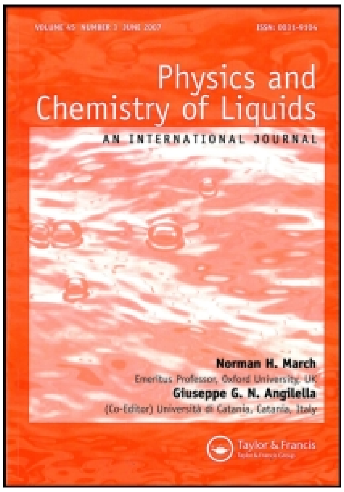

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Dielectric Properties of Isomeric Phenyl Propanols†

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Abstract—The dielectric constant and loss of 1-phenyl-1-, 1-phenyl-2-, 2-phenyl-2-, and 3-phenyl-1-propanol have been measured as a function of temperature for $f < 0.5$ MHz. The equilibrium polarization depends markedly on the proximity of the phenyl and hydroxyl groups, apparently as a steric factor and not because of any specific OH-phenyl interaction. Dielectric relaxation in these liquids can be described in terms of overlapping Debye regions but for the most sterically hindered species the regions overlap so closely that the Davidson–Cole skewed-arc function becomes a more useful description. Activation energies depend on the degree of steric hindrance; this suggests that H-bond breaking is not the rate determining step in the relaxation mechanism.

Introduction

The dielectric properties of a large number of liquid monohydric alcohols have now been studied over extensive ranges of frequency and temperature,(1) concentration in various solvents,(2) and in more limited cases, pressure.(3) The results may be summarized briefly as follows: the equilibrium polarization is a sensitive function of the type and extent of intermolecular association—presumably via H-bonding—which is governed largely by steric factors in the vicinity of the $-$OH group. Dielectric relaxation in pure liquid monohydric alcohols exhibits a general similarity for all species: most of the dispersion is due to a process which may be characterized by a single relaxation time (rate constant) formally in accord with Debye's theory. Deviations from Debye behavior are usually found for $\omega\tau_1 \gg 1$ (τ_1 = relaxation time of the Debye-type dispersion) and attempts have been made to analyze these deviations in terms of additional discrete relaxation processes. The kinetics of the principal

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(lowest frequency) relaxation process depend very much on the size and shape of the hydrocarbon portion of the alcohol. Thus, the original idea that the principal relaxation process is governed by the rate of H-bond breaking has been modified; intermolecular H-bond breaking has been suggested to be a prerequisite, rather than the rate determining step, for dipolar reorientation.(1) However, the most striking feature of the relaxation process is the sufficiency of a single relaxation time to define the major portion of the dispersion, and this fact has never been adequately explained. In this respect, Anderson and Ullman's(4) model calculation based on Kauzmann's fluctuating environment idea is attractive from a conceptual point of view.

There is considerable interest, therefore, in reports that dielectric relaxation in some monohydric alcohols does *not* obey the Debye equation. Davidson(5) has shown that tetrahydrofurfuryl alcohol follows the Davidson–Cole(6) skewed-arc equation; Fujimura and Kamiyoshi(7) have reported that cyclohexanol does too, although Corfield and Davies'(8) data don't bear this out. Bennett,(9) in a brief paper, stated that 3-phenyl-l-propanol and 2-phenylethanol obey the Debye equation but that 1-phenyl-1-propanol does not. Bennett stated that 1-phenyl-1-propanol conforms to the skewed-arc function whose distribution parameter, β, increased with increasing temperature as found for glycerol and alkyl halides-archtypal compounds for the skewed-arc function. Bennett showed that the equilibrium polarization of 1-phenyl-1-propanol was much smaller, and the activation energy for relaxation was much greater, than the corresponding values for 3-phenyl-1-propanol or phenylethanol. He proposed that the effects must be due to the close proximity of the phenyl and hydroxyl group in 1-phenyl-1-propanol.

It was the intent of this investigation to repeat and extend Bennett's studies in the hope that this would help our understanding of the equilibrium and dynamic structure of associated liquids. This paper reports atmospheric pressure dielectric data for four isomeric phenylpropanols; a subsequent communication will discuss an extensive study of the pressure dependence of dielectric relaxation and viscous flow in 1-phenyl-1-propanol.

Experimental

1-phenyl-1-propanol (hereafter designated 1-1), 1-phenyl-2-propanol (1-2), 2-phenyl-2-propanol (2-2) and 3-phenyl-1-propanol (3-1) were obtained from Chemical Samples Co. Their purity is stated to be 98%. 1-1, 2-2, and 3-1 were refluxed over CaH_2; 1-2, which reacted with CaH_2, was dried over $MgSO_4$. All compounds were subsequently vacuum fractionated shortly before use.

Dielectric measurements were performed with bridges and associated apparatus which has been described elsewhere.(10)

The density of 1-1, 1-2, and 2-2 was determined pycnometrically at 25 and 60 °C. The relation $\rho(t) = \rho(0) - \alpha t$ was assumed and $\alpha = 7.5 \times 10^{-4}$ g/cm³-°C was found for each isomer.

Results

The equilibrium dielectric constant was plotted as a function of temperature for each compound. Data interpolated at integral temperatures are listed in Table 1 and plotted in Fig. 1. Our equilibrium data for 1-1 and 3-1 agree well with Bennett's.

By cooling the liquids it was possible to study dielectric relaxation in 1-1, 2-1, and 3-1 at test frequencies less than 0.5 MHz. Some typical Cole–Cole plots are shown in Fig. 2, and pertinent results are listed in Table 2. 2-2 freezes at 20 °C and all attempts to supercool it were unsuccessful; hence we have no relaxation data for this compound.

TABLE 1 Equilibrium dielectric constant as a function of temperature

Temp. °C.	3-phenyl-1-propanol	1-phenyl-2-propanol	1-phenyl-1-propanol	2-phenyl-2-propanol
+100	–	5.37	5.03	4.82
80	–	5.90	5.37	5.07
60	–	6.61	5.66	5.31
40	–	7.68	6.61	5.52
30	10.9	8.45	6.38	5.61
20	11.97	9.35	6.68	–
0	14.35	11.68	7.47	–
–20	17.18	14.92	8.65	–
–40	20.52	19.04	10.70	–
–60	24.36	(23.7)[a]	(14.0)[a]	–

a. Slight extrapolation.

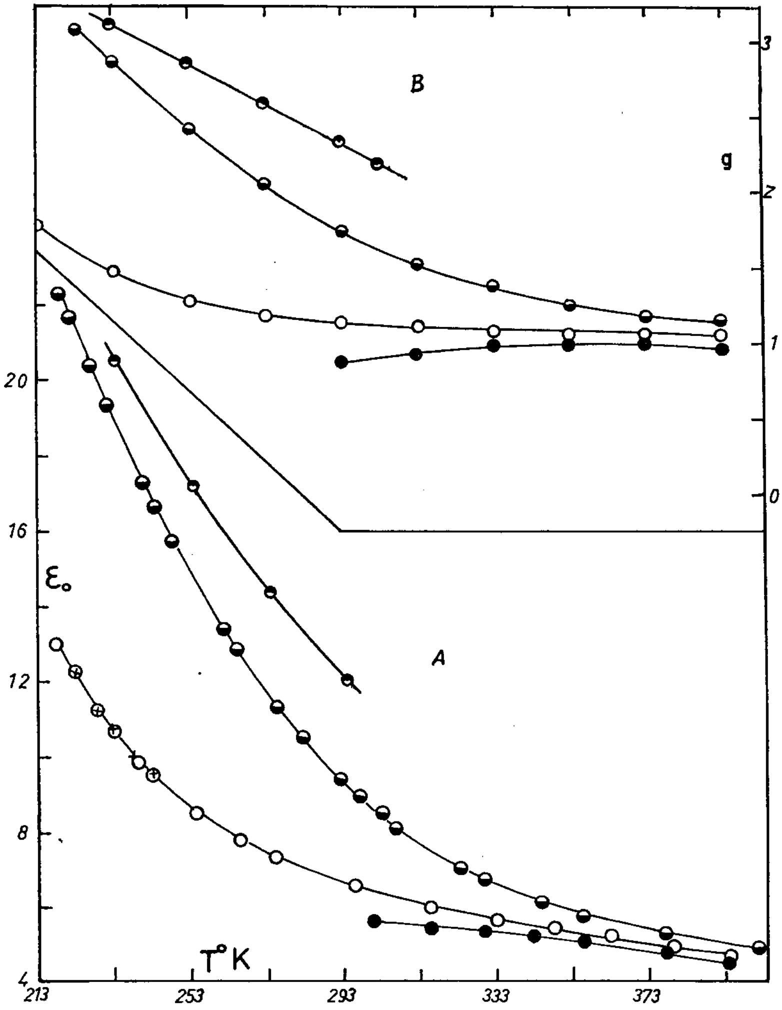

Figure 1. A (bottom): Equilibrium dielectric constant as a function of temperature. ●, 2-phenyl-2-propanol; ○, 1-phenyl-1-propanol; ×, Bennett's results for 1-phenyl-1-propanol; ◒, 1-phenyl-2-propanol; ◓, 3-phenyl-1-propanol. B (top): Kirkwood *g*-factor as a function of temperature. Same symbols as A.

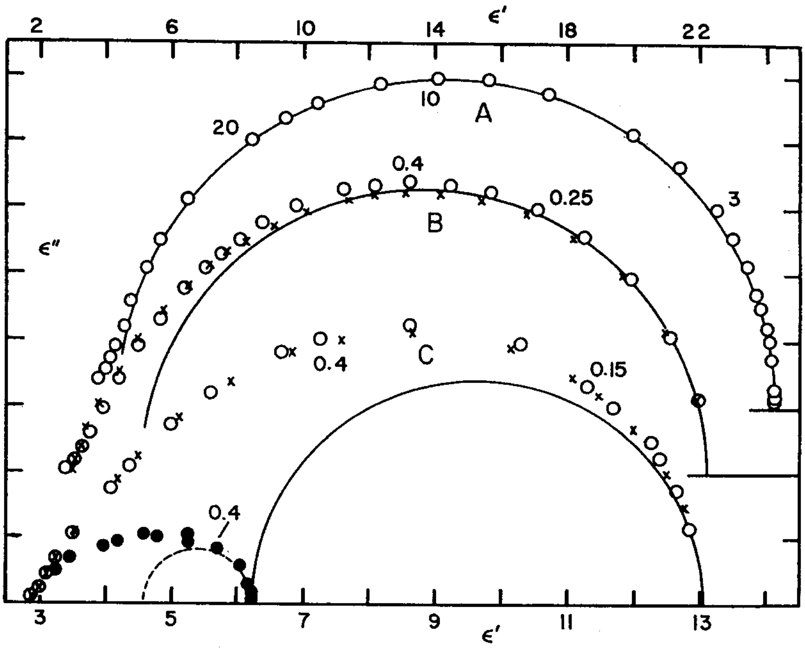

Figure 2. Cole–Cole plots for phenyl propanols. A (upper abscissa): 3-phenyl-1-propanol at 214 °K. ○, experimental points with frequency indicated in KHz. Soid line is best estimate of Debye function with $\epsilon_0 = 24.3$, $\epsilon_1 = 4.4$, $\tau = 15.6\,\mu$s. B (upper abscissa): 1-phenyl-2-propanol at 219 °K. ○, experimental points with frequency indicated in KHz. Solid line is best estimate of Debye function with $\epsilon_0 = 22.12$, $\epsilon_1 = 5.4$, $\tau = 417\mu$s. ×, best fit to Davidson–Cole function with $\epsilon_0 = 22.12$, $\epsilon_1 = 2.82$, $\beta = 0.76$, $\tau_0 = 511\,\mu$s. C (bottom abscissa): 1-phenyl-1-propanol at 218 °K. ○, experimental points with frequency indicated in KHz. Solid line is best estimate of Debye function with $\epsilon_0 = 13.13$, $\epsilon_1 = 6.2$, $\tau = 630\,\mu$s. ●, residual data after subtraction of Debye function. Dashed line is qualitative estimate of a second Debye function. ×, best fit to Davidson–Cole function with $\epsilon_0 = 13.05$, $\epsilon_1 = 2.80$, $\beta = 0.65$, $\tau_0 = 750\,\mu$s.

Discussion

The dependence of the equilibrium polarization on the structure of these isomeric alcohols is most concisely shown by examining the Kirkwood$^{(11)}$ " *g*-factor " (plotted in Fig. 1), a measure of the orientational correlation between dipoles. In lieu of reliable data we have assumed that all isomers have the same dipole moment, 1.68 Debye. As Bennett surmised, increasing the steric interference in the vicinity

TABLE 2. Dielectric relaxation parameters

T °K	ϵ_0	ϵ_{1D}[a]	τ_1[b]	ϵ_{1S}[c]	β	τ_0[d]	$1.1n_D^2$
			1-phenyl-1-propanol				
218	13.13	6.2	630	2.80	0.65	750	2.68
223	12.22	5.6	113	2.80	0.62	156	2.67
229	11.26	5.6	18.6	2.90	0.66	22.4	2.66
233	10.71	5.5	5.74	2.80	0.63	6.99	2.65
239	9.89	–	1.44	–	–	–	2.64
244	9.45	–	0.501[e]	–	–	–	2.63
254	8.54	–	0.0485[e]	–	–	–	2.61
			1-phenyl-2-propanol				
219	22.12	5.4	417	2.82	0.76	511	2.69
223	21.46	6.9?	153	2.88	0.73	175	2.67
227	20.39	4.5	26.4	3.02	0.79	33.2	2.66
232	19.39	4.8	7.59	3.22	0.83	8.78	2.65
236	18.35	–	2.24	–	–	–	2.65
240	17.36	–	0.748[e]	–	–	–	2.64
245	16.67	–	0.350[e]	–	–	–	2.63
249	15.76	–	0.150[e]	–	–	–	2.62
262	13.43	–	0.0180[e]	–	–	–	2.61
			3-phenyl-1-propanol				
207	25.6	4.5	81.0	–	–	–	2.70
214	24.3	4.4	15.6	–	–	–	2.69
233	20.5	–	0.386[e]	–	–	–	2.65
252	17.5	–	0.0428[e]	–	–	–	2.62

a. ϵ_{1D} =high-frequency limit of the principal Debye dispersion; b. Relaxation time (μs) of the principal Debye dispersion. For 1-2, we estimate $\tau_{2D} \approx 0.1\tau_{1D}$ at the lowest four temperatures. For 1-1, we estimate $\tau_{2D} \approx 0.3$–$0.5\tau_{1D}$; c. ϵ_{1S} =high-frequency limit of the Davidson–Cole skewed-arc function; d. Terminal relaxation time (μs) of the skewed-arc function; e. Evaluated from conductance dispersion.

of the –OH group diminishes the extent of intermolecular association, as exemplified by the g's of 2-2 and 1-1 which remain close to unity, indicative of no net correlation, over most of the temperature range. Because chainwise association favors parallel orientations of neighboring dipoles in the chain ($g > 1$) while association to small rings leads to anti-parallel orientations ($g < 1$), it appears that in 2-2 and 1-1 these effects are missing or largely cancel. Whether the lack of extensive association is due only to steric factors or whether the close proximity of the phenyl and –OH groups leads to intramolecular H-bonding which precludes intermolecular association, is not clear. However, for 2-1 and 3-1, the large g's and $\mathrm{d}g/\mathrm{d}T < 1$ are indicative of a favored chainwise association as is found in most "unhindered" aliphatic alcohols.(1,10) If there is intermolecular H-bonding to phenyl groups in 2-1 and 3-1 it seems not to interfere seriously with intermolecular OH · · · H bonding.

Our relaxation data substantiate Bennett's results for 3-1 as the Cole–Cole plot of Fig. 2 illustrates. The major part of the dispersion follows the Debye equation with a slight departure only at the highest frequencies. As shown in Fig. 3, an interpolation of our relaxation times to –60° agrees very well with Bennett's result but we disagree as to the activation energy. The Arrhenius plot for 3-1 may be curved; we estimate E_a to lie between 18 and 23 Kcal compared to Bennett's value of 14.7. This discrepancy notwithstanding, the relaxation process in 3-1 appears entirely "normal" and the mere presence of the phenyl group has no unusual effect.

Moving the –OH group from the terminal to the middle carbon atom of the propane residue changes 3-1 to 1-2. The expected greater steric hindrance is reflected in the somewhat smaller g's (Fig. 1). However, contrary to Bennett's observation for 2-phenylethanol, the Cole–Cole plots for 1-2 no longer look like "simple" Debye loci, as is illustrated in Fig. 2. If, as before, we consider the dispersion to be principally a Debye type with high frequency deviations then, compared to 3-1, the deviations begin at relatively much lower frequencies and are relatively larger in magnitude. Attempts to resolve the dispersion objectively(12) into a low-frequency Debye portion and a residual have been only qualitatively successful: there is a great deal of scatter of the residual data in the region of overlap and consequently it has been impossible to delineate the parameters of the second region precisely. It is clear though that over the temperature range available $\tau_1 \approx 10\tau_2$, a result which is nearly independent of the relative amplitudes of the two dispersion regions. Similar observations have been made for sterically hindered aliphatic alcohols(3,10) so the important factor seems to be the sheer bulk of the sterically hindering group rather than its aromatic character.

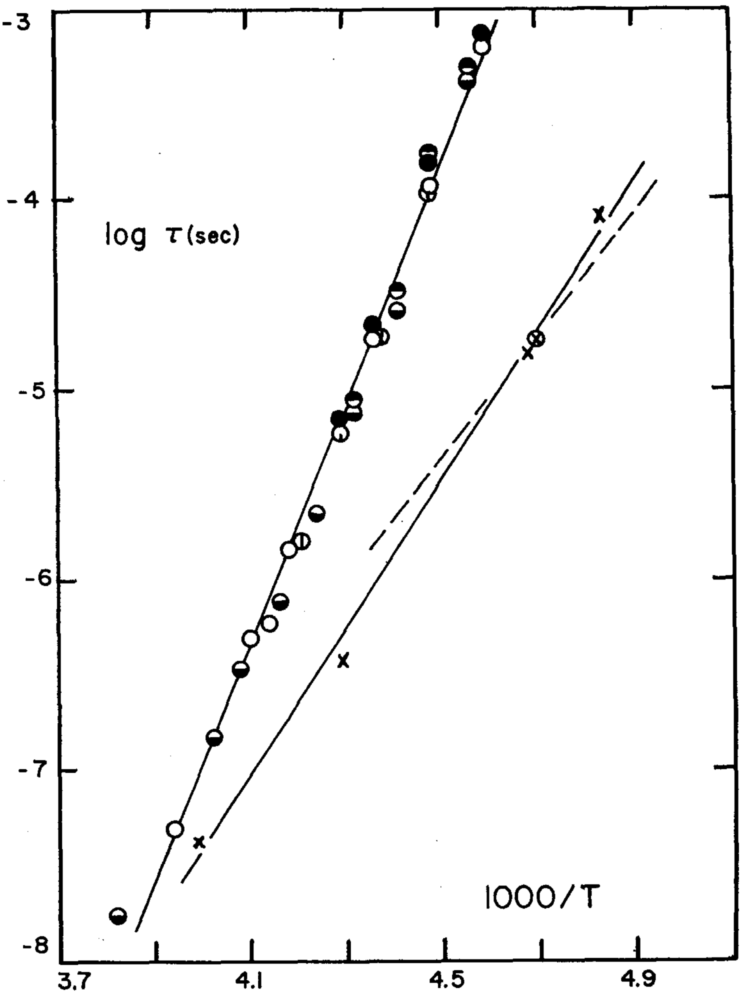

Figure 3. Logarithm of relaxation time as a function of reciprocal temperature. ○, relaxation time of principal Debye dispersion for 1-phenyl-1-propanol. ●, this investigation, and ⦶, Bennett's results, for the Davidson–Cole parameter τ_0 for 1-phenyl-1-propanol. ◒, Debye relaxation time and ◓, Davidson–Cole τ_0, for 1-phenyl-2-propanol. The line corresponds to a molar activation energy of 29 Kcal. ×, Debye relaxation time this investigation, and ⊕, Bennett's results, for 3-phenyl-1-propanol. Solid line corresponds to an activation energy of 18 Kcal; dashed line is Bennett's result, 14.7 Kcal.

The molar activation energy, 29 Kcal, which is about the same for the first and second dispersion, is much greater than that for 3-1. Again, this is in accord with previous observations(1,10) that the activation energy for dielectric relaxation in monohydric alcohols is a sensitive function of the size *and shape* of the hydrocarbon portion of the molecule. As we have discussed previously,(1) such large activation energies can hardly be ascribed to H-bond breaking.

The Cole–Cole loci of 1-2 bear a striking resemblance to Davidson–Cole skewed-arcs. We fit(13) the experimental data to the Davidson–Cole function with the parameters listed in Table 2. The terminal relaxation time, τ_0, is plotted vs. T^{-1} in Fig. 3 for comparison with τ_1, the relaxation time deduced on the basis of superposition of Debye dispersions, and it has the same temperature dependence.

The results for 1-1 are similar in most respects to those for 1-2 although the closer proximity of the phenyl and hydroxyl groups leads to qualitative differences. The Kirkwood g-factor (Fig. 1) is now nearly unity over much of the temperature range, indicative of either very little chain association or a balance between association to short chains and small, slightly polar, rings. Similar behavior has been observed for highly hindered aliphatic alcohols.

Although the Cole–Cole plots for 1-1 and 1-2 seem dissimilar (see Fig. 2), the difference can be ascribed almost entirely to the smaller equilibrium polarization of 1-1. The dispersion may be resolved qualitatively into two very closely overlapping Debye loci plus residual polarization or it may be fit quite adequately by the Davidson–Cole skewed-arc function, as is illustrated in Fig. 2. We can find no reason to prefer one representation (overlapping Debye) to the other (Davidson–Cole skewed-arc) on the basis of our data. It seems that as the hydrocarbon portion of the alcohol molecule becomes bigger and bulkier, the kinetics of the various relaxation processes approach each other so that a description in terms of discrete relaxation times and relaxation mechanisms becomes increasingly awkward while the notion of a distribution of processes becomes increasingly appropriate. Unfortunately, neither way of considering the matter answers the basic question: what is the nature of the various relaxation processes?

Irrespective of the dispersion representation, we conclude that dielectric relaxation in 1-1 and 1-2 is essentially similar despite the substantial difference in equilibrium polarization due to steric hindrance. In contrast, although the equilibrium polarization of 3-1 and 1-2 is quite similar, the relaxational behavior differs greatly. These results are consistent with the premise that the relaxation mechanism of monohydric alcohols, while dependent on the H-bonded intermolecular association, become increasingly influenced by the size and shape of the hydrocarbon portion of the molecule as this becomes large and bulky. The rate of H-bond rupture, which may be rate determining for dipolar reorientation in the lowest aliphatic alcohols, is no longer rate determining in a mechanism which can be schematized as

$$A_m(\text{associated, orientation} \uparrow) = mA\ (\text{monomer, orientation} \uparrow) \quad (1)$$

$$A\ (\text{monomer}, \uparrow) = A\ (\text{monomer}, \downarrow) \quad (2)$$

$$nA\ (\text{monomer}, \downarrow) = A_n\ (\text{associated}, \downarrow) \quad (3)$$

The single relaxation time which defines the kinetics of the major portion of the polarization eliminates the possibility that n-mers reorient as discrete units. The assumption that dipolar reorientation occurs only when a molecule is *not* intermolecularly associated, and the dependence of the activation parameters on the size and shape of the molecule, implies that reaction 1 is a fast equilibration which is prerequisite for reaction 2. Once the individual molecules have equilibrated with the new direction of the field they will again associate—either with the same or with different neighbors than before. The fact that the equilibrium polarization indicates an overall association ensures the existence of equilibria 1 and 3. This mechanism is consistent with Anderson and Ullman's fluctuating environment model for dielectric relaxation: if the association equilibrium is attained rapidly compared to the reorientation, the environment about any specific reorienting molecule will be averaged during the reorientation time and will be essentially the same for all molecules, thus resulting in the single relaxation time. The mechanism also permits the rationalization of the observed dependence of the relaxation time on the size and shape of the molecule. We have shown elsewhere(3) that a large activation enthalpy also implies a large activation volume, i.e., a large pressure coefficient for relaxation. The very large activation enthalpy observed for 1-1 implies that its dielectric relaxation will be extremely pressure dependent. This has indeed been observed and will form the subject of a subsequent paper.

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12. Subjective graphical methods to resolve closely overlapping dispersion regions are notoriously inadequate. See Refs. 5 and 6 for some discussion. We have developed a computerized analysis of permittivity and loss data, based on the linear forms of the Debye equation due to Cole,(6) which yields greatly improved results for a wide variety of synthetic data. All of the experimental results have been analyzed in this manner. See *J. Chem. Phys.* **55**, 629 (1971).
13. We have developed a computer program which, given the equilibrium dielectric constant, ϵ_0, finds the best value for ϵ_1 and β of the skewed-arc function, the value of τ_0 being determined from the frequency where $\tan\{\beta^{-1}\tan^{-1}[\epsilon''/(\epsilon'-\epsilon_1)]\} = \omega\tau_0$ is unity. Our criterion of the " best " fit is minimization of the average absolute error $\Delta = N^{-1}\Sigma[|(\epsilon'_{\mathrm{calc}} - \epsilon_{\mathrm{obs}})/\epsilon'_{\mathrm{obs}}| + |(\epsilon''_{\mathrm{calc}} - \epsilon''_{\mathrm{obs}})/\epsilon''_{\mathrm{obs}}|]$ This function weights the higher-frequency data most heavily (since ϵ' and ϵ'' are both small) at the expense of data near $\epsilon''_{\mathrm{max}}$. Minimization of the average absolute difference, which essentially reverses the weighting, yields nearly the same parameters in most instances.