of relaxation times implied by the broad spectra has been explained in terms of several formal mechanisms, some of which are inherent to a molecular rotation and others to the structure of the liquid. These are, the Glarum's defect diffusion model and its modifications,^{39,40} models for a dynamic heterogeneity,^{12,41,42} and those that require a multiplicity of single relaxation times.^{43–45} A somewhat unrelated mechanism that can account generally for both a single relaxation time and a distribution of relaxation times was proposed by Anderson and Ullman.⁴⁶ These arise from two conditions of the relative rates of fluctuations of the dipole with respect to the potential energy contour of its surroundings. In this fluctuating environment model, the dipolar reorientation occurs faster than the (molecular) environment of the dipole relaxes, i.e., the dielectric relaxation time is less than the structural relaxation time. In this case, the dipolar reorientation would occur in a fluctuating environment of potential energy landscape which itself changes with the angular orientation of the dipole, without the need for co-operativity. 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 Bueche⁴⁷ and the mode-coupling⁴⁸ consideration of the problem. In contrast, when the dipole relaxes slowly with respect to its environment, the averaging of the potential energy contours in the various environments causes the Debye-type relaxation.

Finally, the high-frequency relaxation is the usual⁴⁹ Johari–Goldstein relaxation process,^{11,12} which corresponds to localized motions of molecules, and which occurs over the entire range of the liquid and the vitrified state. Its three characteristics,⁵⁰ namely the broadening of the spectra, the decrease in $\Delta\epsilon$ on cooling, and the Arrhenius temperature dependence of the relaxation rate are consistent with the three features of the faster relaxation process observed for 1-propanol, many non-H-bonded liquids, and 5-methyl-2-hexanol.³

C. Temperature dependence of relaxation rates

Two aspects of the temperature dependence of the relaxation dynamics need be considered here. The first is an analysis of the variation of f_m with T in terms of the Adam and Gibbs configurational entropy theory.⁵¹ The data in Fig. 4 can be described by the empirical Vogel–Fulcher–Tammann equation,^{52–54}

$$f_m = A_{\text{VFT}} \exp[-B/(T - T_0)], \quad (4)$$

where T_0 and B are empirical parameters. As noted in Sec. III and Fig. 4, $A_{\text{VFT}} = 10^{13.32}$ Hz, $B = 1529.3$ K, and $T_0 = 155.1$. As stated earlier,⁵⁵ a further analysis may be done on the premise that the curved shape of the configurational entropy against the 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 terms in the Vogel–Fulcher–Tammann equation are seen as identical to that in the Adam–Gibbs equation,⁵¹

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

where z^* is the number of molecules forming a cooperatively rearranging region, $\Delta\mu$, is "...largely the energy barrier resisting the cooperative rearrangement per monomer segment,⁵¹ and R is the gas constant. Since, $z^* = 1$ in the high temperature limit, it has been shown that parameters of Eq. (3) can be estimated from knowledge of the parameters of Eq. (4) without implying that the temperature T_0 has a thermodynamic significance. This gave,⁵⁵ $\Delta\mu = 8.315B$ and $z^* = [T/(T - T_0)]$. By using the values of B and T_0 , as provided in Sec. III, we obtain $\Delta\mu = 12.7$ kJ/mol, $z^*(198.7 \text{ K}) = 4.56$, and $z^*(T_g)$ for $f_m = 10^{-4}$ Hz) = 5.05 for 1-phenyl-1-propanol. These values seem comparable to the values of 14.5 kJ/mol and 3.4, respectively, for ethylene glycol, 20.6 kJ/mol and 3.2 for glycerol, 15.7 kJ/mol and 4.9 for salol, and 13.1 kJ/mol and 6.4 for *o*-terphenyl, as listed in Tables I and II of Ref. 55, and 23.0 kJ/mol and 2.2 for 5-methyl-2-hexanol. Remarkably, the values for 1-phenyl-1-propanol (12.7 kJ/mol and 5.05) are higher than $\Delta\mu = 7.4$ kJ/mol and $z^*(T_g) = 3.4$ for process I in 1-propanol. They are also higher than the values of 7.8 kJ/mol and 4.3 for 2-methyltetrahydrofuran, of 7.4 kJ/mol and 5.7 for *d*-*l*, propylene carbonate, and 7.1 kJ/mol and 4.4 for 3-bromopentane. (Note that the value of $\Delta\mu$ for 2-methyltetrahydrofuran, *o*-terphenyl, *d*-*l*, propylene carbonate, 3-bromopentane, *n*-propanol and salol in Table II in Ref. 55 should be multiplied by 2.3026 in order to make them comparable with the form of Eq. (4) here and that given in Ref. 55. This error was caused by the use of the notation B in Refs. 1, 21, and elsewhere in a \log_{10} -based rather than the usual \log_e based Vogel–Fulcher–Tammann equation.) It should be stressed that a comparison between Eqs. (4) and (5), which are used to estimate z^* and $\Delta\mu$, require only the matching of the shapes of the plots of $\ln f_m$ against T at $T > T_g$ and this matching was 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 obtained by using a relatively long extrapolation.

The second aspect worth discussing is an analysis of f_m in terms of a temperature-variant Arrhenius energy, which has been recently expressed by Dyre *et al.*,⁵⁶ and Dyre⁵⁷ and in terms of what was called the "shoving model."⁵⁷ They considered that molecular interactions are anharmonic near T_g , with strong short-range repulsion and weak long-range attraction, and that a certain amount of energy is spent in the shoving of the surrounding molecules in a local region be-

fore diffusion can occur at all. This increases the volume of the aggregate from V to $V + \Delta V$. In this manner, a critical volume may be defined as, $V_C = 2(\Delta V)^2/3V$. This consideration ultimately lead to^{56,57}

$$f_m = A_{\text{Dyre}} \exp(-G_\infty V_C/k_B T), \quad (6)$$

where G_∞ is the temperature-dependent shear modulus of a liquid and k_B the Boltzmann constant. They^{56,57} argued that Eq. (6) resembles the expression obtained in the revised mode-coupling model,⁴⁸ when G_∞ is replaced by the zero-frequency bulk modulus. Although both G_∞ and V_C depend upon T , they surmised that the temperature dependence of V_C is negligible in comparison with that of G_∞ . Thus the energy term in the Arrhenius equation, $f_m = A_{\text{Arrhenius}} \exp(-E/RT)$ itself increases with decrease in T . Since the phonon-frequency values of the preexponential terms in Eqs. (5) and (6) are identical, a comparison of Eqs. (5) and (6) leads to $G_\infty V_C = z^* \Delta \mu$ when the quantities are represented in mole units. [It should be noted that neither Eq. (5) nor Eq. (6) implies that $f_m = 0$ at T_0]. For 1-phenyl-1-propanol, we calculate, $G_\infty V_C = 64.1$ (or, $z^* \Delta \mu = 5.05 \times 12.7$) kJ/mol. For comparison, $G_\infty V_C$ for other liquids at their T_g , as calculated from the data given in Tables I and II in Ref. 55 are: 25.1 kJ/mol for process I in 1-propanol, 77.2 for salol, 49.3 for ethylene glycol, 65.92 for glycerol, 50.6 for 5-methyl-2-hexanol, and 83.9 kJ/mol for *o*-terphenyl at T_g . The variation of $G_\infty V_C$ from 25 kJ/mol for 1-propanol to 84 kJ/mol for glycerol would be a reflection of the differences between their respective G_∞ and V_C values according to the shoving model.^{56,57} It should be noted that these values are smaller than those determined from the slopes of their $\ln f_m$ against $1/T$ plots at a specified temperature, according to Eq. (7). This may partly arise from the long extrapolation required to obtain the values of B and T_0 which have been used to estimate $z^* \Delta \mu$ here, and partly due to the poor fit of the data used for obtaining these parameters. It is perhaps more appropriate to determine the magnitude of $z^* \Delta \mu$ directly from the slope of the $\ln f_m$ against $1/T$ plot at a given temperature.

Finally, we consider a further aspect of variation of f_m with T . 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,^{58,59} namely, $f_m \sim (T - T_C)^\gamma$, and the second by Nagel *et al.*,⁶⁰ $f_m \sim [(T - T_C)/T_C]^\gamma$. There is finally the equation based on the mode-coupling theory,^{61,62}

$$f_m = A_{mc} [(T - T_C)/T_C]^\gamma, \quad (7)$$

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 Bertrand⁶³ have provided a somewhat different equation,

$$f_m = A_{SB} [(T - T_C)/T]^\gamma, \quad (8)$$

where A_{SB} , T_C , and γ are also empirical constants. Equations (7) and (8) were fitted to the data for the α -relaxation process in 1-phenyl-1-propanol, and the plots are shown in Fig. 8. The parameters used for fitting are, $A_{mc} = 10^{12.39}$, $T_C = 183.1$, and $\gamma = 13.14$ for Eq. (7), and $A_{SB} = 10^{16.54}$, T_C

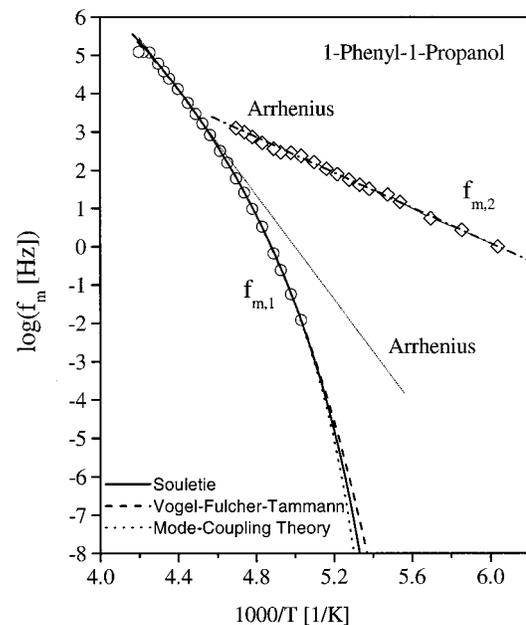


FIG. 8. A comparison of the fits of the Arrhenius equation, $f_m = 10^{34.07} \exp(-31196/RT)$, Vogel-Fulcher-Tammann equation, $f_m = 10^{13.32} \exp[-1529.3/(T - 155.13)]$, power law equation, $f_m = 10^{12.394} [(T - 183.11)/183.11]^{13.14}$, and the Souletie-Bertrand equation, $f_m = 10^{16.54} [(T - 178.65)/T]^{18.56}$ all for process I. The Arrhenius equation, $f_m = 10^{13.98} \exp(-10595/RT)$, is fitted to the $f_{m,2}$ data.

$= 178.65$, and $\gamma = 18.56$ for Eq. (8). Remarkably similar values of the parameters had been obtained for 5-methyl-2-hexanol.³

At first sight, the excellence of the fit seen in Fig. 8 would indicate that the theories on which Eqs. (7) and (8) are based are valid for 1-phenyl-1-propanol and 5-methyl-2-hexanol.³ However, in these theories, it is required that the critical exponent γ must be between 2 and 4. The values of γ observed here is evidently 3 to 4 times as high, which indicates that the theories are not valid, even though the data fit the relevant equations. We conclude that the fit of such equations to the experimental data is a general one. The theories had put a constraint on the value of γ , and that constraint is violated here, making the fit ambiguous and less meaningful in terms of these theories.

There are further implications of Eqs. (7) and (8) that need to be examined here. As discussed earlier,⁶⁴ the approach of f_m toward its high temperature value is quite different for the Vogel-Fulcher-Tammann and power law equations. To elaborate, in the high temperature limit, differentiating the former with respect to $1/T$ yields

$$[\partial(\ln f_m)/\partial(1/T)] \approx -B, \quad (9)$$

which implies that as $T \rightarrow \infty$, $\ln f_m \rightarrow \ln A$. In contrast, by differentiating the power law equations or Eq. (7) with respect to $1/T$ one obtains

$$[\partial(\ln f_m)/\partial(1/T)] \approx -\gamma T, \quad (10)$$

which implies that as $T \rightarrow \infty$, $\ln f_m \rightarrow \infty$.

Third, according to the power law, a plot of $\ln f_m$ against $1/T$ would show a point of inflexion at a temperature $T_x = 2T_C$, where $[\partial^2(\ln f_m)/\partial(1/T)^2]=0$. This point of inflexion has not been observed.⁶⁴

V. CONCLUSION

Replacement of a H atom by a phenyl group in a 1-propanol molecule creates steric hindrance and prevents intermolecular H bonding, and the Debye-type relaxation process which occurs in 1-propanol vanishes in 1-phenyl-1-propanol. The dynamics of the dielectric relaxation in 1-phenyl-1-propanol is found to occur by two processes, both of which have an asymmetric distribution of relaxation times. The predominant process is the α relaxation, which may be described by the Cole–Davidson function, with parameters that remain constant on cooling. The α -relaxation spectra therefore are superimposable, particularly when the Johari–Goldstein relaxation process is well separated from it. The strength of the dielectric polarization is much larger than that observed for the presumed α process in 1-propanol. For 1-phenyl-1-propanol, it is consistent with the conclusion that the α relaxation involves reorientation of H-bond-free molecules. A discussion in terms of the configurational entropy leads to a size of 4.6 molecules for the cooperatively rearranging region at 198.7 K, and 5.5 kJ/mol for the constant value of the potential energy barrier. Dyre *et al.*'s model^{56,57} for a temperature-dependent Arrhenius energy leads to a set of parameters whose values can be estimated by combining with the approximate relations of the configurational entropy theory and the Vogel–Fulcher–Tammann equation without implying an underlying thermodynamic transition in the equilibrium liquid below T_g . However, due to the uncertainty in the extrapolation of the parameters of the Vogel–Fulcher–Tammann equation the slope of the relaxation rate against $1/T$ plots is inconsistent with the slope estimated from the entropy theory. The power law equations fit the data well, but the critical exponent for 1-phenyl-1-propanol is three to four times as high as that required by the mode coupling theory, which had deduced the power law. This indicates that fitting of such power law is ambiguous, and inconsistent with mode-coupling or other theories. The high frequency mode is assigned to Johari–Goldstein^{11,12} relaxation process, since it meets all the relevant criteria,⁵⁰ outlined in section IV B. This process is found to be governed by Havriliak–Negami⁶⁵ distribution of relaxation times for 1-phenyl-1-propanol, as was found before for 5-methyl-2-hexanol,³ isoamyl bromide,¹⁸ and solutions of isoamyl bromide in 2-methylpentane.⁶⁶

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