Asymetric Dielectric Dispersion in Glycols

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Dielectric dispersion studies of two pure liquid glycols, diethylene glycol and 1,3-butane diol, and of 2,2-dimethyl 1,3-propane diol dissolved in dioxane, have been carried out at radio, ultrahigh and microwave frequencies at 30 °C. The dispersion nature of the two pure liquids and the solution conforms to the Cole-Davidson type. The dispersion data on the glycol solution show a significant asymmetric behaviour. Comparison of the dispersion parameter β, and relaxation time τ_0, of the present glycols with those of other glycols reveals that both β and τ_0 increase with the number of intervening carbon atoms between the two hydroxyl groups.

Introduction

The dielectric dispersion behaviour of most liquids can be represented analytically either by the simple Debye equation[1] or the Cole-Cole[2] equation involving a symmetric distribution of relaxation times. But some liquids composed of molecules having two or more hydroxyl groups exhibit an asymmetric behaviour as noticed first by Cole and Davidson[3, 4] for glycerol and 1,2-propane diol. For these liquids, the dispersion locus in the complex plane resembles a semicircle on the low frequency side and approaches a straight line at the high frequency end. The dispersion curve is called a 'Skewed-arc' or asymmetric, the asymmetry being in the distribution of relaxation times. The straight-line part of the skewed-arc on the high-frequency side meets the ε'-axis under an angle $\beta\pi/2$ from which the dispersion parameter, β, is calculated. To describe such a behaviour, Cole and Davidson proposed the following empirical equation:

$$\varepsilon^* = \varepsilon' - \mathrm{j}\,\varepsilon'' = \varepsilon_\infty + \left\{ \frac{\varepsilon_s - \varepsilon_\infty}{(1 + \mathrm{j}\,\omega\,\tau_0)^\beta} \right\}, \qquad (1)$$

where τ_0 is the limiting relaxation time and ε_s and ε_∞ are the static and the limiting high frequency dielectric constants, respectively.

From Eq. (1), the following equations for ε' and ε'' can be obtained:

$$(\varepsilon' - \varepsilon_\infty) = (\varepsilon_s - \varepsilon_\infty)\,[\cos(\Theta/\beta)]^\beta \cos\Theta\,, \qquad (2)$$

and

$$\varepsilon'' = (\varepsilon_s - \varepsilon_\infty)\left[\cos\left(\frac{\Theta}{\beta}\right)\right]^\beta \sin\Theta\,, \qquad (3)$$

where

$$\frac{\Theta}{\beta} = \Phi = \tan^{-1}(\omega\,\tau_0)\,. \qquad (4)$$

Following Cole and Davidson[3, 4], several investivators[5−12] took up the study of the dispersion nature of a number of polyhydroxy alcohols, and the results, plotted in the Cole-Cole complex plane, generally yielded skewed-arcs. The data were analysed and certain new formulations were made concerning the dependence of τ_0 and β on the position and separation of the OH groups, size of the molecule, and temperature. Also some molecular models[13−15] were proposed to explain the asymmetric behaviour.

In the present paper, results of dispersion studies in three glycols, viz., diethylene glycol, 1,3-butane diol, and 2,2-dimethyl 1,3-propane diol are reported. The last substance, which is a solid at room temperature, has been examined in solution in 1,4-dioxane.

Diethylene glycol was investigated earlier by Lakshminarayana[16], and the results were interpreted in terms of two regions of dispersion for this compound. The primary region, contributing most to the polarization, was characterized by a Debye semicircle. The locus of the second dispersion at higher frequencies was a Cole-Cole arc wit $\alpha = 0.18$, where α is a measure of the deviation of the dispersion locus from the normal Debye type. The dispersion characteristics of 1,3-butane diol were examined by Sagal[17] and by McDuffie and Litovitz[9] in the frequency range of 0.01 Mc/sec to 1200 Mc/sec. Sagal's results were fitted into a Cole-Cole arc whereas those of Mc Duffie and Litovitz gave a skewed-arc behaviour for this liquid.

The region of maximum absorption for the liquids discussed here at room temperature is in the

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UHF region. A coaxial line set up is generally employed for the measurement of dielectric constant and loss. Considerable effort was made in developing a coaxial dielectric cell with movable short-circuit [18] for use in this frequency region. It is hoped that, employing this cell, the dispersion nature of these liquids could be acurately determined. The dispersion behaviour of 2,2-dimethyl 1,3-propane diol has not been reported previously. In the present study, a 0.333 mole concentration of this diol in dioxane solution has been employed.

Experimental

Diethylene glycol supplied by Chempure, Calcutta, was of Analar grade of purity. 1,3-Butane diol and 2,2-dimethyl 1,3-propane diol were obtained from Eastman-Kodak organic chemicals. The liquid diols were distilled before use. 2,2-dimethyl 1,3-propane diol was used without further purification. It was kept in a desiccator to protect it from traces of moisture. The solvent dioxane was a BDH Analar sample. It was dried over sodium and fractionally distilled. To check the degree of purity, the boiling point of the liquids and the melting point of the solid were measured. They agree well with literature values.

The static dielectric constant ε_s of the liquids was determined using the conventional resonance method which employed the Franklin Oscillator-wavemeter combination, similar to the one described by LeFevre et al. [19]. The liquid cell was essentially the same as that described by Sugden [20].

The dielectric constant ε' and the loss ε'' of the liquids were measured in the ultrahigh frequency region using a coaxial line set up fitted to a dielectric cell with movable short-circuit. The details of experimental procedure and the method of calculation were described before [18].

For measuring ε' and ε'' at microwave frequencies, wave guide setups employing standing wave methods were used at 3 cm and 1 cm wavelengths. The experimental assemblages and the method of measurement are described elsewhere [21]. All measurements have been made at 30 °C.

Results and Discussion

The static dielectric constant ε_s, the dielectric constant ε', and the loss ε'' of the glycols measured at different frequencies are listed in Table 1. The data are plotted in the Cole-Cole complex plane and the dispersion loci for all three glycols are seen to be skewed-arcs of the Cole-Davidson type. The value of β for diethylene glycol has been obtained by noting the angle the high-frequency end of the skewed-arc makes with the ε'-axis. For the latter two compounds, the high-frequency end of the skewed-arc is not a straight line and β is therefore obtained by employing curve-fitting technique. ε_∞ values for the glycols are obtained from the dispersion loci.

Using β, ε_s, and ε_∞, values of ε' and ε'' are calculated from the Eqs. (2) and (3) for different Θ between zero and $\pi/2$. Empirical Cole-Davidson loci are now drawn using the calculated values which are shown as solid circles in Figure 1. The experimental points are given as empty circles in the same figure.

Values of log tan Φ, where

$$\Phi = \frac{1}{\beta} \tan^{-1} \left\{ \frac{\varepsilon''}{(\varepsilon' - \varepsilon_\infty)} \right\}, \qquad (5)$$

are calculated, and these are also included along with log frequency values in Table 1. A graph is plotted between log tan Φ and log frequency. This is observed to be a straight line with slope equal to unity. From the frequency at which log tan Φ is zero, the limiting relaxation time τ_0 is obtained. The values of β and τ_0 for the three glycols together with similar values for dipropylene glycol and 1,3-propane diol are given in Table 2. The latter values were reported by Murty et al. [12].

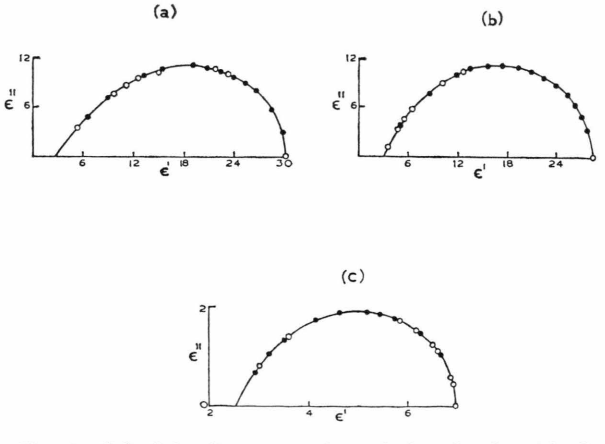

Fig. 1. Cole-Cole dispersion plots of the glycols: (a) diethylene glycol, (b) 1,3-butane diol, (c) 2,2-dimethyl 1,3-propane diol in dioxane. (0) Experimental data, (●) calculated values.

Table 1. Values of ε' and ε'' of diethylene glycol and 1,3-butane diol and the solution of 2,2-dimethyl 1,3-propane diol in dioxane at different frequencies.

Substance	Frequency MHz	ε'	ε''	Log tan Φ	Log frequency
Diethylene glycol	1	30.18	—	—	—
	353	23.30	9.96	$\bar{1}.9618$	8.5477
	483	21.83	10.50	0.0357	8.6842
	900	15.04	10.21	0.3375	8.9542
	1 200	12.86	9.50	0.4638	9.0792
	1 600	11.14	8.62	0.5868	9.2041
	2 000	9.74	7.59	0.6718	9.3010
	9 600	5.40	3.51	1.3900	9.9823
		$\varepsilon_\infty=2.8$			
1,3-butane diol	1	28.18	—	—	—
	353	22.57	10.14	0.2931	8.5477
	483	10.02	8.86	0.4354	8.6842
	1 000	6.47	5.70	0.7642	9.0000
	1 500	5.52	4.46	0.9335	9.1761
	2 000	4.89	3.40	1.0379	9.3010
	9 600	3.68	1.12	1.7886	9.9823
		$\varepsilon_\infty=3.2$			
2,2-Dimethyl 1,3-propane diol in dioxane	1	6.96	—	—	—
	353	6.90	0.45	$\bar{1}.1587$	8.5477
	483	6.86	0.58	$\bar{1}.2743$	8.6842
	900	6.60	1.10	$\bar{1}.5868$	8.9542
	1 200	6.50	1.22	$\bar{1}.6452$	9.0792
	1 600	6.18	1.53	$\bar{1}.7913$	9.2041
	2 000	5.85	1.74	$\bar{1}.9025$	9.3010
	9 600	3.61	1.40	0.5265	9.9823
	24 140	3.02	0.79	0.8690	10.3827
		$\varepsilon_\infty=2.55$			

Table 2. Dispersion parameter (β) and limiting relaxation time (τ_0) of glycols.

Substance	β	$\tau_0 \times 10^{10}$ sec
Diethylene glycol	0.61	3.80
Dipropylene glycol	0.625	12.3
1,3-Propane diol	0.72	1.27
1,3-Butane diol	0.75	8.75
2,2-Dimethyl 1,3-propane diol in dioxane	0.72	0.61

Asymmetric dispersion behaviour was noticed by Muralidhara Rao [10] in ethylene and polyethylene glycols and by Murty et al. [12] in dipropylene glycol. In the light of these observations, the two regions of dispersion reported by Lakshminarayana [16] for diethylene glycol appeared to be doubtful, which prompted the present new investigation on this compound. Indeed the dispersion locus shown in Fig. 1 (a) is a skewed-arc and the experimental points (hollow circles) lie well on the empirical Cole-Davidson curve confirming the value of β and the skewed-arc nature for this compound.

The reports regarding the dispersion nature of 1,3-butane diol were also conflicting. Sagal [17], on the basis of his measurements in the temperature range 5 °C to 50 °C, found that the dispersion showed a symmetric distribution of the relaxation times. He reported at 25 °C a value of a (distribution parameter) equal to 0.05 and a relaxation time of 9.1×10^{-10} sec. McDuffie and Litovitz made measurements between -24 °C and $+10$ °C and noticed asymmetric behaviour in this liquid. They reported that for the glycol β increased from 0.7 to 0.85 and τ_0 decreased from 4.5×10^{-8} sec to 0.24×10^{-8} sec in this temperature range.

It can be seen from Fig. 1 (b) that the experimental points of the present study fit well into a skewed-arc. The value of β (0.75) obtained at 30 °C for 1,3-butane diol appears low when compared with that reported by McDuffie and Litovitz, which means that in this glycol a slightly higher order asymmetry has been observed by the authors. The value of τ_0 (8.75×10^{-10} sec) obtained in the present study, however, is of the same order as the τ value at 25 °C reported by Sagal.

From Fig. 1 (c) it can be seen that the dispersion behaviour of the solution of 2,2-dimethyl 1,3-propane diol in dioxane also conforms to the Cole-Davidson type. The values of β and τ_0 obtained from the dispersion locus are not the true values of the pure glycol. It would have been preferable if measurements were made on solutions of very high concentration. But this was not possible because of the limited solubility of glycol in dioxane. The present observation, however, is significant since so far no solid dissolved in a nonpolar solvent (or a near nonpolar solvent such as dioxane) has shown asymmetric behaviour. The present result is not unexpected since the dipoles in the glycol solution can be assumed to relax in a "Cooperative manner" as they do in a pure glycol. Also the solute and the solvent both containing OH groups in their structure, the solutesolvent hydrogen bonding makes the solution resemble a pure liquid glycol with its intermolecular and intramolecular hydrogen bondings.

It can be seen from Table 2 that both β and τ_0 increase from diethylene glycol to dipropylene glycol and also from 1,3-propane diol to 1,3-butane diol. This shows that, as the number of intervening carbon atoms between the two OH groups is increased, the asymmetry of the diol decreases. Also with this number increasing, the relaxation process is slowed down. But this slowing down can be due to the increase in the size of the relaxing molecule.

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