

Chapter 9

**DIELECTRIC BEHAVIOUR AND
STRUCTURAL ASPECT OF SOME
POLAR LIQUIDS UNDER RADIO
FREQUENCY ELECTRIC FIELD AT
SINGLE AND DIFFERENT
TEMPERATURES**

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1. INTRODUCTION

The experimental determination of the real part of rf conductivity σ'_{ij} of a polar liquid molecule in a non polar solvent is gaining much attention [1-5] as it provides one with an useful tool to estimate the relaxation time τ_j , density of free ions 'n' and dipole moment μ_j at a given temperature in $^{\circ}\text{C}$. High frequency measurement technique gives the valuable information regarding the behaviour of the dielectropolar molecules and their associational aspects. According to Murphy and Morgan [6] the displacement current alone is the only contributing factor to hf conductivity in dielectric liquids. But almost all the dielectropolar liquids specially long chained alcohols deviate from the ideal behaviour due to existence of free ions and electrons in them. The evidence of presence of free ions and electrons in polar-nonpolar liquid mixtures and in pure polar liquids had already been shown by many workers [7-9]. So in case of actual dielectrics under radio frequency (rf) electric fields the conduction and hence the heat produced is for the combined effects of displacement and conduction current. The generation of free ions in both pure polar and polar-nonpolar liquid mixtures has been attributed to many reasons. Cosmic rays, natural radioactivity, thermal dissociation etc. in the insulating dielectrics are the main sources of such ions and electrons. But no specific reasons has, however, yet been reached for such formation of free ions and electrons in dielectropolar liquids which are obviously insulators. Assuming the conduction current due to existence of free ions and electrons and the usual displacement current in a dielectropolar liquid; Sen and Ghosh [10] derived a simple straight forward mathematical relation between the real part σ'_{ij} or σ'_{jk} of the complex rf conductivity σ^*_{ij} or σ^*_{jk} of binary polar nonpolar liquids and pure polar liquids

and solution viscosity η_{ij} or η_{jk} . Rf conductivity was conveniently used to determine the number density 'n' of free charge carriers in a dielectric liquid. The determination of τ_j or τ_{jk} , μ_j from dielectric relaxation solution parameters and polar-polar mixture data at infinite dilution i.e. at $w_j \rightarrow 0$ gives reliable values. In the first case of polar-nonpolar liquid mixture, dipole-dipole interactions, effects of internal field are significantly reduced while in the later case the effect of the j th and the k th solutes on each other remains present. The object of such investigation on some interesting liquids made in this paper is to test the adequacy or otherwise of mathematical formalism so far achieved [10] in order to study the structural aspects and dielectric behaviours of some normal aliphatic alcohols in C_6H_6 and their mixtures at different experimental temperatures in $^{\circ}C$ from the relaxation parameters measured under 1MHz electric field. The variation of the real part of hf conductivity σ'_{ij} in $\Omega^{-1}cm^{-1}$ with the weight fractions w_j 's of the respective alcohols like methanol, ethanol, n-propanol, 2-butanol in C_6H_6 are displayed in Fig. 1. The behaviour of σ'_{ij} in $\Omega^{-1}cm^{-1}$ with $1/\eta_{ij}$ in $poise^{-1}$, are, however, presented in Fig 2, where η_{ij} is the coefficient of viscosity of the solution measured by Oswald's viscometer.

The values of $\ln \sigma'_{jk}$'s of polar-polar mixtures like 2 butanol + n-propanol, n-propanol + ethanol and 2-butanol + ethanol are plotted in Fig. 3 as a function of $1/T$, where T is the temperature in K. The slopes of $\ln \sigma'_{jk}$ vs $1/T$ fitted straight line curves are used to estimate the semiconduction activation energy ΔE_{jk} of the binary polar-polar mixtures as seen in Table2. The $\ln \tau_{jk} T$ against $1/T$ for the three set of polar-polar mixtures illustrated in Fig. 4 was used to estimate the thermodynamic energy parameters due to relaxation and are presented in Table 2 in order to shed more light on their structural configurations. The corresponding τ_{jk} 's at different temperatures are shown in Fig. 5 as a function of mole fraction of the j th solute in jk -mixtures. All the data thus obtained are presented in different Tables 1 to 4 respectively. It is also observed that almost all the alcohols except methanol always showed the

double relaxation times τ_1 and τ_2 for their flexible parts and the whole molecules under GHz electric field [11]. The alcohols were again expected to exhibit the triple relaxation phenomena [12] for different frequencies of electric fields in GHz range. Such long chained liquids under investigation have wide applications in the field of biological research, medicine and industry. Moreover, the study of alcohols under rf electric field of 1 MHz appears to be important to shed more light on their structural configuration. Although much study [2,3] have been made on some of such alcohols having often positive or negative slopes of σ'_{ij} vs $1/\eta_{ij}$ curves in electric field of KHz range. But the present study, however, observes similar facts at even 1 MHz range.

2. RF EXPERIMENTAL DETAILS

The block diagraph of experimental arrangement for measuring the dielectric constant of polar-nonpolar and polar-polar liquid mixtures by the method of variation of resonance has been given in Chapter 2. It consists of a rf meter, tuning condenser and a dielectric cell made up of pyrex glass of diameter 0.02 metre fitted with two circular stainless steel electrodes each of diameter 0.015 metre separated by a distance of 0.01 metre. The dielectric cell was washed several times by chromic acid and then with distilled water and dried. The cell was filled with the respective mixtures of methanol, ethanol, n-propanol, 2-butanol (j) in benzene (i) or polar-polar (jk) binary mixtures of ethanol, n-propanol and 2-butanol. The measurement of resonance currents I_1 and I_2 in the r.f meter is noted when the cell is empty and filled with dielectric liquid mixtures in the different experimental temperatures in the range from 283 K to 323K under 1 MHz electric field.

Using the network theorem, the equivalent impedance of parallel and series combination Z_p is given as

$$Z_p = \frac{R}{1+j\omega CR} \text{ and } Z_p = R' + \frac{1}{j\omega CR'} \quad \text{..... (9.1)}$$

Equating the real part we have

$$R' = \frac{R}{1 + \omega^2 C^2 R^2} \quad \dots\dots (9.2)$$

and hence $I_1 = E/R_0$ \dots\dots (9.3)

where R_0 is radio frequency resistance of the circuit.

Again $I_2 = \frac{E}{R_0 + R'} = \frac{E}{R_0 + \frac{R}{1 + \omega^2 C^2 R^2}}$ \dots\dots (9.4)

Let $\alpha = \frac{I_2}{I_1}$, then

$$(\alpha - 1) = \frac{R}{R_0 + \omega^2 C^2 R^2 R_0}$$

or $R = \frac{1 \pm \sqrt{1 - 4R_0^2 (\alpha - 1)^2 \omega^2 C^2}}{2R_0 (\alpha - 1) \omega^2 C^2}$

In the present experimental set up $4R_0^2 (\alpha - 1)^2 \omega^2 C^2 \ll 1$ hence the rf resistance of polar-nonpolar or polar-polar liquid mixture is

$$R = \frac{1}{R_0 (\alpha - 1) \omega^2 C^2} \quad \dots\dots (9.5)$$

Hence the rf conductivity of dielectric liquid mixture is

$$\sigma' = \frac{1}{4\pi R C_0} \quad \dots\dots (9.6)$$

where C_0 is the capacity of the tuning condenser = $S/4\pi l$, S and l are the area and separation between two condenser plates. The temperature of all the mixture of polar-nonpolar and polar-polar liquids were controlled by a good thermostat coated with thick thermocouples whose accuracy was claimed to be $\pm 1K$. The values of σ'_{ij} and $\sigma'_{jk}(T)$ of polar-nonpolar and polar-polar mixtures were within 2% accuracy.

3. THEORETICAL FORMULATION FOR τ_j AND μ_j

If a bound charged species of a polar molecule moves through a viscous medium under radio-frequency electric field, the equation of motion of charged species is

$$M \frac{dv}{dt} = eE_0 e^{j\omega t} - 6\pi\eta a v \quad \dots\dots (9.7)$$

where M and a are the mass and radius of the polar unit and η is the coefficient of viscosity of the medium.

Equation (9.7) can be solved by assuming the trial solution like

$$v = A e^{j\omega t} \quad \dots\dots (9.8)$$

to get the drift velocity v of the ion as

$$v = \frac{eE_0 e^{j\omega t}}{M(\gamma + j\omega)} \quad \dots\dots (9.9)$$

where $\gamma = 6\pi\eta a / M$ and $j = \sqrt{-1}$, a complex number

$$\text{Hence } v = \frac{eE_0}{M} \left[\frac{\gamma}{\gamma^2 + \omega^2} - j \frac{\omega}{\gamma^2 + \omega^2} \right] e^{j\omega t}$$

$$\text{or, mobility of ion } \mu = \frac{v}{E} = \frac{e}{M} \left[\frac{\gamma^2}{\gamma^2 + \omega^2} - j \frac{\omega}{\gamma^2 + \omega^2} \right]$$

If n be the number of ions per unit volume then the conduction current is

$$i = \frac{ne^2}{M} \left[\frac{\gamma}{\gamma^2 + \omega^2} - j \frac{\omega}{\gamma^2 + \omega^2} \right] E_0 e^{j\omega t} \quad \dots\dots (9.10)$$

The real part of hf conductivity σ'_{ij} is therefore

$$\begin{aligned} \sigma'_{ij} = ne\mu &= \frac{ne^2}{M} \frac{\gamma}{\gamma^2 + \omega^2} = \frac{ne^2}{M} \frac{6\pi\eta a / M}{\left(\frac{6\pi\eta a}{M}\right)^2 + \omega^2} \\ &= \frac{ne^2}{6\pi\eta a} \quad \text{as } \frac{6\pi\eta a}{M} \gg \omega \end{aligned} \quad \dots\dots\dots (9.11)$$

Again Murphy-Morgan relation for the complex hf conductivity σ_{ij}^* is given by :

$$\sigma_{ij}^* = \frac{\omega}{4\pi} \epsilon''_{ij} + j \frac{\omega}{4\pi} \epsilon'_{ij} \quad \dots\dots\dots (9.12)$$

where σ'_{ij} ($= \frac{\omega}{4\pi} \epsilon''_{ij}$) and σ''_{ij} ($= \frac{\omega}{4\pi} \epsilon'_{ij}$) are the real and imaginary

parts of hf conductivity.

Hence the real part of conductivity under rf electric field is

$$\begin{aligned} \sigma'_{ij} &= \frac{\omega}{4\pi} \epsilon''_{ij} + \frac{ne^2}{6\pi\eta a} \\ &= \frac{\omega}{4\pi} \left(\frac{\epsilon_{oij} - \epsilon_{\infty ij}}{1 + \omega^2\tau^2} \right) \omega\tau + \frac{ne^2}{6\pi\eta a} \\ &= \frac{\omega^2\tau}{4\pi} (\epsilon_{oij} - \epsilon_{\infty ij}) + \left(\frac{ne^2}{6\pi a} \right) \cdot \frac{1}{\eta} \end{aligned}$$

because in rf electric field $\omega^2\tau^2 \ll 1$

$$\sigma' = A + \frac{B}{\eta_{ij}} \quad \dots\dots\dots (9.13)$$

where $A = \frac{\omega^2}{4\pi} (\epsilon_{oij} - \epsilon_{\infty ij}) \cdot \tau = \pi f^2 (\epsilon_{oij} - \epsilon_{\infty ij}) \cdot \tau$.

$$\text{and } B = \frac{ne^2}{6\pi a}$$

The slope of fitted linear equation (9.13) yields the number density of free ions 'n' as placed in Tables 1 and 3 respectively for polar-nonpolar and polar-polar liquid mixtures.

To get τ_j of a polar unit we used Einstein - Stoke's relation [3]

$$\tau_j = \frac{2}{3} \frac{a^2 e}{\mu k_B \cdot T} \quad \dots\dots\dots (9.14)$$

where a = molecular radius
 e = electronic charge
 μ = mobility of free ions
 k_B = Boltzmann Constant
 T = temperature in K.

The mobility μ of free ions is related to rf conductivity σ'_{ij} by

$$\mu = \sigma'_{ij} / ne \quad \dots\dots\dots (9.15)$$

From equations (9.14) and (9.15) we have,

$$\tau_j = \frac{2na^2e^2}{3\sigma'_{ij} k_B \cdot T} \quad \dots\dots\dots (9.16)$$

Estimated τ_j and τ_{jk} of polar - nonpolar and polar-polar liquid mixtures are entered in Tables 1 and 3 respectively.

According to Smyth [1] hf σ'_{ij} is written as

$$\sigma'_{ij} = \frac{4\pi^2 f^2 N_A \tau_j \mu_j^2 \rho_{ij} (\epsilon_{oij} + 2) \cdot (n_{Dij}^2 + 2) w_j}{27 M_j k_B T} \quad \dots\dots\dots (9.17)$$

based on the assumption that $c_j = \text{molefraction} = \frac{N_A \rho_{ij}}{M_j} w_j$ and $\omega^2 \tau^2 \ll 1$

where w_j is the weight fraction of solute, N_A is the Avogadro's number, k_B is the Boltzmann constant and ρ_{ij} is the density of solution = $\rho_i (1 - \gamma w_j)^{-1} \simeq \rho_i (1 + \gamma w_j)$, $\gamma = (1 - \rho_j / \rho_i)$, ρ_j and ρ_i are the densities of solute and solvent respectively.

Table. 1: Intercepts (A) and slope (B) of σ_{ij} against $1/\eta_{ij}$ linear equations, coefficients α, β, γ of σ'_{ij} against w_j fitted equation, ion density η , relaxation time τ_j , estimated dipole moment (μ_j) together with theoretical dipole moment μ_{theo} at 25°C under 1 MHz electric field of some normal aliphatic alcohols.

Systems with Sl. Nos. & Molecular weight (M_j)	Intercept & slope of $\sigma'_{ij} \times 10^{-3}$ vs $1/\eta_{ij} \times 10^{-3}$ fitted equation		Coefficient in the equation $\sigma'_{ij} \times 10^{-3} = \alpha + \beta w_j + \gamma w_j^2$			Ion density, $\eta \times 10^{-13}$ /c.c.	Relaxation time $\tau_j \times 10^{10}$ sec.	Dipole moment μ_j in D	Theoretical dipole moment μ_{theo} in D from bond angles and bond moments
	Intercept (A)	Slope (B)	α	β	γ				
I methanol in benzene $M_j = 32$ gm.	-14.1709	88.6940	0.3106	2.2847	-1.9667	12.6760 4.0112*	4.67 6.12*	0.68 0.34*	1.76
II ethanol in benzene $M_j = 46$ gm.	2.4491	-13.7305	0.1033	2.5549	-1.9735	2.1866 2.1460*	3.01 3.16*	1.07 0.76*	1.67
III n-propanol in benzene $M_j = 60$ gm.	0.7599	-5.2762	0.0023	0.7229	-0.1489	0.9264	67.86	0.14	
IV 2-butanol in benzene $M_j = 74$ gm.	0.6189	-2.5520	0.2585	0.5648	-0.3125	0.7243	0.37	1.83	

* Ghosh & Sen, J. Phys. Soc. Japan 48 1219 (1980).

Table. 2 : Temperature variation of rf conductivity $\sigma'_{jk} \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ at different mole fraction, intercept and slope of $\ln \sigma'_{jk}(T)$ against $1/T$ curves and activation energies ΔE_{jk} in eV of binary polar mixture of different alcohols of different concentration.

System with Sl. No.	Mole fraction of jth solute (x_j)	Temperature in Kelvin(T)	Rf-conduc- tivity σ' $\sigma'_{jk} \times 10^{-3}$ in $\Omega^{-1} \text{ cm}^{-1}$ of Polar Solutes	Interest & slope of $\ln \sigma'_{jk}(T)$ vs $1/T$ fitted equation		Activation energy ΔE_{jk} of polar solute in eV
				Intercept (c)	Slope $m \times 10^{-3}$	
I(a) 2-butanol* (5.2c.c) + n-propanol (20.8c.c)	0.1690	298	0.4310	16.69	-3.168	0.27
		308	0.6958			
		313	0.7016			
		318	0.8266			
		323	0.9923			
I(b) 2-butanol* (12.5c.c) + n-propanol (12.5 c.c)	0.4486	298	0.2300	14.97	-2.845	0.25
		308	0.3400			
		313	0.2933			
		318	0.4310			
		323	0.4999			
I(c) 2-butanol* (19.2c.c) + n-propanol (4.8 c.c)	0.7649	298	0.1290	17.81	-3.925	0.34
		308	0.0950			
		313	0.2278			
		318	0.2627			
		323	0.2974			
II (a) n-propanol* (9.6 c.c.) + ethanol (14.4 c.c)	0.3349	283	1.4875	59.67	-14.815	1.28
		285	2.4981			
		287	2.9075			
		289	3.7521			
		291	7.3546			
II (b) n-propanol* (14.4. c.c) + ethanol (14.4 c.c)	0.4302	283	1.0800	66.93	-16.941	1.46
		285	2.1800			
		287	2.6100			
		289	3.4193			
		291	6.7572			
II (c) n-propanol* (14.4 c.c.) + ethanol (9.6 c.c.)	0.5311	283	0.7089	77.19	-19.93	1.72
		285	1.9160			
		287	2.3401			
		289	3.1408			
		291	6.2266			
III (a) 2-butanol* (9.6 c.c) + ethanol (14.4 c.c)	0.2905	283	1.5795	16.01	-2.45	0.21
		285	1.6415			
		287	1.8147			
		289	1.8970			
		291	1.9779			
III (b) 2 butanol* (12 c.c.) + ethanol (12 c.c)	0.3805	283	1.3350	13.82	-1.87	0.16
		285	1.3900			
		287	1.5000			
		289	1.5250			
		291	1.6000			
III (c) 2-butanol* (14.4 c.c.) + ethanol (9.6 c.c.)	0.4795	283	1.1352	11.47	-1.25	0.11
		285	1.1864			
		287	1.2508			
		289	1.2617			
		291	1.2813			

*jth solute

Table. 3: Ion density “n” from rf conductivity σ'_{jk} , relaxation time τ_{jk} , intercept & slope of $\ln \tau_{jk} T$ against $1/T$, enthalpy of activation ΔH_{τ} in K J mole⁻¹ entropy of activation ΔS_{τ} in J mole⁻¹ K⁻¹, free energy of activation ΔF_{τ} in K J mole⁻¹ at different temperatures.

System with Sl. No.	Mole fraction of jth solute x_j	Temp. in Kelvin (T)	rf conductivity of polar solutes $\sigma'_{jk} \times 10^{-3}$ in $\Omega^{-1} \text{cm}^{-1}$	Ion density $n \times 10^{-13}$ per c.c.	Relaxation time $\tau_{jk} \times 10^{11}$ in sec.	Intercept & Slope of $\ln(\tau_{jk} T)$ vs $1/T$ fitted equation		Enthalpy of activation ΔH_{τ} in K J mole ⁻¹	Entropy of activation ΔS_{τ} in J mole ⁻¹ K ⁻¹	Free energy of activation ΔF_{τ} in K J mole ⁻¹
						Intercept (C)	Slope $m \times 10^{-3}$			
I(a) 2-butanol* (5.2 c.c.) + n-propanol (20.8 c.c.)	0.1690	298	0.4310	6.9682	31.98	-33.41	5.178	43.028	81.29	18.80
		308	0.6058	7.7167	24.38					
		313	0.7016	5.7003	15.30					
		318	0.8266	5.0327	11.29					
		323	0.9923	4.3949	8.08					
I(b) 2-butanol* (12.5 c.c.) + n-proanol (12.5. c.c.)	0.4486	298	0.2300	6.9682	59.93	-31.68	4.850	40.299	66.91	20.36
		308	0.3400	7.7167	43.44					
		313	0.2933	5.7003	36.60					
		318	0.4310	5.0327	21.65					
		323	0.4999	4.3949	16.05					
I(c) 2-butanol* (19.2.c.c.) + n-propanol (4.8 c.c.)	0.7649	298	0.1290	6.9682	106.86	-34.55	5.940	49.365	92.53	21.79
		308	0.0950	7.7167	155.47					
		313	0.2278	5.7003	47.13					
		318	0.2627	5.0327	35.52					
		323	0.2974	4.3949	26.97					
II(a) n-propanol* (9.6 c.c.) + ethanol (14.4. c.c.)	0.3349	283	1.4875	20.7080	25.34	-60.99	12.531	104.132	307.22	17.19
		285	2.4981	15.0410	10.88					
		287	2.9075	14.6480	9.04					
		289	3.7521	14.9240	7.09					
		291	7.3546	28.6660	6.90					
II (b) n-propanol* (14.4 c.c.) + ethanol (14.4)	0.4302	283	1.0800	20.7080	34.90	-68.44	14.711	122.246	368.57	17.94
		285	2.1800	15.0410	12.47					
		287	2.6100	14.6480	10.07					
		289	3.4193	14.9240	7.78					
		291	6.7572	28.6660	7.51					

Table. 3 : Contd.

System with Sl. No.	Mole fraction of jth solute x_j	Temp. in Kelvin (T)	rf conductivity of polar solute $\sigma'_{jk} \times 10^{-3}$ in $\Omega^{-1} \text{cm}^{-1}$	Ion density $n \times 10^{13}$ per c.c.	Relaxation time $\tau_{jk} \times 10^{11}$ in sec.	Intercept & Slope of $\ln(\tau_{jk} T)$ vs $1/T$ fitted equation		Enthalpy of activation ΔH_i in K J mole $^{-1}$	Entropy of activation ΔS_i in J mole $^{-1}$ K $^{-1}$	Free energy of activation ΔF_i in K J mole $^{-1}$
						Intercept (C)	Slope $m \times 10^{-3}$			
II(c) n-propanol* (14.4 c.c.) + ethanol (9.6 c.c.)	0.5311	283	0.7089	20.7080	53.17	-78.95	17.775	147.714	455.06	18.93
		285	1.9160	15.0410	14.19				462.32	15.95
		287	2.3401	14.6480	11.23				460.59	15.52
		289	3.1408	14.9240	8.47				459.32	14.97
		291	6.2266	28.6660	8.15				456.07	15.00
III (a) 2-butanol* (9.6 c.c.) + ethanol (14.4 c.c.)	0.2905	283	1.5795	11.4337	15.08	-19.31	0.6542	5.44	-37.21	15.97
		285	1.6415	11.4018	14.37				-37.01	15.98
		287	1.8147	11.5411	13.06				-36.40	15.88
		289	1.8970	12.6766	13.63				-36.95	16.11
		291	1.9779	13.5238	13.85				-37.27	16.28
III(b) 2-butanol* (12 c.c.) + ethanol (12 c.c.)	0.3805	283	1.3350	11.4337	17.84	-17.26	0.0633	0.53	-55.76	16.36
		285	1.3900	11.4018	16.97				-55.62	16.47
		287	1.5000	11.5411	15.80				-55.09	16.34
		289	1.5250	12.6766	16.96				-55.75	16.64
		291	1.6000	13.5238	17.12				-55.90	16.79
III (c) 2-butanol* (14.4 c.c.) + ethanol (9.6 c.c.)	0.4795	283	1.1352	11.4337	20.98	-16.82	0.0421	0.35	-57.93	16.74
		285	1.1864	11.4018	19.88				-57.55	16.75
		287	1.2508	11.5411	18.95				-57.22	16.77
		289	1.2617	12.6766	19.49				-57.52	16.97
		291	1.2813	13.5238	20.38				-57.96	17.21

* jth Solute.

Equation (9.17) on differentiation with respect to w_j and at $w_j \rightarrow 0$ becomes

$$\left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{4\pi^2 f^2 N_A \tau_j \mu_j^2 \rho_i (\epsilon_{oi} + 2) (n_{Di}^2 + 2)}{27 M_j k_B \cdot T},$$

$\left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0}$ represents the linear coefficient of variation of σ'_{ij} against

w_j as shown in Fig. 1 and may be put equal to β . So we have

$$\mu_j = \left[\frac{27 M_j k_B \cdot T \beta}{4\pi^2 f^2 N_A \tau_j \rho_i (\epsilon_{oi} + 2) \cdot (n_{Di}^2 + 2)} \right]^{1/2} \dots\dots\dots (9.18)$$

Rf. dipole moment for alcohol molecules obtained from equation (9.18) are placed in Table 1 in order to compare them with theoretical dipole moment μ_{theo} as estimated from bond angles and bond moments.

Thermodynamic energy parameters are, however, obtained from the following equation of Eyring's rate theory [16]

$$\tau_{jk} = \frac{A'}{T} \exp(\Delta F_\tau / RT)$$

$$\text{or, } \tau_{jk} T = A' \exp. [(\Delta H_\tau - T \Delta S_\tau) / RT]$$

$$\text{or, } \ln(\tau_{jk} T) = A + \frac{B}{T} \dots\dots\dots (9.19)$$

where $A = A' e^{-\Delta S_\tau / R}$ and $B = \frac{\Delta H_\tau}{R}$ are the intercept and slope of fitted straight line equation of $\ln(\tau_{jk} T)$ against $1/T$. The estimated ΔS_τ , ΔH_τ and ΔF_τ are presented in Table 3.

4. Results and Discussions

4.1 Dielectric behaviour of polar-nonpolar liquid mixture :

The real part of rf conductivity σ_{ij}' in $\Omega^{-1}\text{cm}^{-1}$ for different weight fractions w_j 's of polar solutes like (i) methanol, (ii) ethanol, (iii) n-propanol and (iv) 2-butanol in benzene at 25°C under 1 MHz electric field are shown in Fig.1. The dependence of σ_{ij}' 's on the coefficient of viscosity (η_{ij}) of the solution are, however, illustrated in Fig. 2 along with the data measured by Ghosh and Sen [2] on methanol and ethanol in benzene at 30°C under 800 KHz electric field. The later experimental datas were placed on dotted lines of Fig. 2. The least square fitted straight line equatons of σ_{ij}' against $1/\eta_{ij}$ for different systems under investigation are computed and the respective equations are given by

$$\sigma_{ij}' \times 10^{-3} = -14.1709 + 88.6940 (1/\eta_{ij} \times 10^{-3}) \text{ for [methanol]}$$

$$\sigma_{ij}' \times 10^{-3} = 2.4491 - 13.7305 (1/\eta_{ij} \times 10^{-3}) \text{ for [ethanol]}$$

$$\sigma_{ij}' \times 10^{-3} = 0.7599 - 5.2762 (1/\eta_{ij} \times 10^{-3}) \text{ for [n-propanol]}$$

$$\sigma_{ij}' \times 10^{-3} = 0.6189 - 2.5520 (1/\eta_{ij} \times 10^{-3}) \text{ for [2-butanol]}$$

The linear equations as computed were drawn by solid lines with the experimental points placed on them. It is evident from Fig. 2 that both our experiental data of σ_{ij}' for methanol, ethanol, n-propanol and 2-butanol together with those of Ghosh and Sen [2] for methanol and etahnol shows excellent linear dependence on reciprocal of solution viscosity ($1/\eta_{ij}$). The slopes of linear curves of σ_{ij}' against $1/\eta_{ij}$ has been utilised to estimate free ion density 'n' from equation (13). With the knowledge of a from Kinetic theory, n is obtained. n is , however, used to estimate relaxation time τ_j of a polar solute from equation (16). n and τ_j so obtained are entered in columns 7 and 8 of Table 1 to compare them with available data of Ghosh and Sen [2]. Fig. 2 shows that σ_{ij}' decreases with the increase of $1/\eta_{ij}$ exhibiting negative slope of the linear curves for all the alcohols except methanol. This sort of behaviour observed elsewhere [2] may be explained on the basis of the fact that methanol is less viscous than solvent benzene in comparison to other alcohols.

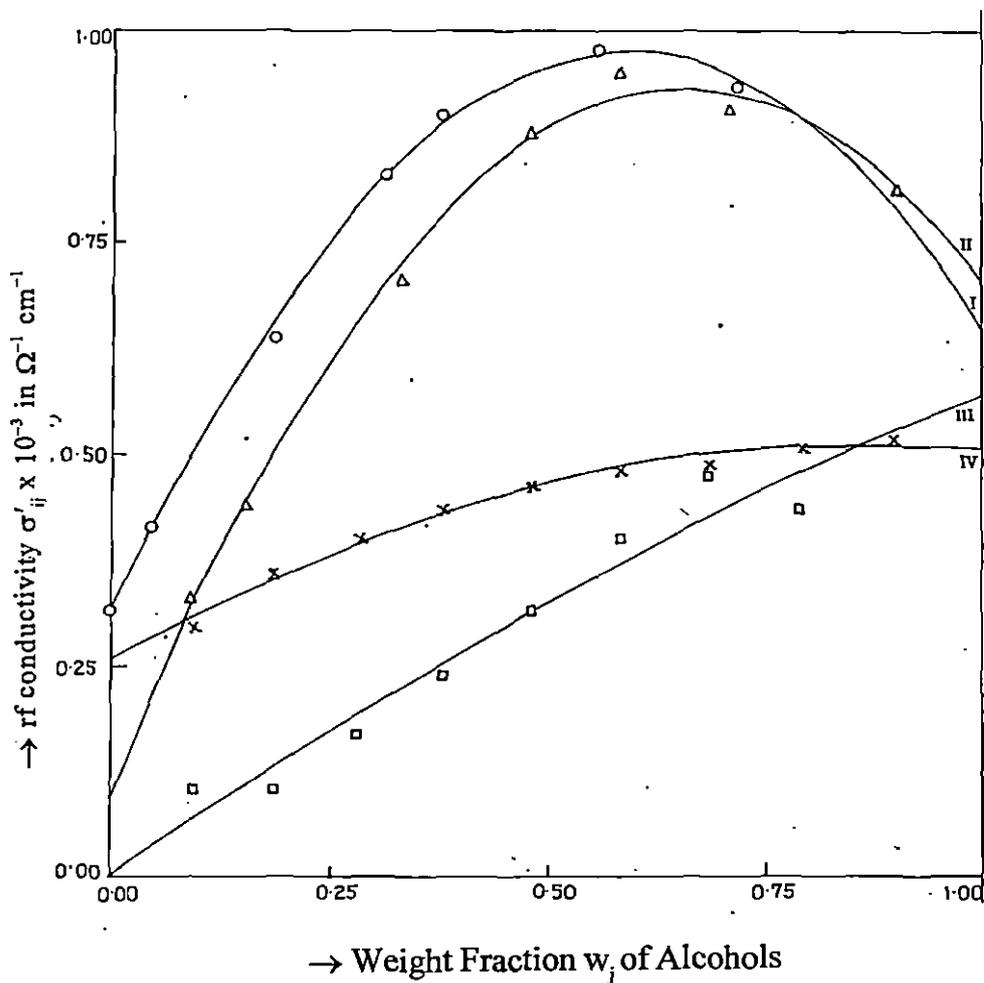


Fig. 1. Variation of r.f. conduction σ'_{ij} in $\Omega^{-1} \text{ cm}^{-1}$ with weight fraction w_j

methanol —○—○—, ethanol —△—△—,
 n-propanol —□—□—, 2-butanol —x—x—

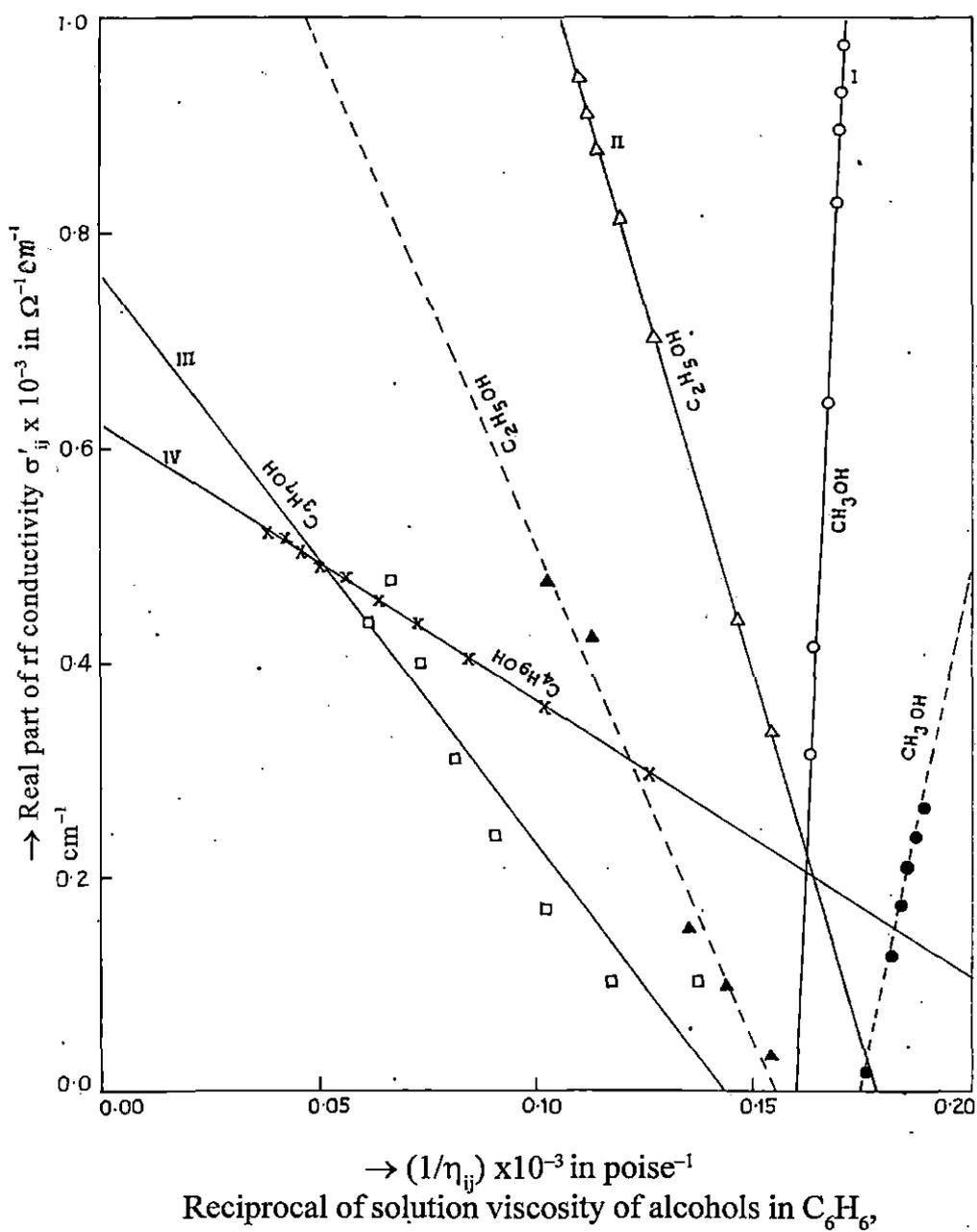


Fig. 2. Variation of r.f. conduction σ'_{ij} in $\Omega^{-1} \text{cm}^{-1}$ with reciprocal of solution viscosity $1/\eta_{ij} \times 10^{-3}$ in poise^{-1} .

methanol —○—○—, ethanol —△—△—,
 n-propanol —□—□—, 2-butanol —x—x—

It is seen that σ_{ij}' for all systems except n-propanol increases gradually with w_j attaining a maximum value at $w_j = 0.5$ indicating there by the change of phase beyond a certain concentration (Fig.1). n-propanol may show its change of phase in higher concentration. σ_{ij}' involved with w_j may be put by a polynomial equation of the form $\sigma_{ij}' = \alpha + \beta w_j + \gamma w_j^2$ whose linear coefficient β evaluated by least squares fitting technique has been utilised to get rf dipole moment μ_j of a polar unit. μ_j thus estimated are placed in Table 1 for comparison with μ_j values obtained by Ghosh and Sen [2] for methanol and ethanol. Theoretical dipole moment estimated from available bond angles and bond moments of substituent polar groups of alcohol molecules as sketched in Fig. 6 are, however, placed in column 10 of Table 1. This study, therefore, gives a deep insight into the structural configuration of the alcohol molecules as shown in Fig. 6.

4.2. RF CONDUCTIVITY OF POLAR-POLAR MIXTURES

The plot of $\ln \sigma_{jk}'(T)$ against $1/T$ was, however, displayed in Fig 3 with the measured data of $\sigma_{jk}'(T)$'s presented in the 4th column of Table 2 at three different concentrations x_j , where x_j is the mole fraction of the jth solute. The computed linear equations of $\ln \sigma_{jk}'(T)$ against $1/T$ were also worked out for different respective systems as noted below.

2-butanol + n-propanol mixture

$$(I a) \ln \sigma_{jk}'(T) = 16.6895 - 3167.7484 (1/T)$$

$$(I b) \ln \sigma_{jk}'(T) = 14.9709 - 2844.6878 (1/T) \text{ and}$$

$$(I c) \ln \sigma_{jk}'(T) = 17.8118 - 3925.1169 (1/T)$$

n-propanol + ethanol mixture

$$(IIa) \ln \sigma_{jk}'(T) = 59.6722 - 14814.9073 (1/T)$$

$$(IIb) \ln \sigma_{jk}'(T) = 66.9322 - 16940.9227 1/T \text{ and}$$

$$(IIc) \ln \sigma_{jk}'(T) = 77.1874 - 19931.2778. 1/T$$

2-butanol + ethanol mixture

$$(IIIc) \ln \sigma_{jk}'(T) = 16.0104 - 2447.4359. 1/T$$

$$(IIIb) \ln \sigma_{jk}'(T) = 13.8157 - 1872.4399. 1/T \text{ and}$$

$$(IIIc) \ln \sigma_{jk}'(T) = 11.4705 - 1251.8801 . 1/T$$

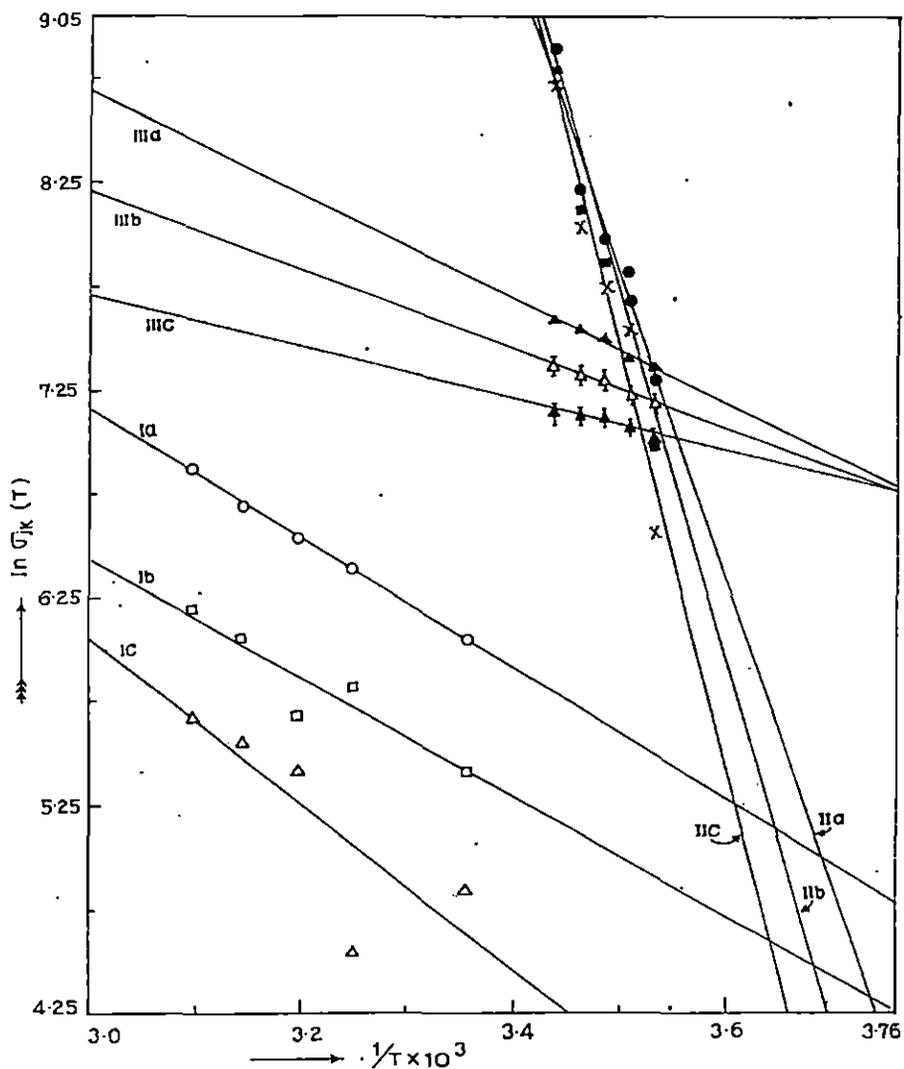


Fig. 3. Plot of $\ln \sigma'_{jk}(T) - 1/T$ fitted equations

For 2-butanol + n-propanal mixture

I (a) —○—○— I (b) —□—□— I (c) —△—△—

For n-propanol + ethanol mixture

II (a) —●—●— II (b) —■—■— II (c) —x—x—

For 2-butanol + ethanol mixture

III (a) 40% 60% —▲—▲—

III (b) 50% 50% —△—△—

III (c) 60% 40% —▲—▲—

The conduction that arises due to mobility of free ions or electrons in such dielectropolar liquids is an additional term to the dielectric loss ϵ_{ij}'' and is expressed as the real part of conductivity [15]. The rf conductivity $\sigma_{jk}'(T)$'s of 2-butanol + n-propanol, n-propanol + ethanol and 2-butanol + ethanol at various concentrations as reported in Table 2 under 1 MHz electric field of experimental temperature range 283 K to 323 K were measured. It is evident from Table 2 and Fig 3 that the addition of n-propanol in the first mixture, ethanol in the last two mixtures there are marked decrease in the rf conductivities as $1/T$ increases. The temperature dependence of $\sigma_{jk}'(T)$ of the polar-polar mixtures of j and k may be expressed as

$$\sigma_{jk}'(T) = \sigma_1' \exp. \left(\frac{-\Delta E_{jk}}{k_B \cdot T} \right) \dots\dots\dots (9.20)$$

where σ_1' is the pre-exponential factor which is assumed to be constant for a given liquid mixture, ΔE_{jk} is the activation energy of j th and k th polar liquid mixture and k_B is the Boltzmann constant. σ_1' and ΔE_{jk} for the mixtures can be evaluated from the intercepts and slopes of the linear equation (9.20). The activation energies of polar-polar mixtures are placed in column 7 of Table 2. The plot of $\ln \sigma_{jk}'(T)$ of polar-polar mixtures against $1/T$ of the respective solutes were, however, drawn with the various mole fractions x_j 's of the j th solute. The plots were found to be strictly linear as they were supported by the experimental data of σ_{jk}' of Table 2. The extrapolation of linear curves of $\ln \sigma_{jk}'(T)$ against $1/T$ in K^{-1} of Fig 3 shows that all straight lines for respective systems have a tendency to meet in the neighbourhood of certain values of $1/T$ depending upon the nature of the respective mixtures under investigation.

4.3 RELAXATION BEHAVIOUR OF POLAR-POLAR LIQUID MIXTURES :

The dielectric relaxation time τ_{jk} of polar-polar liquid mixtures of various concentrations at different experimental temperatures were also found out by using the following relation [15].

$$\tau_{jk} = \frac{2na^2e^2}{3 \sigma_{jk}' k_B \cdot T} \dots\dots\dots(9.21)$$

where n is the ion density, e is the electronic charge and a is the radius of rotating unit which is of the order of 10^{-8} cm. The values of ion density of different rotating units at different temperatures were obtained from the slope of $(\sigma'_{jk} - 1/\eta_{jk})$ linear equations and placed in 5th column of Table 3. The estimated values of τ_{jk} of the polar mixtures from equation (9.21) for different mole fractions x_j at different experimental temperatures are placed in 6th column of Table 3. In order to get an idea of the variation of τ_{jk} of the binary polar mixture with the three different mole fraction x_j of the j th solute plots are drawn for three binary polar mixtures keeping temperature constant and shown in Fig.5. $(\tau_{jk} - x_j)$ curves are drawn according to the following equations obtained from values of x_j , keeping experimental temperature constant and corresponding values of τ_{jk} as reported in Table -3.

For 2-butanol + n-propanol mixture

1. $\tau_{jk} \times 10^{11} = 21.244 + 49.794 x_j + 81.234 x_j^2$ at 298 K,
2. $\tau_{jk} \times 10^{11} = 49.264 - 228.255 x_j + 479.968 x_j^2$ at 308 K
3. $\tau_{jk} \times 10^{11} = -3.030 + 120.628 x_j - 71.970 x_j^2$ at 313 K
4. $\tau_{jk} \times 10^{11} = 5.893 + 30.007 x_j + 11.408 x_j^2$ at 318 K
5. $\tau_{jk} \times 10^{11} = 3.747 + 24.560 x_j + 6.387 x_j^2$ at 323 K

For n-propanol + ethanol mixture

6. $\tau_{jk} \times 10^{11} = 51.272 - 215.683 x_j + 412.847 x_j^2$ at 283 K
7. $\tau_{jk} \times 10^{11} = 5.558 + 15.273 x_j + 1.845 x_j^2$ at 285 K
8. $\tau_{jk} \times 10^{11} = 5.927 + 8.119 x_j + 3.514 x_j^2$ at 287 K
9. $\tau_{jk} \times 10^{11} = 4.369 + 8.813 x_j - 2.055 x_j^2$ at 289 K
10. $\tau_{jk} \times 10^{11} = 4.714 + 6.627 x_j - 0.296 x_j^2$ at 291 K

For 2-butanol + ethanol mixture

11. $\tau_{jk} \times 10^{11} = 6.781 + 26.962 x_j + 5.526 x_j^2$ at 283 K
12. $\tau_{jk} \times 10^{11} = 6.268 + 27.124 x_j + 2.636 x_j^2$ at 285 K
13. $\tau_{jk} \times 10^{11} = 5.015 + 25.59 x_j + 7.240 x_j^2$ at 287 K
14. $\tau_{jk} \times 10^{11} = -3.85 + 77.839 x_j - 60.821 x_j^2$ at 289 K
15. $\tau_{jk} \times 10^{11} = 1.286 + 48.518 x_j - 18.138 x_j^2$ at 291 K

All the curves are shown in Fig. 5

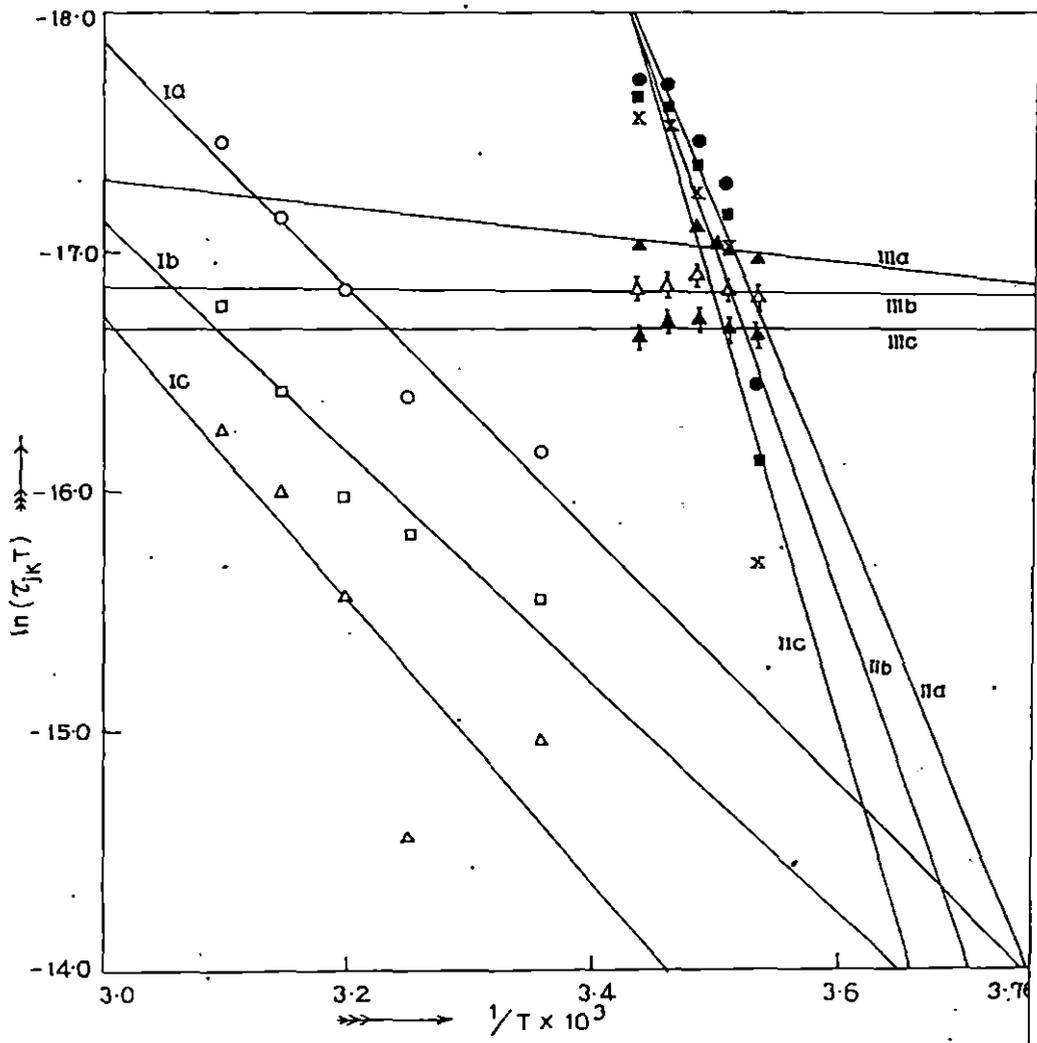


Fig. 4. Plot of $\ln(\tau_{jk} T) - 1/T$ fitted equations

For 2-butanol + n-propanol mixture.

I. (a) —○—○—, I (b) —□—□— I (c) —△—△—

For n-propanol + ethanol mixture.

II (a) —●—●—, II (b) —■—■— II (c) —x—x—

For 2-butanol + ethanol mixture.

III (a) 40% 60% —▲—▲—

III (b) 50% 50% —△—△—

III (c) 60% 40% —▲—▲—

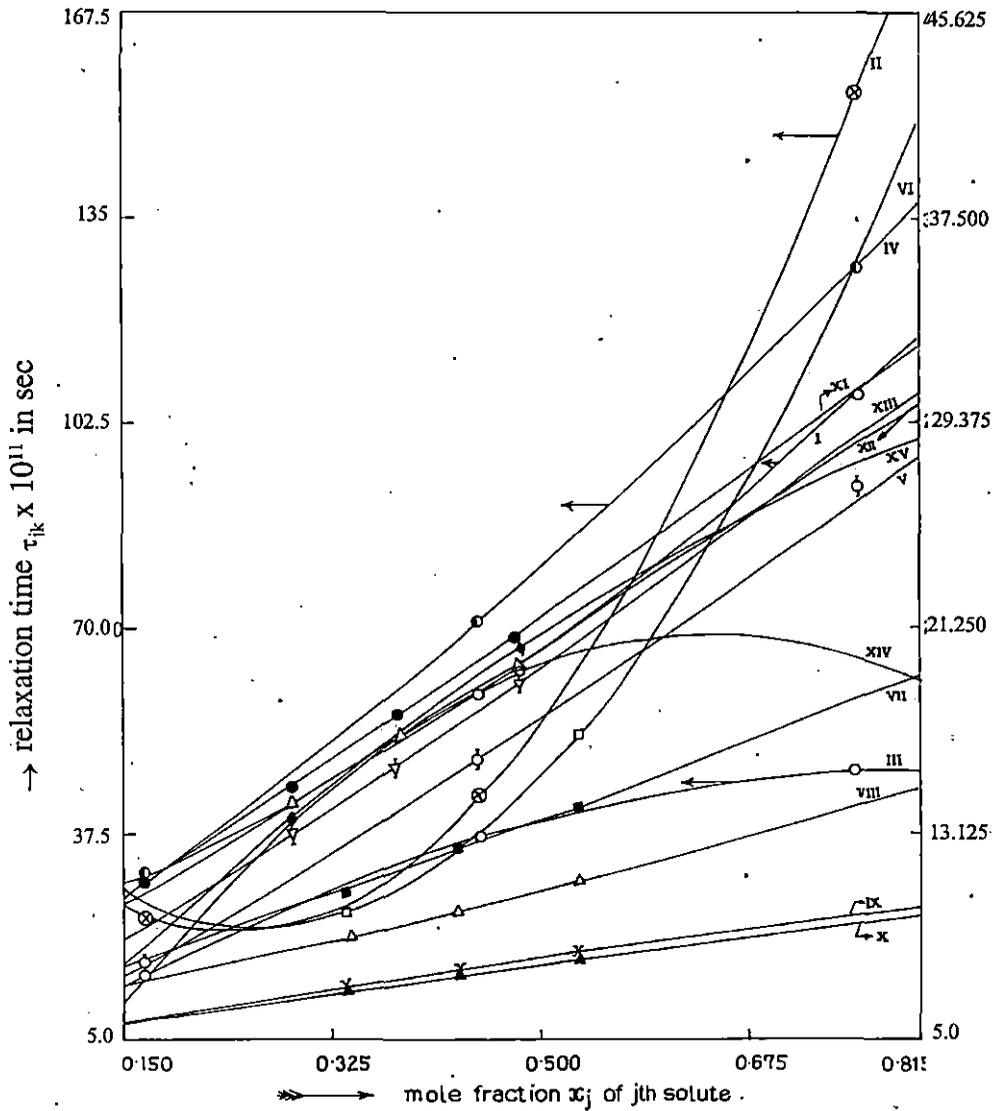


Fig. 5.

Fig. 5. : Plot of $\tau_{jk} \times 10^{11} - x_j$ fitted equations at different constant temperature with serial number of equations. For 2-butanol + n-propanol mixture :

1. —○—○— at 298K, 2. —⊕—⊕— at 308K, 3. —⊗—⊗— at 313 K,
 4. —⊙—⊙— at 318K, 5. —⊚—⊚— at 323K

For n-propanol + ethanol mixture.

6. —□—□— at 283K, 7. —■—■— at 285K, 8. —△—△— at 287K,
 9. —X—X— at 289, 10. —▲—▲— at 291K.

For 2 butanol + ethanol mixture

11. —⊖—⊖— at 283K, 12. —△—△— at 285K, 13. —▽—▽— at 287K.
 14. —▼—▼— at 289K, 15. —◆—◆— at 291K.

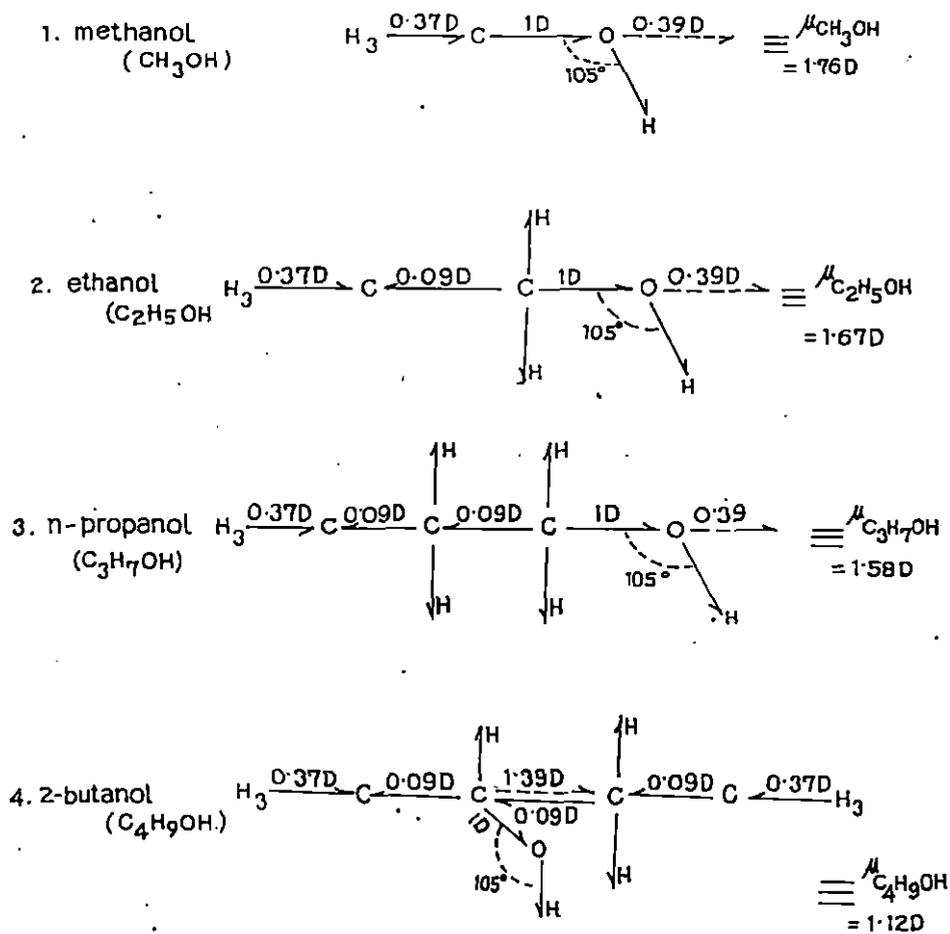


Fig. 6. Conformational structure of some alcohols.

The results show that τ_{jk} increases monotonically with x_j at all temperatures. It is found that τ_{jk} 's are of constant values when $x_j < 0.325$ for all the system under investigation. The individual relaxation time τ_j or τ_k of the j th and k th solute for all the systems at different experimental temperatures can thus be obtained by extrapolating the curves at $x_j \rightarrow 0$ and $x_k \rightarrow 1.0$ and τ_j and τ_k values thus obtained are reported in Table 4. τ_k values were found to be negative for the system 2-butanol + n-propanol mixture and for the system 2-butanol + ethanol mixture at temperatures 313 K and 289 K respectively. Relaxation time were also calculated from mixing rule from the values of x_j and x_k obtained by extrapolating $(\tau_{jk} - x_j)$ curves of Fig.5 and are placed in the 5th and 6th columns of Table 4. Experimental relaxation time as calculated from eq. 9.21 is also reported in the 8th column of Table 4 for comparison. Experimental values of relaxation time are found to agree excellently well with the values calculated from mixing rule for the system 2-butanol + n-propanol (Syst.I) of $x_j = 0.1690, 0.4486$ and 0.7649 at 318 K, 323K respectively; for the system n-propanol + ethanol (Syst.II) of $x_j = 0.3349, 0.4302$ and 0.5311 at temperatures 285 K, 287 K, 289K, 291 K and for the system 2-butanol + ethanol (Syst. III) of $x_j = 0.2905, 0.3805$ and 0.4795 at temperatures 283 K, 285 K and 287 K which indicates obeying of colligative property at these temperatures. Experimental relaxation times are found to differ highly for System I 2-butanol + n-propanol mixture at temperature 298 K, 308 K and 313 K; for system II at 283 K and for System III at temperature 289 K and 291 K which shows that the systems do not obey colligative property at those temperatures. Comparatively high values of τ_{jk} shows that more association between j th and k th solute molecules has occurred at that temperatures and mole fractions where as low values of τ_{jk} indicate less association between solute and solvent units.

This sort of behaviour indicates that the intermolecular interactions among binary polar species in higher concentration occurs to increase τ_{jk} . This behaviour also invites further study to see the value of τ_{jk} for 1 : 1 binary mixture.

It is interesting to note that the relaxation time τ_{jk} of the mixtures decreases with the rise of temperature except for the mixture 2-butanol + ethanol This may probably due to experimental uncertainty introduced in its rf conductivity

Table. 4 : Relaxation time $\tau_k \times 10^{11}$ of kth solute and $\tau_j \times 10^{11}$ of jth solute at different experimental temperature from $\tau_{jk} - x_j$ fitted equation for $x_j = 0$ and $x_j = 1$, mole fraction x_j and $x_k (=1-x_j)$, relaxation time τ_{jk} for the mixture as obtained from mixing rule $\tau_{jk} = x_j \tau_j + x_k \tau_k$ and from equation (9.21).

Systems with Sl. No.	Temp. in Kelvin	Value of Relaxation time in sec. obtained from $(\tau_{jk} - x_j)$ fitted equations		Mole fraction		Relaxation time from mixing rule $\tau_{jk} \times 10^{11} =$ $x_j \tau_j + x_k \tau_k$	Experimental relaxation time in sec. $\tau_{jk} \times 10^{11}$ from equation (9.21)
		$\tau_k \times 10^{11}$ for $x_j = 0$	$\tau_j \times 10^{11}$ for $x_j = 1$	x_j	x_k		
I 2-butanol + n-propanol	298	21.244	152.272	0.1690	0.8310	43.39	31.98
				0.4486	0.5514	80.02	59.93
				0.7649	0.2351	121.47	106.86
	308	49.264	300.977	0.1690	0.8310	91.80	24.38
				0.4486	0.5514	162.18	43.44
				0.7649	0.2351	241.80	155.47
	313	- 3.030	45.628	0.1690	0.8310	5.244	15.30
				0.4486	0.5514	18.80	36.60
				0.7649	0.2351	34.19	47.13
	318	5.893	47.308	0.1690	0.8310	12.89	11.29
				0.4486	0.5514	24.47	21.65
				0.7649	0.2351	37.57	35.52
323	3.747	34.694	0.1690	0.8310	8.98	8.08	
			0.4486	0.5514	17.63	16.05	
			0.7649	0.2351	27.42	26.97	
II. n-propanol + ethanol	283	51.272	248.436	0.3349	0.6651	117.30	25.34
				0.4302	0.5698	136.09	34.90
				0.5311	0.4689	155.98	53.17
	285	5.558	22.676	0.3349	0.6651	11.29	10.88
				0.4302	0.5698	12.92	12.47
				0.5311	0.4689	14.65	14.19
	287	5.927	17.56	0.3349	0.6651	9.82	9.04
				0.4302	0.5698	10.93	10.07
				0.5311	0.4689	12.10	11.23
	289	4.369	11.127	0.3349	0.6651	6.63	7.09
				0.4302	0.5698	7.28	7.78
				0.5311	0.4689	7.96	8.47
291	5.368	11.699	0.3349	0.6651	7.49	6.90	
			0.4302	0.5698	8.09	7.51	
			0.5311	0.4689	8.73	8.15	
II. 2-butanol + ethanol	283	6.781	39.269	0.2905	0.7095	16.22	15.08
				0.3805	0.6195	19.14	17.84
				0.4795	0.5205	22.36	20.98
	285	6.268	36.028	0.2905	0.7095	14.91	14.37
				0.3805	0.6195	17.59	16.97
				0.4795	0.5205	20.54	19.88
	287	5.015	37.845	0.2905	0.7095	14.55	13.06
				0.3805	0.6195	17.51	15.80
				0.4795	0.5205	20.76	18.95
	289	- 3.85	13.168	0.2905	0.7095	1.09	13.63
				0.3805	0.6195	2.62	16.96
				0.4795	0.5205	4.31	19.49
291	1.286	31.666	0.2905	0.7095	10.11	13.85	
			0.3805	0.6195	12.84	17.12	
			0.4795	0.5205	15.85	20.38	

measurement. Therefore, the plots of $\ln(\tau_{jk} T)$ against $1/T$ are, however, given in Fig 4 to study the molecular dynamics as well as the molecular environment of various binary polar mixtures. The variation of $\ln(\tau_{jk} T)$ against $1/T$ were also worked out for the systems as noted below.

2-butanol + n-propanol mixture

$$(Ia) \quad \ln(\tau_{jk} T) = -33.4143 + 5177.878. 1/T$$

$$(Ib) \quad \ln(\tau_{jk} T) = -31.6779 + 4849.4750. 1/T$$

$$(Ic) \quad \ln(\tau_{jk} T) = -34.5532 + 5940.4530. 1/T$$

n-propanol + ethanol mixture

$$(IIa) \quad \ln(\tau_{jk} T) = -59.9616 + 12235.015. 1/T$$

$$(IIb) \quad \ln(\tau_{jk} T) = -66.9761 + 14290.552. 1/T$$

$$(IIc) \quad \ln(\tau_{jk} T) = -77.4549 + 17345.073. 1/T$$

2-butanol + ethanol mixture

$$(IIIa) \quad \ln(\tau_{jk} T) = -19.3109 + 654.2014. 1/T$$

$$(IIIb) \quad \ln(\tau_{jk} T) = -17.1234 + 81.2733. 1/T$$

$$(IIIc) \quad \ln(\tau_{jk} T) = -16.8236 + 42.0596. 1/T$$

The variation of $\ln(\tau_{jk} T)$ against $1/T$ obeys Eyring's rate theory [16] for almost all systems as shown in Fig.4. The system I and II showed steeper fall of $\ln(\tau_{jk} T)$ with $1/T$ while system III showed almost horizontal curves which had tendency to meet at lower temperature.

Different thermodynamic energy parameters like enthalpy of activation $\Delta H_{\tau_{jk}}$, entropy of activation $\Delta S_{\tau_{jk}}$ and free energy of activation $\Delta F_{\tau_{jk}}$ of the polar-polar mixture for dielectric relaxation process were obtained from Eyring's rate theory [16] and are placed in Table 3.

$$\tau_{jk} = [h/k_B \cdot T] \exp [\Delta F_{\tau_{jk}} / RT] \quad \dots\dots\dots (9.22)$$

$$\Delta F_{\tau_{jk}} = \Delta H_{\tau_{jk}} - T \Delta S_{\tau_{jk}} \quad \dots\dots\dots (9.23)$$

For the system 2-butanol + n-propanol mixture the enthalpy of activation $\Delta H_{\tau_{jk}}$ in K.J mole⁻¹ are almost the same as shown in Table 3. It is also confirmed by the nearly parallel straight line curves. Free energy of activation $\Delta F_{\tau_{jk}}$ of the systems increases with x_j while entropy of activation $\Delta S_{\tau_{jk}}$ decreases with x_j assuming minimum value indicating the orderliness of the system at different temperatures. $\Delta S_{\tau_{jk}}$ for system II increases with x_j . This is due to the fact that molecular environment becomes more disordered with the increase of concentration of n-propanol + ethanol polar mixture. The negative values of $\Delta S_{\tau_{jk}}$ for 2-butanol + ethanol mixture indicates the co-operative process for such systems which is also supported by the low values of $\Delta H_{\tau_{jk}}$ for the aforesaid system at different x_j .

CONCLUSION

Relaxation parameters viz n , τ_j , μ_j (and if possible μ_{jk}) for polar - nonpolar liquid mixtures and ΔE_{jk} , τ_{jk} for polar-polar mixtures obtained under rf electric field of frequency 1 MHz at 25°C within the framework of Debye -Smyth model shows close agreement with the values estimated by previous workers [2,5]. This investigation establishes the validity of the theoretical formulations so far achieved. Although large disagreement has been observed in τ_j and μ_j values for n-propanol, probably due to experimental uncertainty. Thermodynamic energy parameters $\Delta H_{\tau_{jk}}$, $\Delta S_{\tau_{jk}}$ and $\Delta F_{\tau_{jk}}$ provides one with important information regarding stability of the systems and molecular environment around polar solutes. Study of theoretical dipole moment μ_{theo} gives a deep insight into the distribution of bonds and rotation of -OH groups of alcohol molecules under rf electric field. Invariably this investigation gives valuable information regarding structural configuration of polar molecules.

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