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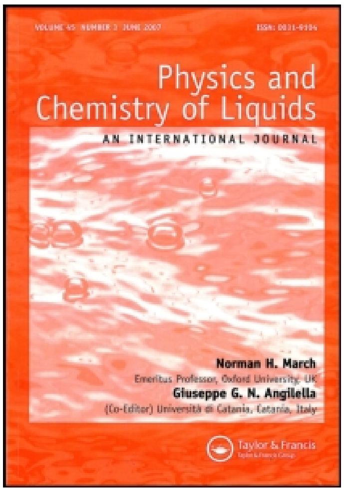

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INFLUENCE OF SOLVENT ENVIRONMENT ON LINEAR CORRELATION FACTOR AND DIELECTRIC RELAXATION TIME OF ETHANEDIOL, 1,2 PROPANEDIOL, DIETHYLENE GLYCOL AND CYCLOHEXANOL

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The values of static dielectric constant at 1 KHz (ε_0) and complex permittivities at 8.336 GHz (ε' and ε'') of Ethanediol, 1,2 Propanediol, Diethylene glycol and Cyclohexanol in 1,4 Dioxane, at different concentrations at 298 K, 308 K and 318 K were reported. These data have been utilised to compute the Kirkwood-Frolich linear correlation factor, the dielectric relaxation time and distribution parameter. The results are discussed on the basis of various association models of alcohols. The free energy of activation due to dielectric relaxation is larger than that expected from theoretical considerations. It is due to a translational motion arising out of the rotational motion of nonspherical molecules.

KEY WORDS: Kirkwood correlation factor, dielectric relaxation time, activation energy.

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INTRODUCTION

It has been realised in recent times that the kinetics of fast chemical reactions is very much related to the macroscopic solvent parameters like viscosity and polarity and hence, there is renewed interest in understanding the relaxation mechanisms of solvents like alcohols. Bottcher and his co-workers[1] and several earlier investigators treated alcohols as mixtures of multimers, whose dielectric behaviour as a function of temperature, pressure and concentration could be described in terms of g, the Kirkwood correlation factor[2]. However it cannot give specific information as to the sizes of multimers. Recent work in this area is excellently reviewed by Schuster *et al*[3]. Dielectric relaxation measurements provide a different approach to this problem. The frequency dependent dielectric constant $\varepsilon(\omega)$ of a structureless fluid of dielectric continuum is normally given by Debye's formula[4]. Alcohols have a more complex dielectric response[5]. The Debye relaxation times of alcohols are commonly associated with at least three important molecular motions (i) hydrogen bonded dynamics of molecular aggregates, (ii) monomer rotation, (iii) rotation of the terminal O–H group. The concentration dependence of relaxation times of monoalcohols are well studied by several workers and the causes of variations are analysed by Smyth[6]. However much less work has been done in diols in dilution which exhibit considerable viscosity. In this work, we have studied the temperature and concentration dependence of

Kirkwood correlation factor and Debye relaxation time of Ethanediol, 1-2 Propanediol, Diethylene glycol and Cyclohexanol in dilute solutions of 1,4 dioxane.

EXPERIMENT

The static dielectric constants ε_0 were determined at 1 KHz by a bridge method using VLCR-7 of Vasavi electronics, India. The refractive indices were measured by using an Abbe's refractometer. ε' and ε'' were measured at 8.336 GHz using a standard liquid cell supplied by M/s. SICO Ltd., Allahabad, in conjunction with a X-band microwave set up. The viscosities were measured with Ostwald's viscometer. A constant temperature circulating bath was used to keep the liquids at the desired temperature within ± 1 K. All liquids studied were of research grade and were used with prior distillation. No reduction in volume upon mixing was assumed or observed.

(i) Calculation of linear correlation factor

As a reaction field exists even in the absence of external field, the internal moment of a polar solute in dilute solutions may differ considerably from the moment 'μ' of the molecule in vacuua. The total polarization of a small volume of solution depends on the total energy of interaction between molecules namely solvent–solvent, solvent-solute and solute–solute molecules. If the interaction between solvent molecules which are non polar could be ignored, the interaction between the solvent and solute molecules at high dilution of the solute could be considered as equivalent to that when keeping the solute in the gaseous state, *albeit* the dispersion forces. Only the interaction between the solute species among themselves with progressive dilution may be considered for short range correlations. Hence for dilute solutions Onsager equation may be written as

$$B(T)=\frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)T}{3\varepsilon_0 d}$$

$$=\frac{4\pi}{3k}N_A\left[\langle P_1M_1^*\rangle\frac{w_1}{M_1}+\langle P_2M_2^*\rangle\frac{w_2}{M_2}\right] \quad (1)$$

where w_1, M_1 and w_2, M_2 are the weight fractions and molecular weights of the solvent and solute respectively. M_1^* and M_2^* are the total moments of a sphere having a solvent or solute species located at its centre, while P_1 and P_2 are the moments of the solvent and solute respectively. In a dilute solution there are many more solvent–solvent contacts than solvent-solute contacts so that $\langle P_1M_1^*\rangle$ may be assumed to be practically equal to its value in the pure state. Hence,

$$B_1(T)=\frac{(\varepsilon_1-\varepsilon_{1\infty})(2\varepsilon_1+\varepsilon_{1\infty})T}{3\varepsilon_1 d_1}\approx\frac{4\pi N_A}{3kM_1}\langle P_1M_1^*\rangle \quad (2)$$

d and d_1 are the densities at temperature T for solution and solvent respectively.

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Combining equations (1) and (2)

$$B(T)-w_1B_1(T)=\frac{4\pi N_A w_2}{3kM_2}\langle P_2M_2^*\rangle \tag{3}$$

If the average angular correlation between the polar species is represented by "g'"

$$\langle P_2M_2^*\rangle = g'\mu_2^2\left[\frac{\varepsilon_{1\infty}+2}{3}\right]^2 \tag{4}$$

The definition of g' here is most general in the sense that it is a measure of the angular correlation of the dipole vector of the molecule with the neighbouring molecules in the solution, while the effect of the short range correlation between solvent molecules are also accounted for[7]. Hence combining equations (3) and (4)

$$g'=\frac{27kM_2}{4\pi N_A w_2\mu_2^2(\varepsilon_\infty+2)^2}[B(T)-w_1B_1(T)]. \tag{5}$$

It can be seen that for pure polar liquids the equation (5) reduces to Onsager equation. The values of g' are reported here for the first time.

(ii) Calculation of relaxation time

The following expressions[8] were used for obtaining ε' and ε''

$$\varepsilon'=\left(\frac{\lambda_0}{\lambda_c}\right)^2+\left(\frac{\lambda_0}{\lambda_d}\right)^2 \tag{6}$$

$$\varepsilon''=\frac{2}{\pi}\left(\frac{\lambda_g\lambda_0^2}{\lambda_d^3}\right)\left(\frac{d\rho}{dn}\right) \tag{7}$$

where λ_d is the wavelength in the dielectric medium, λ_g, the guide wavelength, λ_0, the free space wavelength, λ_c, the cut off wavelength and $1/\rho$ is the standing wave ratio obtained by using a short circuited movable plunger. The uncertainties in the measurement of ε_0, ε_∞ and ε' were 1% and ε'' was 5%.

The relaxation time for various solutions of diols and cyclohexanol was also obtained in terms of two Debye relaxation mechanisms with the help of the following equations[9] for dilute solution of weight fraction w_2,

$$\varepsilon_0=\varepsilon_1+w_2a_0 \tag{8}$$

$$\varepsilon'=\varepsilon_1+w_2a' \tag{9}$$

$$\varepsilon''=a''w_2\colon \varepsilon_\infty=\varepsilon_{1\infty}+a_\infty w_2$$

$$\tau(1)=\frac{a''}{\omega(a'-a_\infty)} \tag{10}$$

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$$\tau(2) = \frac{a_0 - a'}{\omega a''} \tag{11}$$

ω is the angular frequency;
The distribution parameter α

$$\alpha = 1 - \frac{2}{\pi}\tan^{-1}\left(\frac{a''(a_0 - a_\infty)}{(a_0 - a')(a' - a_\infty)}\right) \tag{12}$$

$\tau(2)$ given by equation (11) corresponds to the dielectric relaxation time for overall rotation of the whole molecule and $\tau(1)$ given by equation (10) is a sort of intramolecular relaxation time depending on both the weight factor of such mechanism at a given concentration and temperature[10].

The free energy of activation for dipolar and viscous forces have been calculated using Eyring's Equation[11]

$$\tau = \frac{h}{kT}\exp(\Delta F_\tau/RT) \tag{13}$$

$$\eta = \frac{Nh}{V}\exp(\Delta F_\eta/RT) \tag{14}$$

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RESULTS AND DISCUSSION

The variations of g' with molefractions of the alcohols in 1,4 Dioxane are given in Figure 1. It is found that g' decreases with increase of dilution, reaches a minimum and again increases with further increase of dilution which is a common behaviour for most of the alcohols[1]. This suggests that the smallest multimers are linear, somewhat greater ones are cyclic and the greatest multimers are linear again. It is found that the curve of g' versus the molefraction of the alcohol (X_2) flattens significantly with the decrease in the number of polar molecules per unit volume of alcohols. The interference of the solvent with the preferred packing of hydroxylic solute and the inhibition of free rotation are some of the factors that are responsible for the said effects.

It may therefore be concluded that the high values of g' at very high dilutions may be explained by the linear association model (LAM) proposed by Cole and Dannhauser[12], while the low value of g' at a definite concentration may be explained by the model proposed by Bordewijk *et al.*[13] which assumes a cyclic α-multimer with out-of-plane bond moments.

The relaxation behaviour of these alcohols were also studied in the concentration ranges where significant changes in g' occur. The relaxation times $\tau(1)$ and $\tau(2)$ obtained for these alcohols in dilution with 1,4 Dioxane at three different temperatures are given in Tables 1–4. It is a known fact that the relaxation time is a function of viscosity even though it does not increase in the proportion in which viscosity

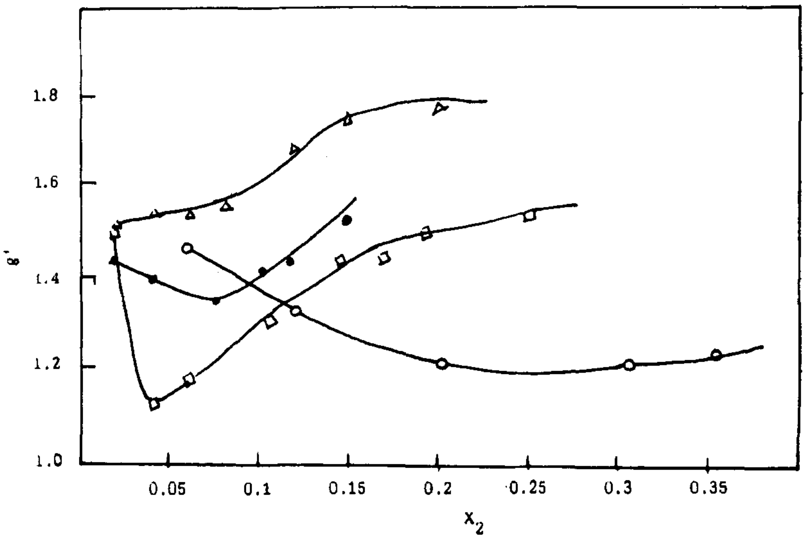

Figure 1 Variation of g' with mole fraction of Ethanediol, 1,2 Propanediol, Diethylene glycol and Cyclohexanol in 1,4 Dioxane.
—□— Ethanediol; —●— 1,2 Propanediol; —△— Diethylene Glycol; —○— Cyclohexanol.

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increases[14–15]. In our present investigation the viscosity of the solutions is almost a constant at a given temperature.

The distribution parameter α for all the systems are appreciable which implies the existence of more than one relaxation mechanism. For Diethylene glycol and Cyclohexanol it decreases with dilution. This behaviour is normal in the sense that the

Table 1 Values of dielectric constants, distribution parameter, relaxation times and activation energies for various mole fractions of Ethanediol at 298 K, 308 K and 318 K in 1,4 Dioxane.

Temp.	X_2	ε_0	ε_∞	ε'	ε''	α	$\tau(1)$ PS	$\tau(2)$ PS	ΔF_τ KJ/M	ΔF_η KJ/M
298 K	0.06	2.940	2.018	2.74	0.18	0.30	7.0	20.9	9.36	13.81
	0.08	3.098	2.021	2.91	0.22	0.24	6.3	15.9	9.10	13.84
	0.10	3.390	2.022	3.08	0.27	0.35	6.2	22.3	9.06	13.86
	0.12	3.760	2.024	3.35	0.32	0.39	5.6	24.3	8.83	13.92
308 K	0.06	2.860	2.011	2.72	0.14	0.32	5.5	19.3	9.13	13.79
	0.08	3.028	2.012	2.87	0.17	0.30	5.1	17.1	8.93	13.84
	0.10	3.300	2.014	3.05	0.21	0.40	4.8	22.6	8.80	13.91
	0.12	3.680	2.016	3.30	0.26	0.47	4.6	28.0	8.66	13.93
318 K	0.06	2.800	2.003	2.69	0.12	0.32	4.7	17.7	9.11	13.85
	0.08	2.950	2.005	2.85	0.16	0.21	4.6	12.4	9.05	13.89
	0.10	3.220	2.006	3.02	0.19	0.38	4.4	21.0	8.09	13.93
	0.12	3.590	2.008	3.23	0.22	0.51	4.2	30.8	8.83	13.98

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Table 2 Values of dielectric constants, distribution parameters relaxation times and activation energies for various mole fractions of 1-2 propanediol at 298 K, 308 K and 318 K in 1,4 Dioxane.

Temp.	X_2	ε_0	ε_∞	ε'	ε''	α	$\tau(1)$ PS	$\tau(2)$ PS	ΔF_τ KJ/M	ΔF_η KJ/M
298 K	0.04	2.624	2.019	2.55	0.13	0.09	8.1	11.5	9.71	13.81
	0.06	2.820	2.020	2.63	0.15	0.32	7.5	23.2	9.53	13.87
	0.08	3.086	2.021	2.79	0.20	0.39	7.0	27.8	9.37	13.97
	0.10	3.380	2.023	2.95	0.24	0.46	6.5	34.2	9.19	14.05
308 K	0.04	2.576	2.010	2.51	0.11	0.11	7.3	11.4	9.90	13.91
	0.06	2.786	2.012	2.61	0.14	0.37	6.6	24.9	9.63	13.96
	0.08	3.038	2.013	2.77	0.16	0.48	5.5	32.0	9.13	14.03
	0.10	3.290	2.014	2.92	0.18	0.54	5.1	38.6	8.93	14.10
318 K	0.04	2.528	2.001	2.47	0.10	0.13	6.9	11.8	10.14	13.94
	0.06	2.752	2.002	2.58	0.12	0.41	5.9	26.9	9.72	14.01
	0.08	3.004	2.003	2.74	0.14	0.51	5.1	34.5	9.31	14.07
	0.10	3.214	2.004	2.87	0.17	0.55	4.9	38.8	9.20	14.17

Table 3 Values of dielectric constants, distribution parameters, relaxation times and activation energies for various mole fractions of Diethylene glycol at 298 K, 308 K and 318 K in 1,4 Dioxane.

Temp.	X_2	ε_0	ε_∞	ε'	ε''	α	$\tau(1)$ PS	$\tau(2)$ PS	ΔF_τ KJ/M	ΔF_η KJ/M
298 K	0.06	3.100	2.038	2.81	0.18	0.45	6.2	31.6	9.06	13.90
	0.10	3.632	2.041	3.10	0.36	0.36	8.3	28.5	9.78	14.22
	0.12	3.926	2.042	3.20	0.47	0.33	9.6	29.9	10.16	14.36
308 K	0.06	3.024	2.025	2.74	0.16	0.47	6.0	33.4	9.39	13.97
	0.10	3.528	2.031	3.06	0.30	0.40	7.1	29.4	9.81	14.22
	0.12	3.836	2.032	3.17	0.40	0.40	8.2	32.3	10.18	14.31
318 K	0.06	2.940	2.016	2.70	0.13	0.50	5.2	33.5	9.38	14.06
	0.10	3.452	2.019	3.01	0.26	0.45	6.4	32.1	9.92	14.29
	0.12	3.732	2.022	3.10	0.34	0.44	7.3	34.0	10.28	14.36

probability of alcohol molecules to be grouped as multimers of different kinds of molecular rotations is smaller when the dilution is increased[16]. However the relaxation time $\tau(1)$ for ethanediol and 1,2 Propanediol increases with dilution. Similar observations in primary alcohols were made by other authors[17-18]. The relaxation time $\tau(2)$ decreases with dilution for all the systems due to either the destruction of the coupling of polar molecules preventing the co-operative process of relaxation or due to the progressive monomerisation of alcohols or both.

With increase of temperature, $\tau(1)$ for a given concentration decreases for all the systems studied implying progressive domination of monomers. However $\tau(2)$ decreases with increase of temperature for lower concentration and reverses at higher concentration which requires further investigation.

The insight into the condition for the appearance of a rotatory phase is given by the comparison of the free energy of activation for dielectric relaxation, ΔF_τ and free

Table 4 Values of Dielectric constants, distribution parameters, relaxation times and activation energies for various mole fractions of cyclohexanol at 298 K, 308 K and 318 K in 1,4 Dioxane.

Temp.	X_2	ε_0	ε_∞	ε'	ε''	α	$\tau(1)$ PS	$\tau(2)$ PS	ΔF_τ KJ/M	ΔF_η KJ/M
298 K	0.06	2.682	2.036	2.60	0.09	0.30	5.0	16.9	8.54	13.69
	0.10	2.890	2.038	2.74	0.14	0.35	5.5	20.8	8.76	13.81
	0.12	3.016	2.040	2.83	0.18	0.30	6.2	19.2	9.07	14.38
308 K	0.06	2.618	2.020	2.58	0.07	0.17	4.0	10.0	8.35	13.63
	0.08	2.716	2.023	2.66	0.10	0.19	4.4	11.1	8.55	13.65
	0.10	2.814	2.025	2.71	0.12	0.32	4.7	17.4	8.73	13.70
	0.12	2.968	2.030	2.77	0.14	0.43	5.3	26.4	9.04	14.16
318 K	0.06	2.584	2.008	2.54	0.06	0.27	3.3	12.9	8.20	13.43
	0.08	2.682	2.011	2.59	0.07	0.46	3.6	25.0	8.45	13.66
	0.10	2.794	2.016	2.68	0.09	0.42	3.8	22.1	8.54	13.78
	0.12	2.948	2.020	2.72	0.11	0.57	4.2	39.1	8.80	14.32

energy of activation for viscous flow, ΔF_η. For non-polar liquids[19]

$$\Delta F_\tau < 0.5\,\Delta F_\eta \tag{15}$$

In the present study ΔF_τ is larger than that expected from equation (15). For non spherical molecules the rotation necessarily requires a translational motion of the neighbours and hence there is an increased dipolar activation energy as is observed in the present investigation.

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