DIELECTRIC RELAXATION AND THERMODYNAMIC PARAMETERS OF N-PROPYL ALCOHOL, ETHYLENEDIAMINE AND THEIR BINARY MIXTURES IN 1,4-DIOXAN

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ABSTRACT

The values of dielectric constant ($\in'$) and dielectric loss ($\in''$) have been calculated for n-propyl alcohol, ethylenediamine and their binary mixtures in 1,4-dioxan at different temperatures using X-band microwave bench. The relaxation time (τ) and dipole moment (μ) have been calculated by employing Gopala Krishna's method. Values of relaxation time (τ) compared with calculated values from different methods. The thermodynamic parameters also have been calculated for dielectric relaxation as well as for viscous flow process. Observed values of Debye's factor and Kalman's factor shows that Kalman's formula satisfactorily explains the relationship between dielectric relaxation time and the viscosity. The non-linear behaviour of relaxation time with mole fraction reveals the presence of solute-solute molecular association in the mixture.

Key words: Dielectric relaxation, Relaxation time, Energy parameters, Solute-solute association.

INTRODUCTION

Dielectric relaxation data obtained from the microwave absorption studies are expected to throw light on various types of molecular associations present in the solution. Dielectric relaxation studies of polar molecules in non-polar solvent from microwave absorption have been frequently attempted by number of research workers[1-7]. In the present paper, the dielectric relaxation study of n-propyl alcohol (*nPA*), ethylenediamine (*EDA*) and their binary mixtures in 1,4-dioxan were carried out for different mole fraction of *EDA* at different temperatures. The study is expected to provide better understanding of the nature of molecular association in the mixture.

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EXPERIMENTAL

n-Propyl alcohol (*nPA*), ethylenediamine (*EDA*) and 1,4-dioxan (all AR grade) were procured from S.D. Fine Chemicals, Mumbai and used without further purification. The liquids were mixed according to their proportion by volume. The *X*-band microwave bench[2] was used to measure voltage standing wave ratio (*VSWR*) and wavelength in dielectrics (λ_d) at temperatures 293, 303, 313 and 323 K. The dielectric constant ($\in'$) and dielectric loss ($\in''$) were computed from these measurements. The dielectric relaxation time (τ) and dipole moment (μ) were calculated using Gopala Krishna's[8] method. The free energy of activation (ΔF_τ, ΔF_η), enthalpy of activation (ΔH_τ, ΔH_η) and entropy of activation (ΔS_τ, ΔS_η) for dielectric relaxation process and viscous flow process have been estimated using Eyring's equation[9]. The values of Debye factor (*C*) and Kalman's factor (*C'*) were calculated using equations[10]. Values of dipole moment (μ) have been compared with values calculated by using relation

$$\mu^2 = X_1\mu_1^2 + X_2\mu_2^2 \qquad \qquad …(1)$$

where X_1 and X_2 are the mole fractions of two constituents in the mixture.

The values of relaxation time (τ) compared with the values obtained by various methods such as.

(i) Simple mixing method[11-14] (*S.M.*)

$$\tau_{\min} = \sum_{i=1}^{n} X_i\tau_i \qquad \qquad …(2)$$

(ii) Reciprocal mixing method[11-14]

$$\frac{1}{\tau_{Mix}} = \sum_{i=1}^{n} \frac{X_i}{\tau_i} \qquad \qquad …(3)$$

(iii) Yadav and Gandhi[13] method (*Y. & G.*)

$$\left(\tau_{Mix}\right) = \sqrt{\frac{\sum_{i=1}^{n} X_i\tau_i^2}{\sum_{i=1}^{n} X_i}} \qquad \qquad …(4)$$

where τ_t is relaxation time of ith component of mole fraction X_i in the mixture.

(iv) Madan's[15] method

$$\frac{1}{\tau_{mix}} = \left(\frac{c_1 \mu_1^2}{[c_1 \mu_1^2 + (1-c_1)\mu_2^2]^{\tau_1}} + \frac{(1-c_1)\mu_2^2}{[c_1 \mu_1^2 + (1-c_1)\mu_2^2]^{\tau_2}} \right) \qquad \ldots(5)$$

Where C_1 is mole fraction of *EDA*, μ_1 and μ_2 are dipole moments of *EDA* and *nPA* respectively. τ_1 and τ_2 are relaxation time of *EDA* and *nPA*, respectively.

The excess inverse relaxation time $\left(\dfrac{1}{\tau}\right)^e$ may be evaluated using the following relation[16,17].

$$\left(\frac{1}{\tau}\right)^e = \left(\frac{1}{\tau_m}\right) - \left[X_1 \left(\frac{1}{\tau_1}\right) + X_2 \left(\frac{1}{\tau_2}\right) \right] \qquad \ldots(6)$$

Where symbols *m,* 1 and 2 are related to mixture, liquid 1 and liquid 2, respectively.

RESULTS AND DISCUSSION

Values of relaxation time (τ) for pure liquids and their mixtures are presented in Table 1. The values of relaxation time are observed to decrease systematically with increase in temperature from 20°C to 50°C. This may be due to increase in temperature, which causes change in molar volume and rate of loss of energy due to large number of collisions. Hence, molecules reorient with faster rate. Similar kind of results are presented by Rewar and Bhatnagar[18]. Fig. 1 shows the variation of relaxation time with increasing mole fraction of *EDA*. The non-linear variation of relaxation time with mole fraction of one of the constituents is interpreted as possible solute-solute molecular association in the binary mixture. The molecular entities become much more voluminous than the individual molecules due to this association.

The values of Debye factor (*C*), Kalman's factor (*C'*) and dipole moment (μ) are reported in the Table 1. The dipole moment values are found to increase with increase in temperature. This may be due to increase of dipole length for higher temperature. The variation of dipole moment with temperature may be attributed to solute-solvent association[19]. Fig. 2 shows variation of dipole moment with mole fraction of *EDA*. This non-

linear variation of (μ) suggests the solute-solute molecular association[20]. The survey of table 1 shows that Debye factor (*C*) varies with temperature where as Kalman's factor (*C'*) remains almost constant with temperature. This shows that Kalman's equation for dielectric relaxation time (τ) as a function of viscosity is superior to the Debye equation and the quantity η^x is a better representation of inner friction coefficient for dipolar rotation. Similar results were observed earlier by Khatri and Gandhi[21], Khameshara and Sisodia[22] and Singh and Sharma[10].

Table 1: The values of relaxation time (τ), Debye constant (C), Kalman's factor (C'), experimental values of dipole moment (μ exp.) and calculated values of dipole moment (μ cal) of n-propyl alcohol, ethylenediamine and their mixtures in dilute solution of 1,4-dioxan at different temperatures

Solute %	Temp. K	τ ps	C x 10^{-8}	C^η x 10^{-8}	μ exp. *D*	μ cal. *D*	μ^2 exp.	μ^2 cal.	% Deviation in μ^2
	293	5.39	13.19	0.209	1.685	--	2.840	--	--
nPA	303	5.04	15.46	0.205	1.751	--	3.066	--	--
100%	313	4.94	18.99	0.213	1.796	--	3.225	--	--
	323	4.69	24.08	0.209	1.802	--	3.247	--	--
nPA (73%) + EDA (23%)	293	5.74	14.07	0.206	1.684	1.683	2.835	2.832	0.10
	303	5.61	17.20	0.209	1.730	1.739	2.993	3.027	-1.13
	313	5.23	20.53	0.208	1.738	1.787	3.179	3.195	-0.50
	323	5.08	26.08	0.206	1.798	1.798	3.232	3.233	-0.05
nPA (47%) + EDA (53%)	293	4.34	10.62	0.174	1.681	1.680	2.825	2.825	0.00
	303	4.27	13.09	0.177	1.721	1.729	2.961	2.991	-1.01
	313	4.20	16.15	0.182	1.774	1.779	3.147	3.167	-0.63
	323	4.13	21.21	0.187	1.796	1.794	3.225	3.221	-0.12
nPA (23%) + EDA (77%)	293	4.00	9.79	0.133	1.689	1.679	2.819	2.818	-0.35
	303	3.80	11.66	0.131	1.716	1.719	2.944	2.956	-0.40
	313	3.72	14.30	0.133	1.772	1.772	3.133	3.140	-0.22
	323	3.56	18.30	0.133	1.791	1.790	3.211	3.208	-0.09

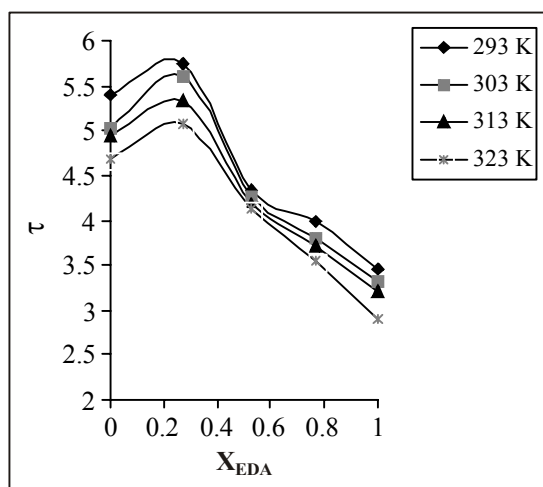| Solute %	Temp. K	τ ps	C x 10^{-8}	C^{η} x 10^{-8}	μ exp. *D*	μ *cal. D*	μ^2 exp.	μ^2 *cal.*	% Deviation in μ^2
	293	3.46	8.47	0.162	1.673	--	2.844	--	--
EDA	303	3.32	10.18	0.164	1.710	--	2.924	--	--
(100%)	313	3.20	12.30	0.167	1.765	--	3.112	--	--
	323	2.91	14.94	0.161	1.786	--	3.197	--	--

Fig. 1: Variation of relaxation time versus mole fraction of EDA in the binary mixture
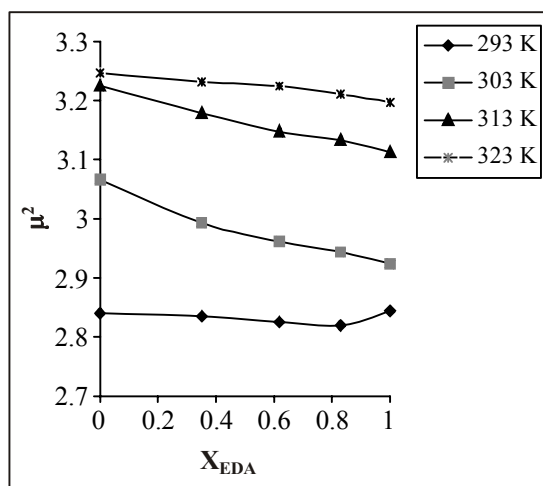

Fig. 2: Variation of square of dipole moment versus mole fraction of EDA in the binary mixture

The values of relaxation time obtained experimentally and values obtained by equations (2 to 5) are presented in Table 2. These values show that Yadav and Gandhi[13] method gives better fit with experimental results in comparison to other methods. The negative deviation of excess inverse relaxation time $\left(\dfrac{1}{\tau}\right)^e$ suggest the solute-solvent interaction in such a way that binary mixture of (*nPA + EDA*) produces a field in which effective dipoles rotates slowly.

Table 2*:* Comparison of experimental values and computed values of relaxation time (τ) using different theoretical methods and excess inverse relaxation time $\left(\dfrac{1}{\tau}\right)^e$ for binary mixtures of n-propyl alcohol, ethylenediamine and their binary mixtures at different temperatures

Temp. K	Mole fraction of *EDA*	τ *exp* (ps)	Theoretical values of τ calculated by				Excess inverse relaxation time $\left(\frac{1}{\tau}\right)^e$
			S. M. method	R. M. Method	Y. and G. method	Madan's method	
	0.00	5.39	--	--	--	--	--
	0.27	5.75	4.87 (-18.14)	4.68 (-22.86)	4.94 (-16.36)	4.70 (-22.34)	-0.03967
293	0.53	4.34	4.54 (4.4)	4.16 (-4.32)	4.48 (3.12)	4.17 (-4.07)	-0.0100
	0.77	4.00	3.90 (-2.46)	3.77 (-6.1)	3.98 (-0.31)	3.77 (-6.1)	-0.0152
	1.00	3.46	--	--	--	--	--
	0.00	5.04	--	--	--	--	--
	0.27	5.61	4.57 (-22.67	4.42 (-26.92)	4.63 (-21.03)	4.42 (-26.92)	-0.0447
303	0.53	4.27	4.13 (-3.30)	3.96 (-7.82)	4.22 (-1.18)	3.96 (-7.82)	-0.0184
	0.77	3.80	3.72 (-2.27)	3.60 (-5.5)	3.78 (-0.38)	3.60 (-5.5)	-0.0144
	1.00	3.32	--	--	--	--	--

Temp. K	Mole fraction of EDA	τ exp (ps)	Theoretical values of τ calculated by				Excess inverse relaxation time $\left(\frac{1}{\tau}\right)^\epsilon$
			S. M. method	R. M. Method	Y. and G. method	Madan's method	
	0.00	4.94	--	--	--	--	--
	0.27	5.34	4.47 (-19.5)	4.31 (-23.90)	4.54 (-17.72)	4.30 (-24.2)	-0.0450
313	0.53	4.20	4.02 (-4.4)	3.84 (-9.38)	4.11 (-2.08)	3.84 (-9.38)	-0.0224
	0.77	3.72	3.60 (-3.33)	3.48 (-6.8)	3.67 (-1.25)	3.48 (-6.8)	-0.0184
	1.00	3.20	--	--	--	--	--
	0.00	4.69	--	--	--	--	--
	0.27	5.08	4.21 (-20.70)	4.03 (-26.05)	4.28 (-18.68)	4.03 (-26.05)	-0.0520
323	0.53	4.13	3.75 (-10.10)	3.55 (-16.38)	3.85 (-7.15)	3.55 (-16.38)	-0.0400
	0.77	3.56	3.32 (-7.25)	3.19 (-11.60)	3.40 (-4.62)	3.19 (-11.60)	-0.0330
	1.00	2.91	--	--	--	--	--

*(bracket terms indicates % deviation)

The energy parameters for dielectric relaxation process and viscous flow process are presented in Table 3. The free energy of activation (ΔF_τ) for dielectric relaxation process is found to increase with increase in temperature. This may be due to the fact that with increase in temperature; the thermal agitation increases and dipole require more energy to be activates. It is found that the free energy of activation (ΔF_τ) for dielectric relaxation process is less than free energy of activation (ΔF_η) for viscous flow process. This is because of the dielectric relaxation process, which involves rotation of molecules only whereas in viscous flow process, the rotation as well as translational motion of the molecules is involved[20].

The enthalpy of activation (ΔH_η) for viscous flow process is found to be greater than the enthalpy of activation (ΔH_τ) for dielectric relaxation process and their ratio is found to be

$\dfrac{\Delta H_\tau}{\Delta H_\eta} < 0.5$, suggesting the solid rotator phase[23]. The entropy of activation (ΔS_τ) for dielectric relaxation process is found to be negative, suggesting that activated state is more ordered than the normal state[24]. In activated state, the dipoles are more aligned than in normal state.

Table 3: The values of free energy of activation (ΔF_τ, ΔF_η), enthalpy of activation (ΔF_τ, ΔF_η) and entropy of activation (ΔS_τ, ΔS_η) for n-propyl alcohol, ethylenediamine and their binary mixtures in 1,4-diaxon at different temperatures

Solute %	Temp. K	ΔF_τ Kcal/mole	Δh_τ Kcal/mole	ΔS_τ cal/mole	ΔF_η Kcal/mole	Δh_η Kcal/mole	Δs_η cal/mole
nPA (100%)	293	2.03		-6.06	3.231		2.738
	303	2.06	0.255	-5.96	3.232	4.033	2.644
	313	2.16		-6.08	3.225		2.581
	323	2.22		-6.08	3.167		2.680
nPA (73%) + *EDA* (23%)	293	2.07		-5.59	3.231		2.738
	303	2.15	0.183	-5.64	3.232	4.033	2.644
	313	2.21		-5.71	3.225		2.581
	323	2.27		-5.75	3.167		2.680
nPA (47%) + *EDA* (53%)	293	1.91		-5.59	3.231		2.738
	303	1.98	0.272	-5.64	3.232	4.033	2.644
	313	2.06		-5.71	3.225		2.581
	323	2.13		-5.75	3.167		2.680
nPA (23%) + *EDA* (77%)	293	1.86		-5.56	3.231		2.738
	303	1.91	0.144	-5.93	3.232	4.033	2.644
	313	1.98		-5.96	3.225		2.581
	323	2.04		-5.97	3.167		2.680
EDA (100%)	293	1.78		-4.60	3.231		2.738
	303	1.83	0.429	-4.63	3.232	4.033	2.644
	313	1.89		-4.67	3.225		2.581
	323	1.91		-4.58	3.167		2.680

CONCLUSION

The values of dielectric relaxation parameters and thermodynamic parameters have been reported for n-propyl alcohol, ethylenediamine and their binary mixtures. These studies suggest the dipole-dipole molecular association in the mixture through hydrogen bonding.

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