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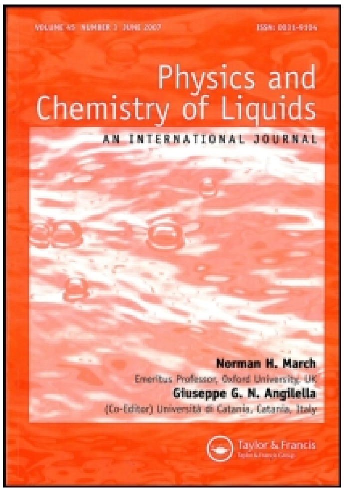

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Liquid Structure and Dielectric Relaxation of Some Isomeric Methylheptanols‡

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Abstract—The dielectric permittivity and loss of 6-, 4-, and 2-methyl-1-heptanol have been measured over a wide range of frequency and temperature. The equilibrium polarization of all three isomers and its temperature dependence is similar, which suggests that the type and extent of intermolecular association is also similar. A model of H-bond association to chain n-mers is proposed. Dielectric relaxation is Debye-like for all three liquids; the activation parameters are shown to be sensitive functions of the isomer structure. A qualitative model of relaxation in which H-bond rupture is a prerequisite rather than a rate determining step is proposed. Relaxation in other isomeric octanols and monoalcanols is discussed from this point of view.

Introduction

Monohydric alcohols are one of the most thoroughly studied[1–3] class of compounds as far as dielectric relaxation is concerned. The earliest experiments seemed to substantiate Debye's viscous-damped sphere-in-continuum model of relaxation because the polarization decayed exponentially, as predicted by the theory. Subsequently it became apparent that the agreement was fortuitous, that Debye's model was really inapplicable because either unrealistic molecular radii or an empirical "microviscosity" had to be invoked to achieve agreement. As it became clear that liquids which are believed to be unassociated—alkyl halides, ketones, etc.—also do not obey the Debye equation, Debye-type relaxation came to be considered a consequence of the associated nature of the liquid. This point of view naturally emphasized the hydrogen-bonded intermolecular interactions as the fundamental structural feature of the liquid, and the nature of the remainder of the molecule, i.e., the structure of the alcohol's alkyl group, was generally accorded little attention.

Recently,[4–5] however, it has become increasingly evident that the specific nature of the alkyl group—the overall size and shape—plays an

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important role in determining both the equilibrium and dynamic electric polarization of alcohols. While the existence of intermolecular association remains a crucial factor, it is also clear now that a molecular theory of dielectric polarization will have to take into account the "fine structure" of the alcohol. Since a satisfactory theory still has not been proposed, a wide variety of experimental data is desirable to spur efforts in that direction.

We report equilibrium and dynamic dielectric data for three isomeric octyl alcohols and summarize data now available for several others.

Experimental

Bridges and Cells.[5] A transformer ratio-arms impedance bridge was used for the frequency range 0.050–500 kHz and an ultra-low frequency (ULF) bridge served for the range 0.1–200 Hz. The cell is a three terminal, guarded, parallel plate type of nominal cell constant 15 pf. Corrections for the small stray capacitance and the temperature coefficient of the cell constant were applied; we estimate the permittivity accurate to 0.1% and the loss to 1%. The cell was immersed in a well stirred regulated bath whose temperature could be controlled to better than ± 0.1° during the course of a run. Temperature was monitored with a Cu-constantan thermocouple inside the cell.

Samples. 6-Methyl-1-, 4-methyl-1-, and 2-methyl-1-heptanol, referred to hereafter as 6; 1, 4; 1, and 2; 1, respectively, were prepared by Chemical Samples Company, the products stated to be 98% pure. Because the only literature reference[6] pertaining to these compounds is of questionable veracity, and because the essence of our investigation is to probe the effect of small structural changes on physical properties, we undertook the synthesis of these alcohols by hydroboration of the appropriate alkenes in order to ensure the identity of our test samples. Products of the hydroboration were separated by preparative GC. IR and NMR spectra served to differentiate the three isomers uniquely and to intercompare both sets of alcohols. We are confident that the samples used for dielectric studies are pure.

Results

Equilibrium Polarization. The equilibrium dielectric constant of the three isomers, interpolated from large scale graphs, is tabulated as a function of temperature in Table 1. Our results agree well with Smyth and Stoops' data[7] for 6;1 but disagree markedly for 4;1 and 2;1.

Dielectric Relaxation. The dielectric dispersion loci plotted in the complex plane are similar for all three isomers: a low frequency, semicircular arc of the Debye type accounts for more than 95% of the dispersion. At the lowest temperatures and for the highest frequencies a small residual dispersion, which seems to be characteristic of unhindered alcohols,[1-3] was found. The relaxation times of the principal, low frequency, dispersion were obtained from the frequency of maximum loss or from the slope of the linear test plots proposed by Cole.[8] These data are plotted in Fig. 1 according to the equation

$$\tau = A \exp(E_a/RT) \qquad (1)$$

and literature data for closely related isomers are also plotted for comparison. The relaxation parameters A and E_a are listed in Table 2. No attempt was made to analyze the high frequency residual dispersion except to note qualitatively that subtraction of the contribution of the low frequency dispersion resulted in a broad arc whose center frequency was about 100 times greater than the critical frequency of the primary dispersion.

TABLE 1 Equilibrium dielectric constant as a function of temperature.

t, °C	2-methyl-1-heptanol	4-methyl-1-heptanol	6-methyl-1-heptanol
130	3.86	4.30	4.30
110	4.25	4.78	4.80
90	4.63	5.46	5.54
70	5.42	6.43	6.52
50	6.54	7.65	7.86
30	8.48	9.37	9.50
20	9.77	10.36	10.45
10	11.20	11.44	11.42
-10	14.05	13.85	13.72
-30	17.02	16.43	16.22
-50	20.35	19.33	18.90
-70	23.81	22.32	21.91
-90	(27.7)[a]	(26.1)[a]	(24.7)[a]

[a] Slight extrapolation.

Discussion

Equilibrium Polarization. A comparison with literature[9] data for 7;1

TABLE 2 Parameters of the dielectric relaxation equation

$\tau = A \exp(E_a/RT)$

	E_a, Kcal/mole	$-\log A$
6-methyl-1-heptanol	10.8	16.9
4-methyl-1-heptanol	11.4	17.5
2-methyl-1-heptanol	12.5	18.0
1-octanol[a]	8.65	15.2
2-ethyl-1-hexanol[b]	12.4	17.9
2, 2-dimethyl-1-hexanol[c]	20.0	24.4

[a] Ref. 9 of text. [b] Ref. 11 of text. [c] Ref. 12 of text.

(1-octanol) shows that 7 ; 1, 6 ; 1, and 4 ; 1 are essentially equivalent as far as their equilibrium polarization and its temperature dependence is concerned. Because all octanol isomers have virtually identical densities, thermal expansivities, and (presumably) dipole moments, this implies that 7 ; 1, 6 ; 1, and 4 ; 1 have the same Kirkwood correlation factor, *g*, and the same value for dg/dT over this large temperature range. This behavior is entirely consistent with our previous results[10] which predict that if the $-$OH group of an alcohol is "unhindered" sterically, the correlation factor should be greater than unity and increase with decreasing temperature, its magnitude and temperature dependence being determined by the equilibrium constant for the intermolecular association into linear chain species

$$\mathrm{ROH} + (\mathrm{ROH})_n = (\mathrm{ROH})_{n+1}.$$

The model previously developed assumes that ΔH of association is constant for all the isomeric octanols and that differences in the association constant—and hence in *g* and dg/dT—are due to differences in ΔS of chain association which are determined largely by steric factors. Thus, we interpret our results to imply that intermolecular association is not appreciably affected by moving a branch methyl group along the hydrocarbon chain from the 7- to the 4-position if the $-$OH group is far removed, viz., on the terminal group. On the basis of our experience, we predict that literature[7] dielectric data for 5-methyl-1-heptanol and 3-methyl-1-heptanol are incorrect, presumably because of sample impurities as we have suggested for others of the samples prepared by Reid.

The dielectric constant and thus, too, the correlation factor of 2 ; 1 is slightly less than that of 4 ; 1 or 6 ; 1 at high temperatures but becomes greater at low temperatures. We interpret this, as before,[10] to be due to increased steric interference of the neighboring methyl group in 2;1, leading to a more negative ΔS for chain association. However, the more restricted conformations available for the chain are those that favor parallelism of near-neighbor dipoles in the chain, thus enhancing the dielectric polarization at low temperature. Concomitantly, they favor disruption of the chain structure at high temperatures.

In summary, we believe that both the type (linear chain) and extent of intermolecular association in pure liquid 7;1, 6;1, and 4;1, are similar over the entire range of temperature covered in our study. Based on previous[10] calculations, we estimate that ΔH° of chain association is about -6.7 Kcal/mole; $\Delta S^\circ \approx -16$ eu. The steric interference of the methyl group in 2;1 decreases the extent of chain association slightly, but we believe the similarity in behavior to the other three isomers to be more significant than this small difference.

Dielectric Relaxation. In view of the similarity of the equilibrium liquid structure adduced above, the difference in the relaxation behavior indicated in Fig. 1 and Table 2 is striking. It is obvious that even the subtle change of moving a methyl group from the terminal 7- to the adjacent 6-position affects the kinetics of the polarization, while bringing the methyl group to the 2-position, adjacent to the $-OH$ group, has a profound influence. Substitution of an ethyl group in the 2-position (2-ethyl-1-hexanol)[11] for the methyl group is relatively ineffective, but dimethyl substitution (2, 2-dimethyl-1-hexanol)[12] causes another large change in the activation parameters. As shown in previous work,[5] still more drastic structural changes, such as moving the $-OH$ to an interior position of the chain and bringing a branch methyl group nearby, as exemplified by 5-methyl-3-heptanol for instance, causes relatively little additional change in the relaxation parameters as long as the steric interference about the $-OH$ group is not so large as to change the *type* of intermolecular association.

The present results tend to bolster the belief that H-bond breaking is *not* the rate determining step in the relaxation process. Rather, they lend credence to the qualitative model which considers H-bond rupture a prerequisite for dipolar reorientation. It is envisaged that a particular H-bond will break and reform many times without reorientation of either the donor or acceptor molecule. Because the local liquid alcohol structure remains, on average, chain associative, the dipolar reorientation is necessarily cooperative and occurs relatively seldom. When it does occur,

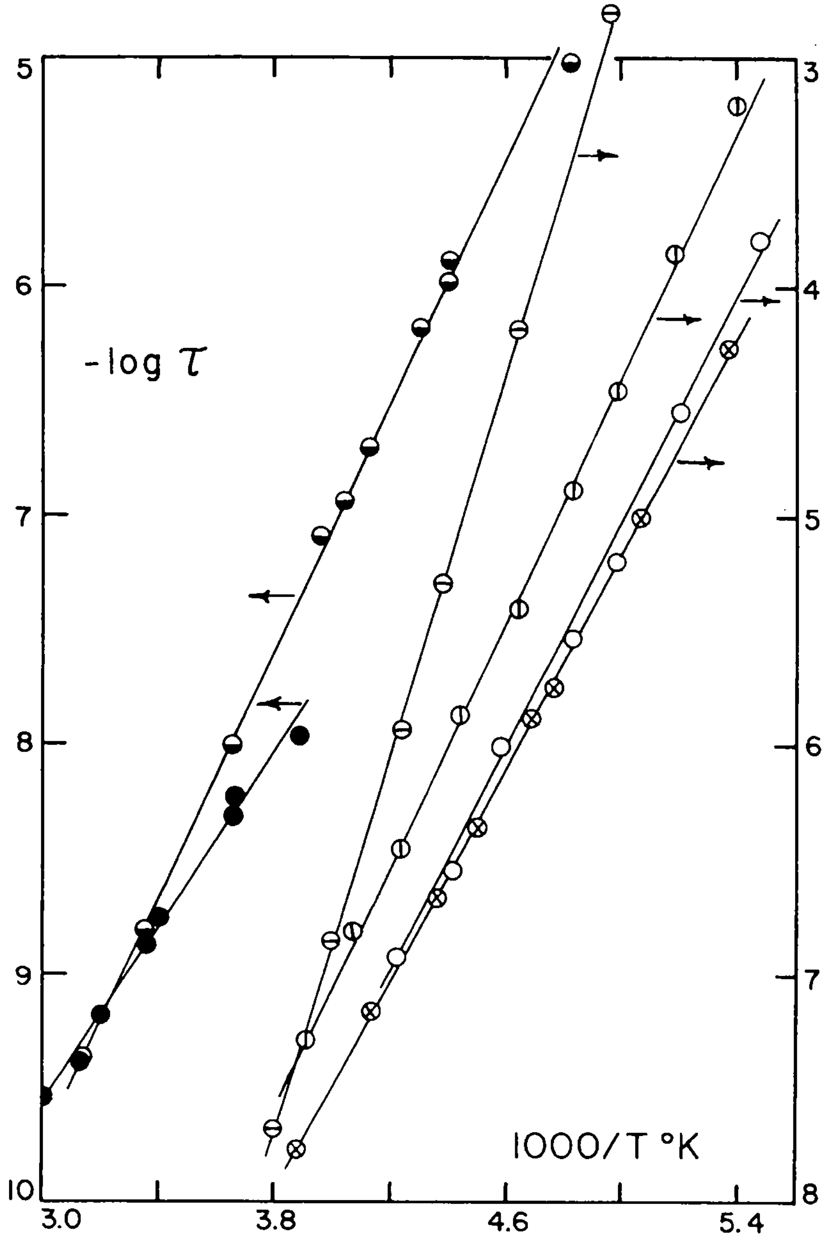

Fig. 1. Logarithm of the dielectric relaxation time as a function of reciprocal absolute temperature. *Left ordinate:* ●, 1-octanol, Ref. 9; ◒, 2-ethyl-1-hexanol, Ref. 11. *Right ordinate:* ⊗, 6-methyl-1-heptanol; ○, 4-methyl-1-heptanol; ⦶, 2-methyl-1-heptanol; ⊖, 2, 2-dimethyl-1-hexanol, Ref. 12.

the rate of reorientation depends on the size and shape of the entire molecule insofar as this determines the interaction of a specific molecule with its "surroundings" and also because the structure of the molecule determines the nature of the surroundings. The more highly branched the alkyl group and the more sterically hindered the $-OH$ group, the greater will be the required degree of cooperation.

If the alkyl group is small and unbranched, and/or the amount of "free volume" available is large (high temperature, low pressure), then reorientation may occur so easily that H-bond breaking becomes the rate-determining step. On the basis of the Kirkwood correlation factor, we conclude that methanol is more extensively associated than *n*-decanol but the relaxation time in pure methanol (ca. 6 psec at 20 °C)[13] is not much more than methanol in very dilute benzene solution (1 psec)[14] where H-bonding and other intermolecular interactions are presumably absent. The corresponding relaxation times for *n*-decanol are 2000[1] and 36 psec,[14] respectively. The highly associated nature of liquid methanol only perturbs the reorientation slightly while it dominates the behavior of decanol even though the extent of intermolecular association is apparently less.

Dielectric relaxation in the lower alcohols is strongly non-Arrhenius[3]—the apparent activation energy increasing with decreasing temperature—while relaxation in the higher alcohols, and especially in the sterically hindered species, follows the Arrhenius equation over the same range of relaxation times. The temperature dependent activation parameters of the former class of compounds reflects a transition from the relatively free reorientation, rate-determined in the limit by H-bond breaking, to the mechanism suggested above. In the latter class of alcohols, the molecular reorientation depends strongly on the nature of the alkyl group; they are effectively in the "low temperature" region at all accessible temperatures. If this conjecture is correct, the relaxation behavior of this latter class should become non-Arrhenius at *higher* temperatures than studied so far, and the distinction between isomers should largely disappear under those conditions.

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