

CHAPTER VI

CONDUCTIVITY, RELAXATION TIME AND ENERGY OF ACTIVATION OF SOME ALCOHOL + BENZENE MIXTURE AT RADIO FREQUENCY FIELD.

INTRODUCTION:

Alcohols presents a complex and interesting problem in liquid structure because of the possibility of strong hydrogen bonding between adjacent molecules. The dielectric properties of alcohol was initially carried out by Mizushima (1927) and then by Debye (1929). Lateron many workers extensively investigated the dielectric properties of pure aliphatic alcohols and also of dilute solution in different nonpolar solvents. Measurement over a very large frequency range later on showed that in aliphatic alcohols, the anomalous dispersion and absorption cannot be described by a single relaxation time. The different behaviour of the alcohols in pure state and in dilute solution in nonpolar solvent indicates that the dipole orientation is essentially determined by the association of -OH groups via hydrogen bridge and not by the properties of the individual group. Garg and Smyth (1965) measured the dielectric constant and losses of the normal alcohols at

various temperatures and frequencies and obtained three different relaxation times for each alcohol viz. (a) in the low frequency region it is around 1 to 22×10^{-10} sec. (b) in the intermediate frequency region it is about the order of 1.7 to 5×10^{-11} sec. and (c) in the high frequency region it is around 1.7 to 4×10^{-12} sec. which can be taken as dipole rotation of single molecule. Sen and Ghosh (1972) estimated the time of relaxation of some pure normal alcohol in radio frequency region which fall in the low frequency region. As there is no suitable expression for finding out the relaxation time for normal alcohols in dilute solution of nonpolar solvents from radio frequency conductivity data, we used the Debye dispersion equation (Smyth, 1955)

$$K' = \frac{\mu^2 N e_{ij} F_{ij}}{3 M_j k T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) W_j \quad \dots 6.1$$

where r.f. conductivity $K' = \frac{\omega \epsilon''}{4\pi}$ and ϵ'' is the dielectric loss. It has already been established that the dielectric properties of the liquid varies with temperature, concentration in nonpolar solvent as well as with frequency in the dispersion region. Therefore a relatively large change in dielectric relaxation is expected by decreasing or by increasing the viscosity of liquids, either by temperature variation or by varying the concentration of the polar molecules in nonpolar solvents.

So in the present paper an attempt has been taken to study the nature of variation of dipolar relaxation time of three normal alcohols such as methyl, ethyl and propyl alcohols at various concentrations in benzene and at different temperatures from radio frequency conductivity measurements. The activation energy which characterised the dipole relaxation process in reaction kinetic energy consideration can be determined by using Eyring (1941) rate equations

$$\tau = \frac{A}{T} \exp\left(\frac{\Delta F_{\tau}}{RT}\right) \quad \dots 6.2$$

This equation has been utilised to calculate the variation of thermodynamical quantities of orientation, such as free energy of activation ΔF_{τ} , enthalpy of activation ΔH_{τ} and entropy of activation ΔS_{τ} of the three normal alcohols.

Experimental Arrangement:

The schematic diagram of the experimental arrangement and the method of determination of radio frequency conductivity at 1 MHz. has been described in detail in chapter II section 1.

The dielectric cell was made up of a pyrex glass tube of diameter 2 cms. with a pair of stainless steel circular electrodes of diameter 1.5 cms., sepa-

rated by a distance of 1 cm. Before filling the dielectric liquids, the glass cell was cleaned with chromic acid, then with distilled water and finally with benzene. The liquids under investigation such as methyl alcohol ethyl alcohol, propyl alcohol and benzene were all Analar grade obtained from Messrs, British Drug House, London. The viscosity of the liquids were measured with an Ostwald viscometer taking water as a standard liquid for comparison. The temperatures in all the experiments were controlled within $\pm 1^\circ\text{C}$ by a thermostat. The method of measurement of viscosity and purification of chemicals are given in chapter II section 2.5 and 2.6 respectively.

Results and Discussion:

The high frequency conductivity of polar dielectric liquid in nonpolar solvent is expressed (Smyth, 1955) as

$$K_{ij}^* = K'_{ij} + jK''_{ij} \quad \dots 6.3$$

where K'_{ij} is the real part and K''_{ij} is the imaginary part of the r.f. conductivity of the dielectric solution. Assuming there is no free ion present in the dielectric liquid, the real part of the conductivity has been expressed by the relation

$$K'_{ij} = \frac{\omega \epsilon''_{ij}}{4\pi} \quad \text{where} \quad \epsilon''_{ij} \quad \text{and} \quad \omega$$

are the dielectric loss and angular frequency of the applied field respectively. Now the number of experimental facts has established that, polar liquids especially alcohols contain atleast some percentage of free ions which are responsible for their higher conductivity. But in our present experiment we have tactfully eliminated the effect of free ions by estimating the r.f. conductivity at infinite dilution of alcohols in nonpolar solvent.

The r.f. conductivity (K'_{ij}) in esu of polar and nonpolar liquid mixture of different weight fractions (W_j) and temperatures can be expressed by the three terms polynomial equation in weight fraction W_j as

$$K'_{ij} = \alpha + \beta W_j + \gamma W_j^2 \quad \dots 6.4$$

where α , β and γ are the constants. The computed values of the K'_{ij} in esu of various weight fractions at different temperatures of the three systems (1) methanol + benzene, (2) ethanol + benzene and (3) propanol + benzene are given in the table (6.1.a,b,c) Table (6.2.a,b,c,d) and Table (6.3.a,b,c) respectively.

System 1Methanol in Benzene.

$$K'_{ij} \times 10^{-3} = 0.552 - 1.499 W_j + 2.792 W_j^2 \quad \text{at} \\ \text{temp. } t = 30^\circ\text{C}$$

$$K'_{ij} \times 10^{-3} = 1.269 - 3.91 W_j + 4.93 W_j^2 \quad \text{at} \\ \text{temp. } t = 40^\circ\text{C}$$

$$K'_{ij} \times 10^{-3} = 1.192 - 3.986 W_j + 5.471 W_j^2 \quad \text{at} \\ \text{temp. } t = 50^\circ\text{C.}$$

System 2Ethanol in Benzene.

$$K'_{ij} \times 10^{-2} = 2.178 - 8.321 W_j + 10.515 W_j^2 \quad \text{at temp.} \\ t = 30^\circ\text{C}$$

$$K'_{ij} \times 10^{-2} = 3.922 - 14.37 W_j + 16.87 W_j^2 \quad \text{at temp.} \\ t = 40^\circ\text{C}$$

$$K'_{ij} \times 10^{-2} = 4.356 - 15.404 W_j + 18.527 W_j^2 \quad \text{at temp} \\ t = 50^\circ\text{C}$$

$$K'_{ij} \times 10^{-2} = 3.624 - 12.195 W_j + 17.059 W_j^2 \quad \text{at temp.} \\ t = 60^\circ\text{C.}$$

and System 31-Propanol in Benzene

$$K'_{ij} \times 10^{-2} = 4.851 - 8.624 W_j + 6.119 W_j^2 \quad \text{at temp.} \\ t = 30^\circ\text{C}$$

$$K'_{ij} \times 10^{-2} = 4.39 - 7.065 W_j + 5.771 W_j^2 \quad \text{at temp.} \\ t = 40^\circ\text{C}$$

$$K'_{ij} \times 10^{-2} = 3.684 - 5.539 W_j + 6.266 W_j^2 \quad \text{at temp.} \\ t = 50^\circ\text{C}$$

The coefficients of W_j of the above equations are important to evaluate the relaxation time τ_s of polar solute in dilute solution of nonpolar solvent.

Eq. (6.1) on being differentiated with respect to W_j as $W_j \rightarrow 0$ takes the following form:

$$\left(\frac{dK'_{ij}}{dW_j} \right)_{W_j \rightarrow 0} = \frac{\mu^2 N \rho_i F_i}{3 M_j k T} \left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} \right) = \beta \quad \dots 6.5$$

since $\omega^2 \tau_s^2 \ll 1$ in the radio frequency region so eq. (6.5) finally becomes

$$\tau_s = \frac{3 M_j k T \beta}{\mu^2 N \rho_i F_i \omega^2} \quad \dots 6.6$$

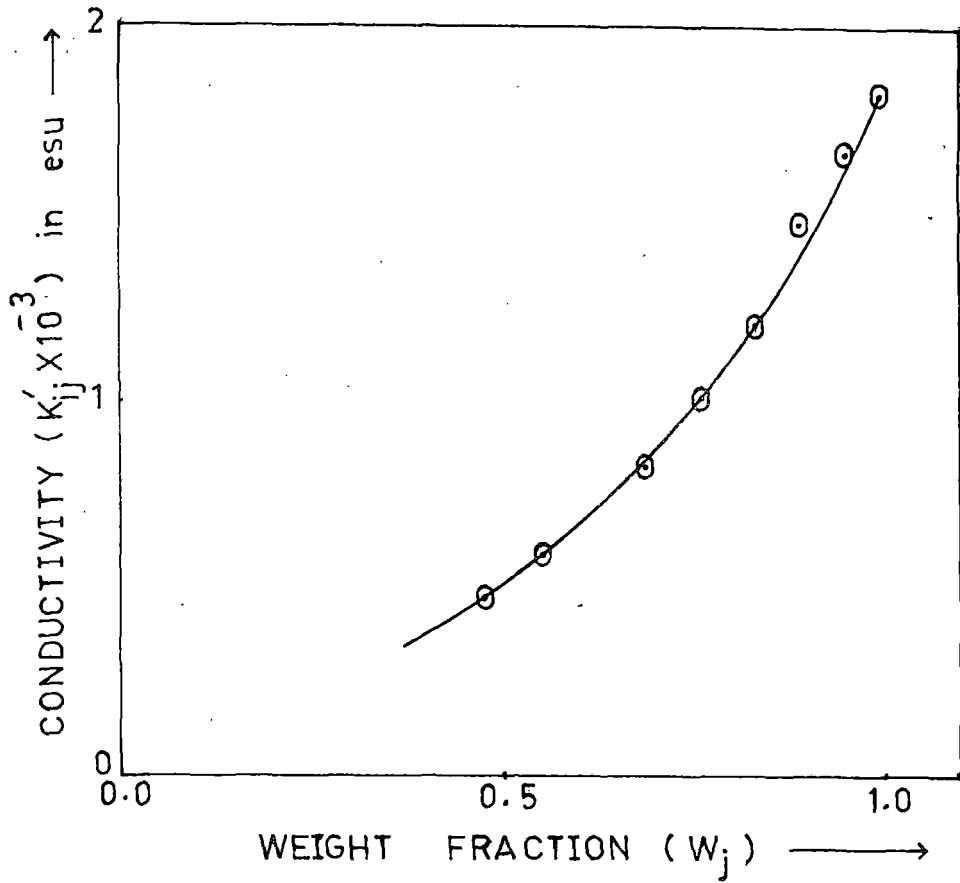


Fig-6.1 Conductivity K'_{ij} is plotted against Weight fraction W_j for methanol in benzene at 30°C .

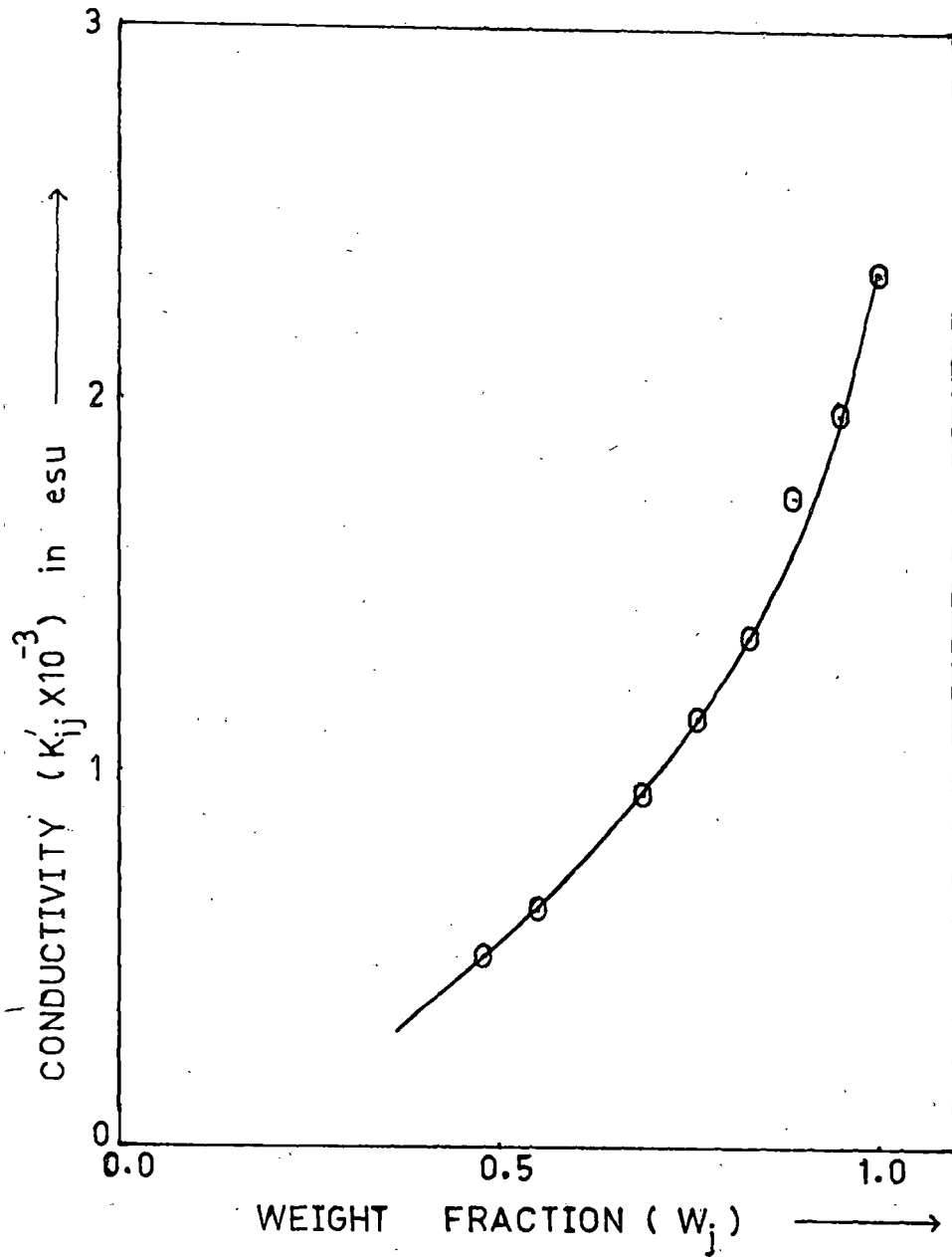


Fig-6.2 Conductivity K'_{ij} is plotted against Weight fraction W_j for methanol in benzene at 40°C .

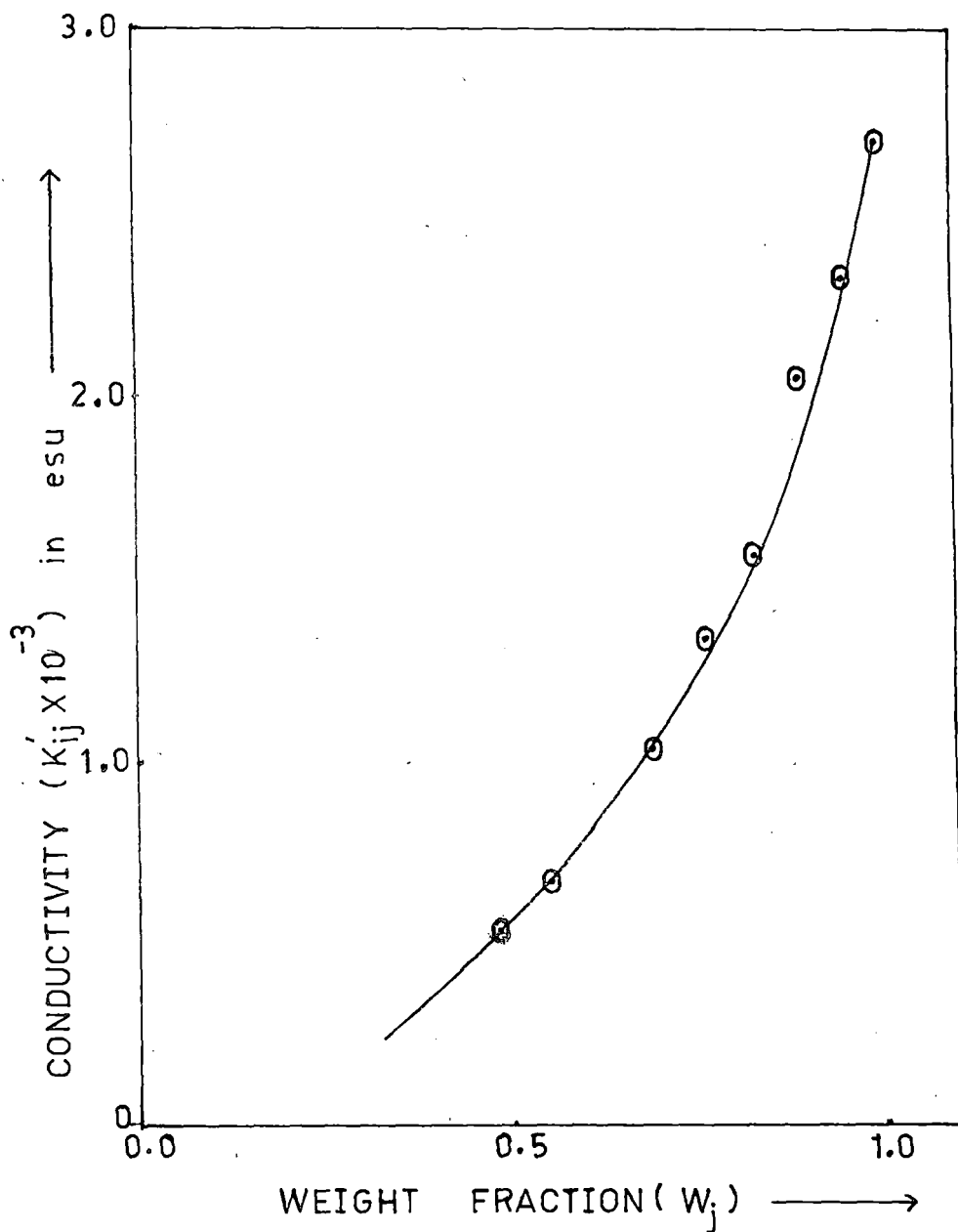


Fig-6.3 Conductivity K'_{ij} is plotted against Weight fraction W_j for methanol in benzene at 50°C .

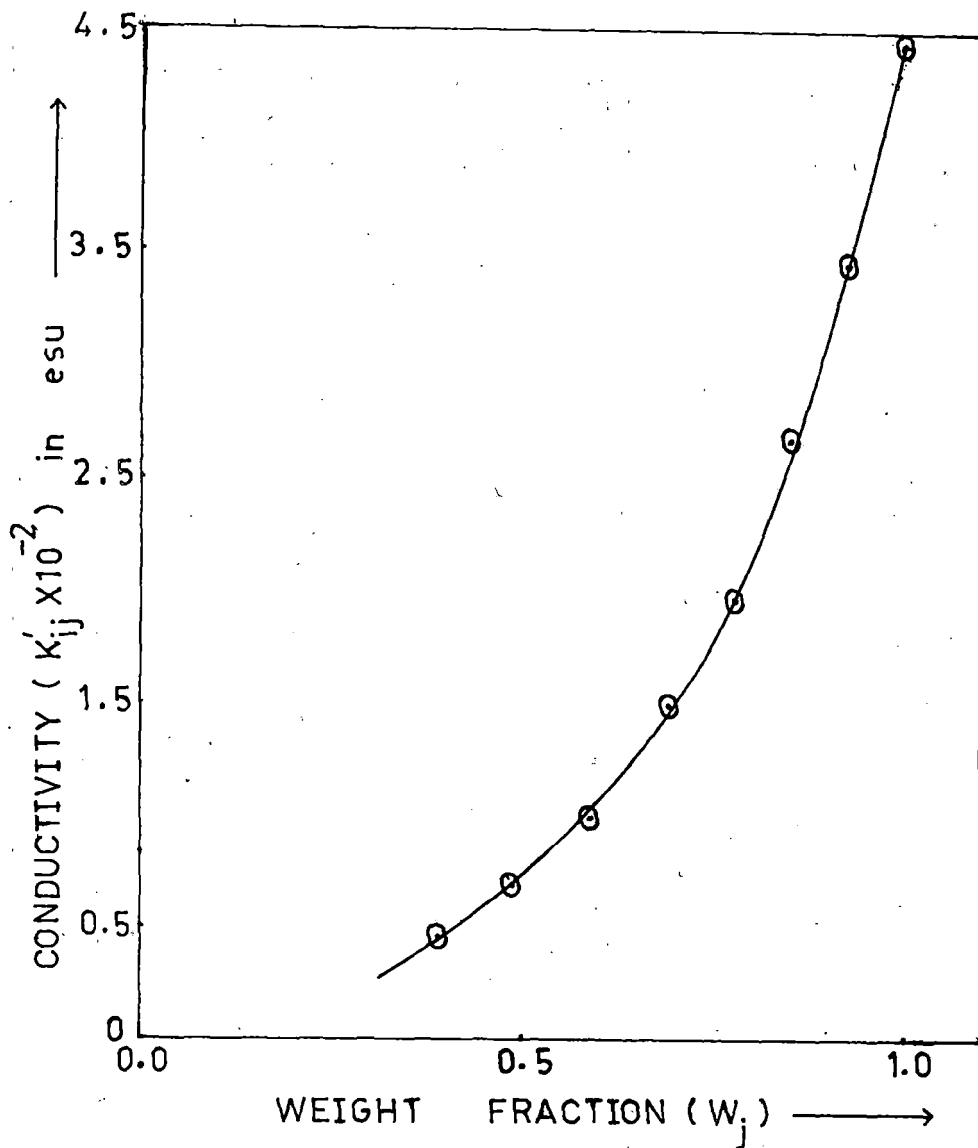


Fig-6.4 Conductivity K'_{ij} is plotted against Weight fraction W_j for ethanol in benzene at 30°C .

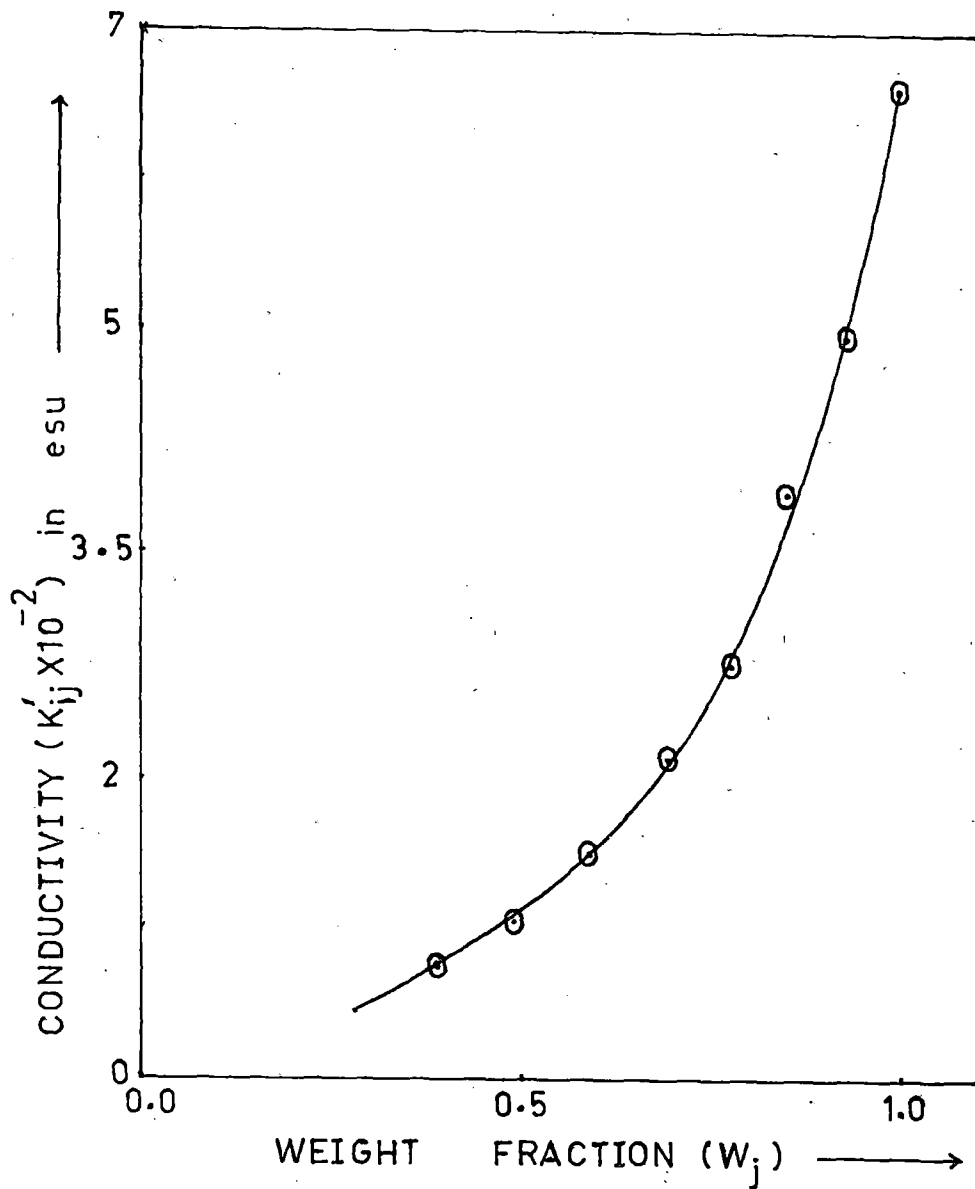


Fig-6.5 Conductivity K'_{ij} is plotted against Weight fraction W_j for ethanol in benzene at 40°C .

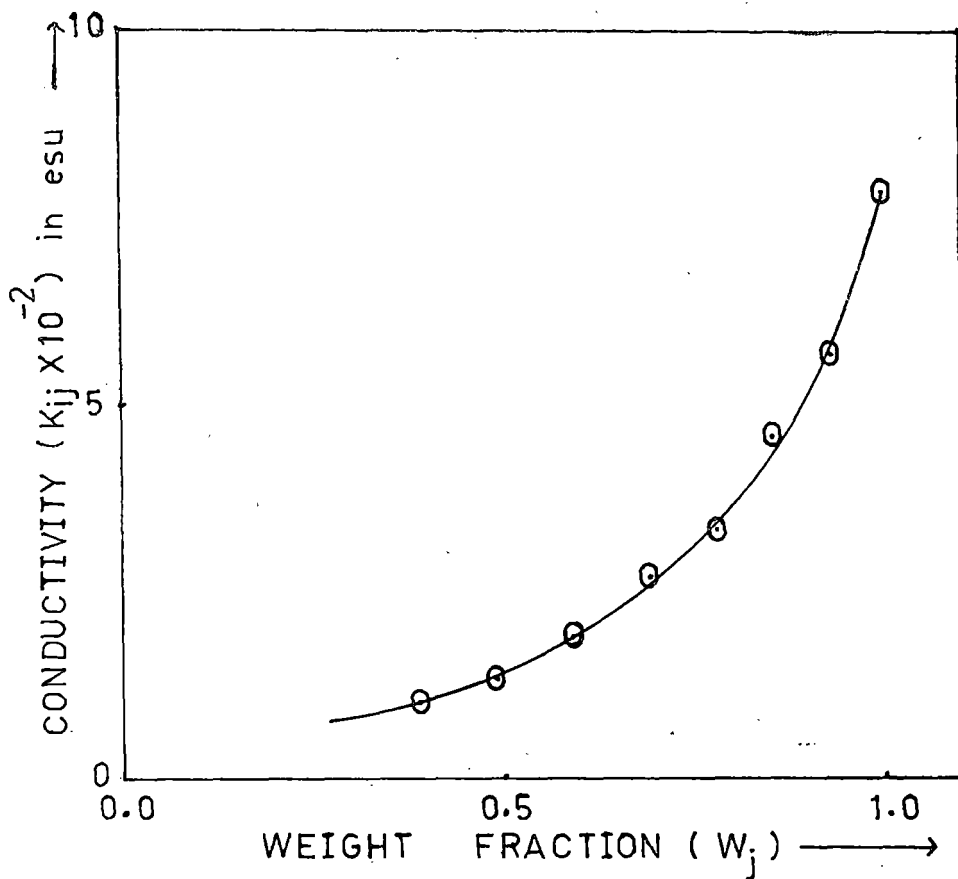


Fig-6.6 Conductivity K'_{ij} is plotted against Weight fraction W_j for ethanol in benzene at 50°C .

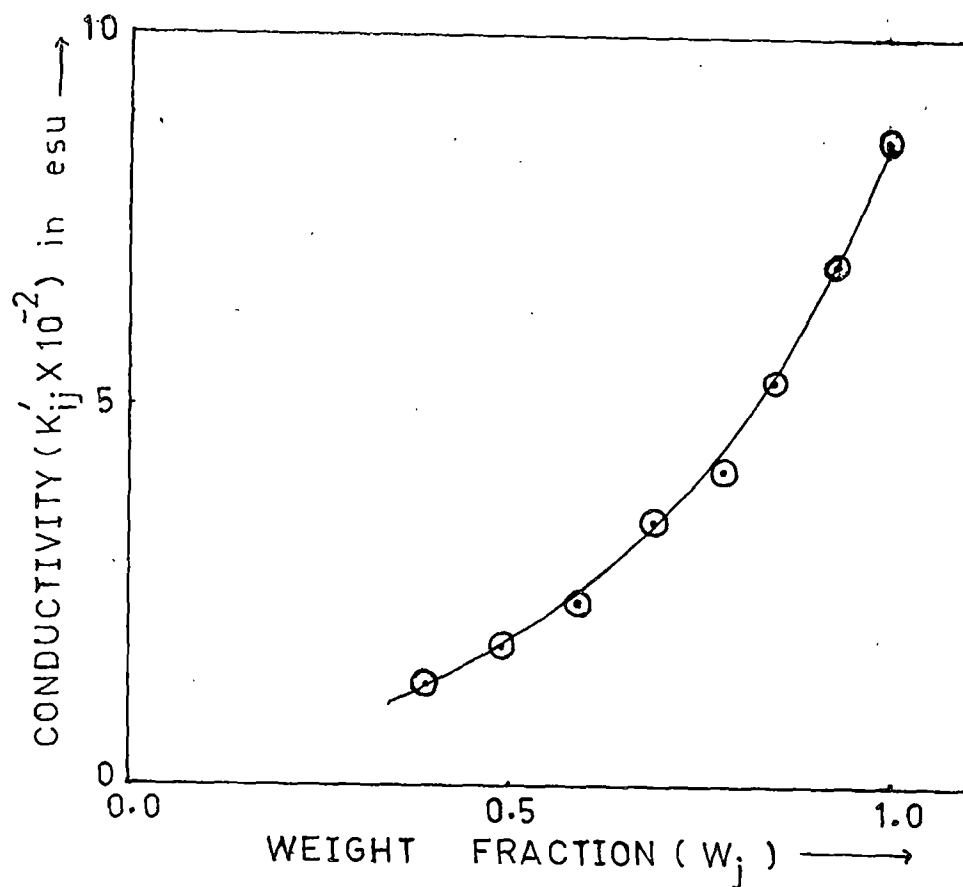


Fig-6.7 Conductivity K'_{ij} is plotted against Weight fraction W_j for ethanol in benzene at 60°C .

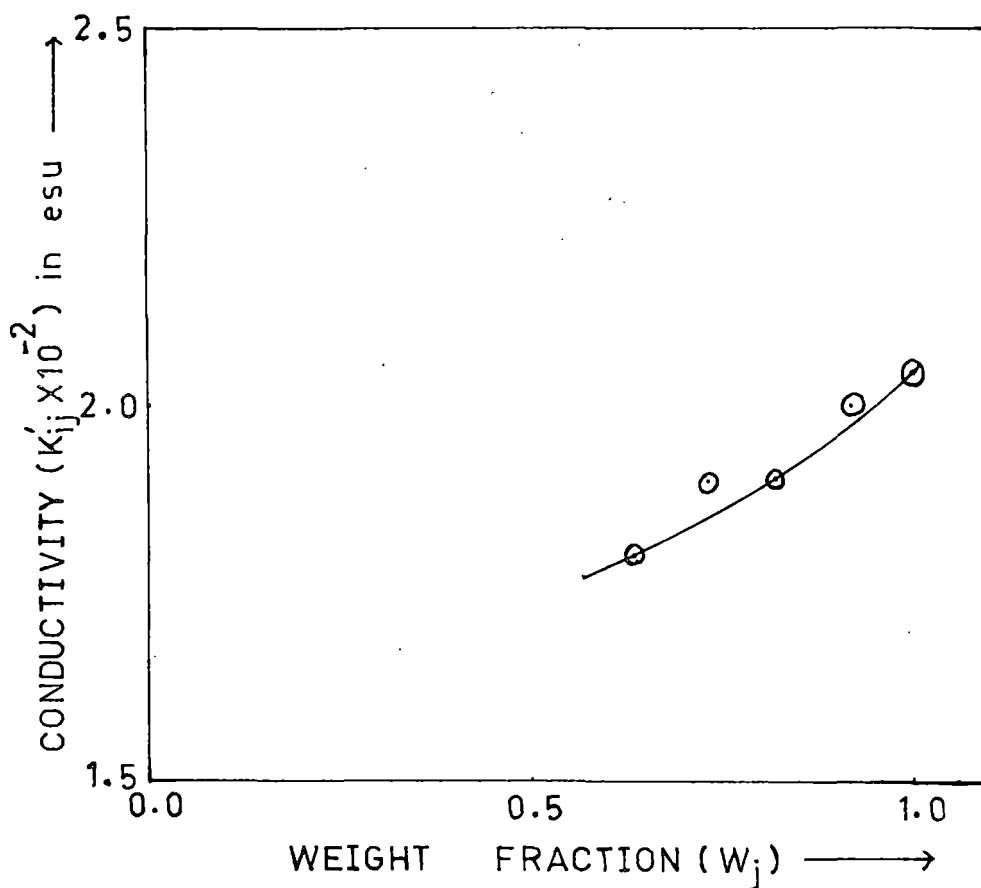


Fig-6.8 Conductivity K'_{ij} is plotted against Weight fraction W_j for 1-propanol in benzene at 30°C .

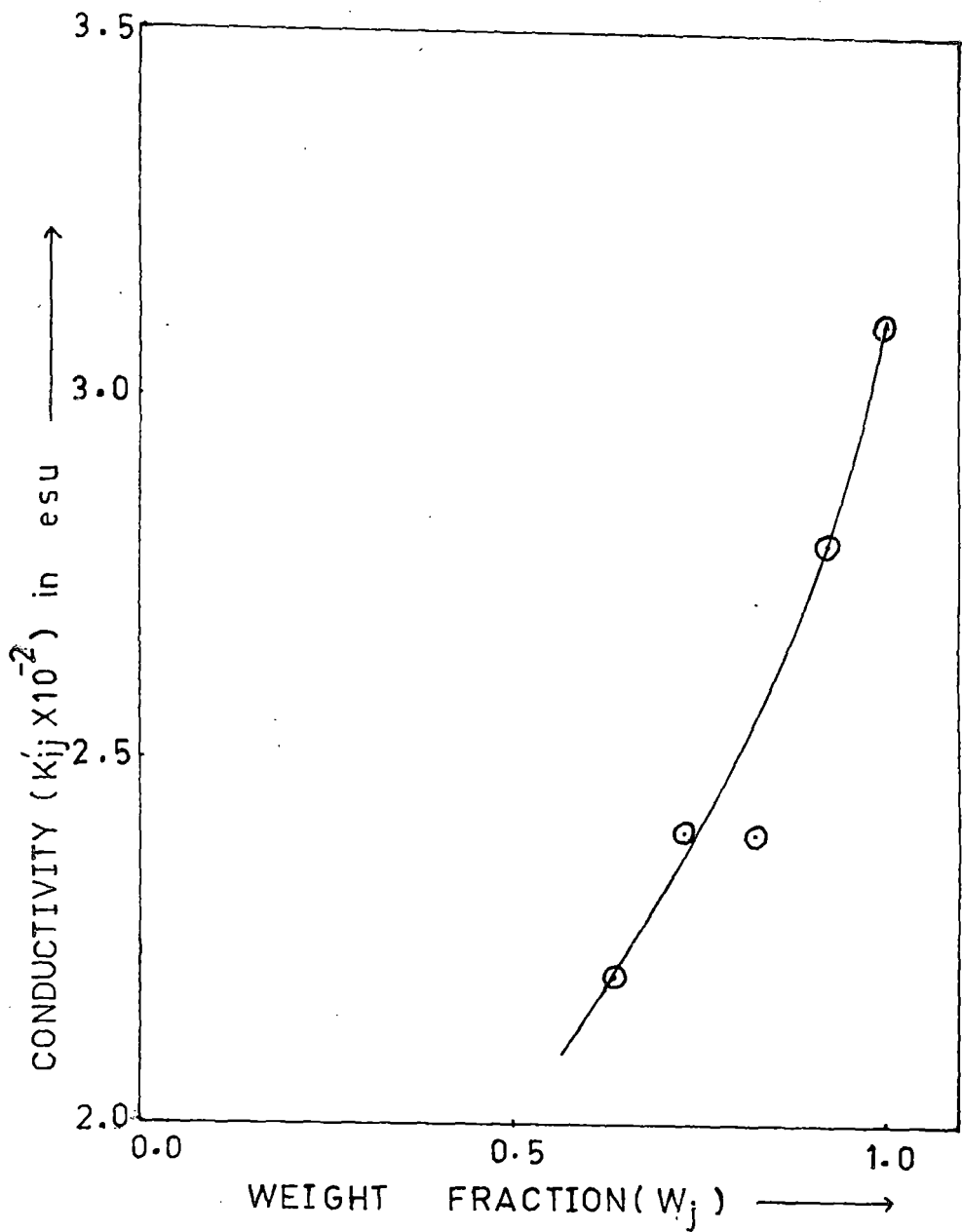


Fig-6.9 Conductivity K'_{ij} is plotted against Weight fraction W_j for 1-propanol in benzene at 40°C .

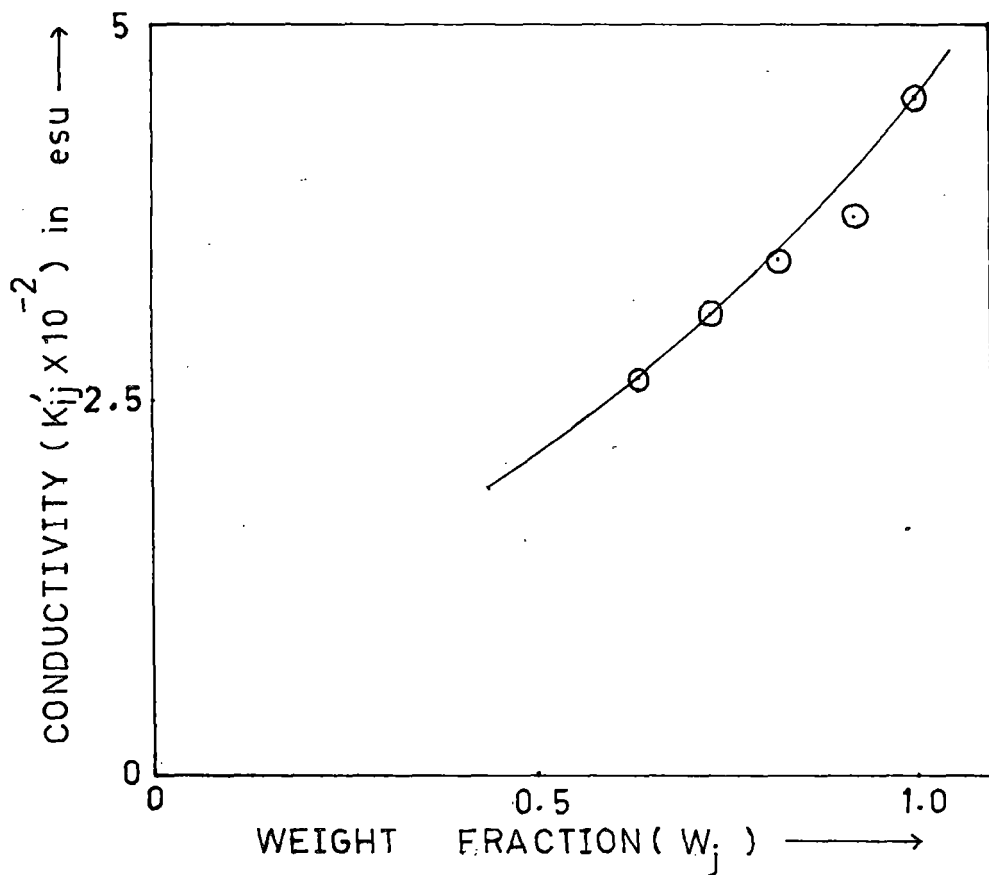


Fig-6.10 Conductivity K'_{ij} is plotted against Weight fraction W_j for 1-propanol in benzene at 50°C .

where β is the slope of $K'_{ij} - W_j$ plot at $W_j \rightarrow 0$ and ρ_i the density of the solvent, F_i the local field, μ the dipole moment of the solute, M_j , N and k are the molecular weight, Avogadro's number and Boltzmann's constant respectively.

It is evident that the dielectric properties of polar liquid varies with temperature, concentration and also with the frequency in the dispersion region. Therefore relatively a large change in dielectric relaxation time is expected by decreasing or by increasing the microscopic viscosity of the liquid either by temperature variation or by variation of concentration of polar molecules in nonpolar solvents. So in this paper an attempt has been made to study, the nature of variation of dipole relaxation time of some monohydric alcohol at various temperatures and concentration in nonpolar liquid benzene. The values of relaxation time τ_s for various concentrations of alcohol in benzene solution and at different temperatures (T) have been computed from the equation (6.6). The time of relaxation at infinite dilute (τ_∞) has been calculated from the relation,

$$\tau_\infty = \left(\frac{\eta_0}{\eta_s} \right) \tau_s \quad \dots 6.7$$

where η_0 and η_s are viscosities of nonpolar solvent and of the extremely low concentration of solute respectively. Again the Onsager (N.E.Hill et al, 1969) model $\tau'_\infty = \left(\frac{2}{3}\right) \tau_s$ has been applied to calculate the molecular relaxation τ'_∞ of the polar molecule. All these calculated values of relaxation time are placed in the Table 6.4. It is observed from the table that the calculated values of relaxation times agrees fairly well with literature (Böttcher, 1952) values and also indicate the tendency of decreasing with the increase of temperature. Further it is observed that τ_∞ slightly varies with number of carbon atoms. The effect of solvent on the measurement of dipole moment of polar solute is well known and with this view in mind the solvent effect of benzene on the relaxation time of polar molecules at infinite dilution τ_∞^* has been calculated from the relation

$$\tau_\infty^* = \frac{\tau_\infty}{[1 - C(\epsilon - 1)^2]^2} \quad \dots 6.8$$

where C is the constant for which Müller (Smyth; 1955) gave a value of 0.038 and ϵ is the dielectric constant of the solvent. The values of τ_∞^* thus calculated for each alcohol molecules from eq. (6.8) are entered in table 6.4. The higher values of τ_∞^* for a particular temperature indicate that the variation of

local environment has a definite influence upon relaxation time. It is further observed that the computed values of relaxation times of polar molecules at infinite dilution are much lower than those of the pure compound, which indicates that at an infinite dilute solution in nonpolar solvent the rotation of a dipole molecules is not hindered by the interaction with other neighbouring dipole molecules.

The dielectric mechanism may be explained in terms of absolute rate theory (Glasstone et al, 1941) by treating the dipole orientation as a rate process in which polar molecules rotate from one equilibrium position to another. The process of rotation requires an activation energy sufficient to overcome the energy barrier separating the two mean equilibrium position and is given by

$$\tau = \frac{A}{T} \exp\left(\frac{\Delta F_{\tau}}{RT}\right) \quad \dots 6.9$$

where A is known as frequency factor and is given by $A = \frac{h}{k}$ where h and k are Plank's constant and Boltzmann's constant respectively and R is the universal gas constant.

The enthalpy of activation ΔH_{τ} and the entropy of activation ΔS_{τ} for dipole relaxation are related with free energy of activation ΔF_{τ} by

the equation

$$\Delta F_{\tau} = [\Delta H_{\tau} - T\Delta S_{\tau}] \quad \dots 6.10$$

Hence from the equation (6.9), we can get

$$\tau = \frac{A}{T} \exp\left(-\frac{\Delta S_{\tau}}{R}\right) \exp\left(\frac{\Delta H_{\tau}}{RT}\right) \quad \dots 6.10a.$$

or

$$\tau = \frac{A'}{T} \exp\left(\frac{\Delta H_{\tau}}{RT}\right) \quad \dots 6.10b.$$

where $A' = A \exp\left(-\frac{\Delta S_{\tau}}{R}\right)$

Further the molar free energy of activation for viscous flow ΔF_{η} , the heat activation energy ΔH_{η} and the entropy of activation ΔS_{η} for viscous flow of the infinitely dilute solution of alcohol in benzene also have been calculated for the purpose of comparison by using the relation

$$\eta = B \exp\left(\frac{\Delta F_{\eta}}{RT}\right) \quad \dots 6.11a$$

or

$$\eta = B \exp\left(-\frac{\Delta S_{\eta}}{R}\right) \exp\left(\frac{\Delta H_{\eta}}{RT}\right) \quad \dots 6.11b$$

Here $B = \frac{hN}{V}$ known as the frequency factor, where N is the Avogadro's number, V is the molar volume, h is the Plank's constant and η is the coefficient of viscosity of the liquid.

In this chapter the temperature dependence of relaxation time have been utilized for determining the molar free energy of activation ΔF_{τ} , enthalpy of activation energy ΔH_{τ} and the entropy of activation energy ΔS_{τ} for the dipole orientation of polar molecules in nonpolar solvent. The computed values of $\Delta H_{\tau_{\infty}}$ for the three alcohols, methanol, ethanol and propanol, have been determined from the slope of the usual plot $\log_e (\tau_{\infty} T)$, against $(\frac{1}{T})$, shown in the figure, (6.11, 12, 13) The intercept of the plot of the curves gives the values of the factor A' , which have been used for computing the values of entropy $\Delta S_{\tau_{\infty}}$ and the magnitudes of $\Delta F_{\tau_{\infty}}$ for different systems have been determined from equation (6.10). The computed values of $\Delta F_{\tau_{\infty}}$, $\Delta H_{\tau_{\infty}}$ and $\Delta S_{\tau_{\infty}}$ for the three different systems at various temperatures are tabulated in table (6.4). The values of $\Delta H_{\tau_{\infty}}$ are very nearly same to the values as refer by Bordewijk and Böttcher (1978). Similarly the heat of activation energy for viscous flow $\Delta H_{\eta_{\infty}}$ has been calculated from the linear plot of $\log_e \eta$ against $1/T$

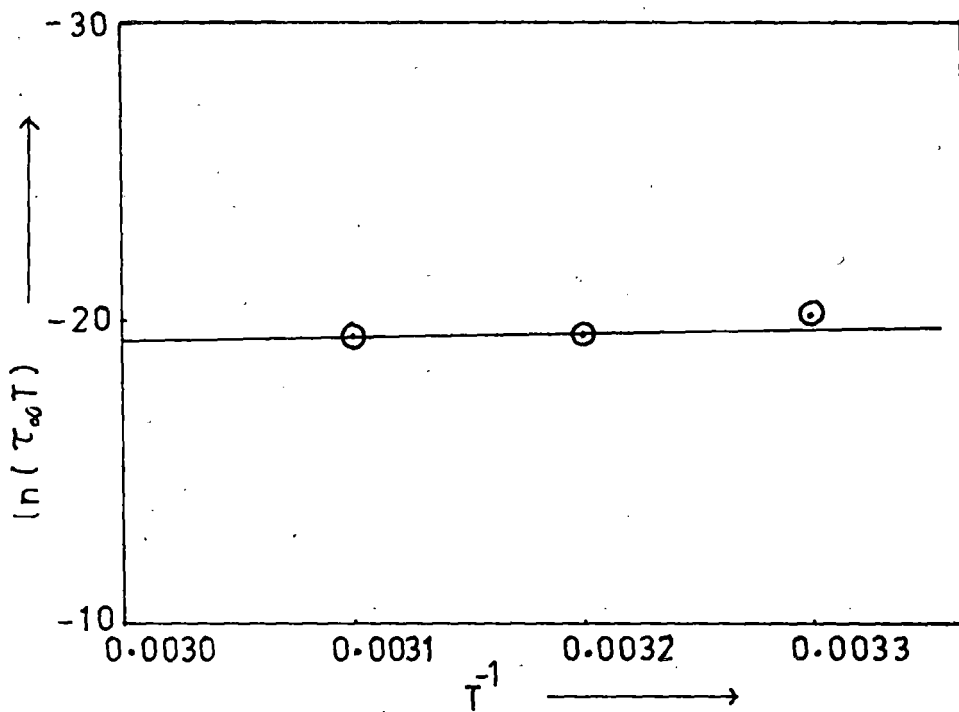


Fig-6.11 Value of $\ln(\tau_{\infty}T)$ versus reciprocal of absolute temperature (T^{-1}) for methanol in benzene.

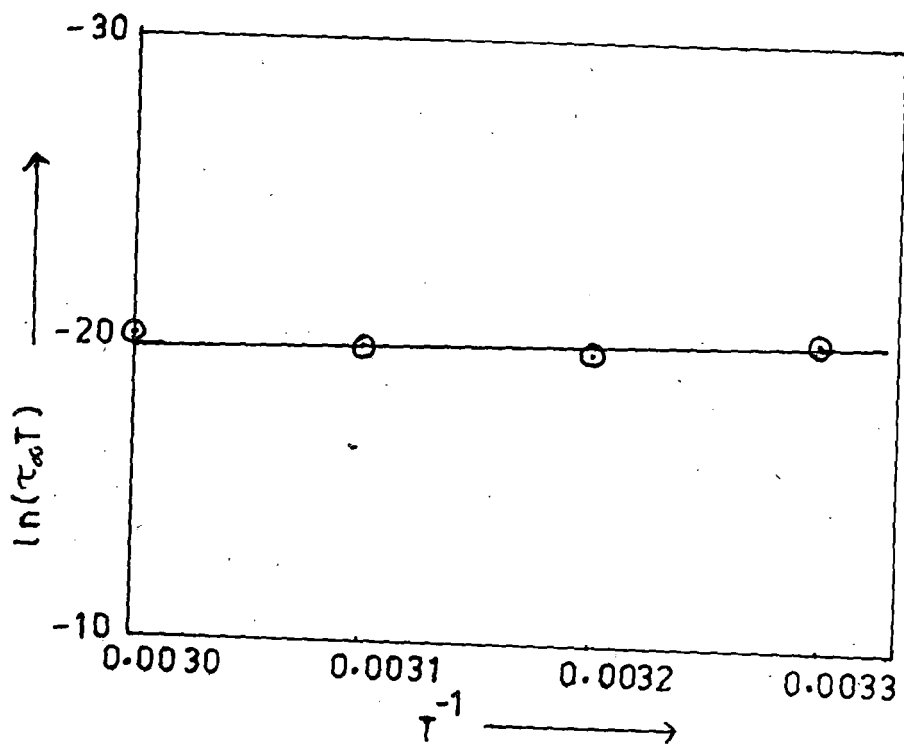


Fig-6.12 Value of $\ln(\tau_0 T)$ versus reciprocal of absolute temperature (T^{-1}) for ethanol in benzene.

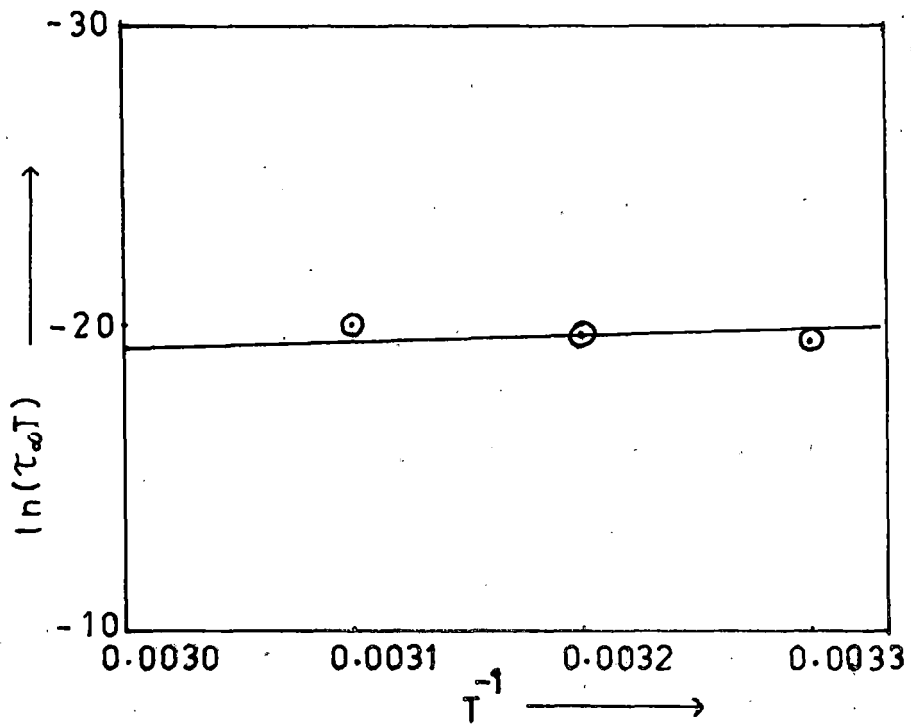


Fig-6.13 Value of $\ln(\tau_0 T)$ versus reciprocal of absolute temperature (T^{-1}) for 1-propanol in benzene .

shown in figure (6.14). Here the activation energy for viscosity ΔH_{η} has been considered due to the effect of viscosity of unit mole fraction of benzene in alcohol benzene solution, which is eventually the viscosity of benzene at pure state. The activation energy for relaxation of dipole orientation is often compared with that for the activation energy for viscosity and it is found that these are approximately equal ($\Delta F_{\eta} \approx \Delta F_{\tau_{\infty}}$) for rigid molecules. From the table (6.4), we observed that $\Delta H_{\tau_{\infty}}$ and ΔH_{η} are approximately equal for the first two systems whereas it differ widely in the case of 1-propanol, the third system. It is further observed from the table (6.4) that the heat activation energy $\Delta H_{\tau_{\infty}}$ for methanol, ethanol and 1-propanol gradually increases with the increase of chain length or with carbon atoms and the values are closely agree with the values given by other workers (Bordewijk, et al, 1978). The slightly higher value of ΔH_{η} compare to $\Delta H_{\tau_{\infty}}$ for methanol and ethanol may be interpreted as that for viscous flow the molecules involves both translational as well as rotational motion whereas for dipole relaxation it is only related to orientational motion of the dipole molecules. But the very high value of $\Delta H_{\tau_{\infty}}$ for 1-propanol compare to ΔH_{η} indicate that the energy concentration due to its higher chain length.

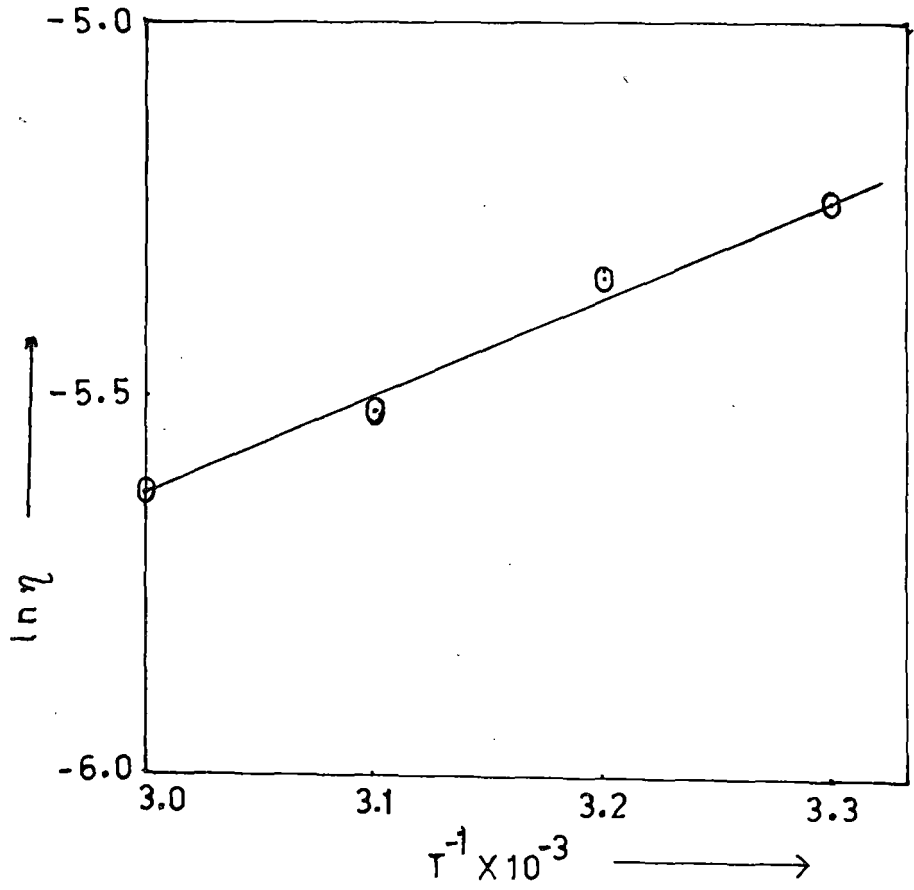


Fig-6.14 Value of $\ln \eta$ versus reciprocal of absolute temperature (T^{-1}) .

The positive value of $\Delta S_{\tau_{\infty}}$ implies that, certain number of molecules surrounding the one, rotates during the process of orientation, but, momentarily, complete discharge occurs between one another under the applied field. But again they resume their configuration with net displacement orientation in the new-direction, which exhibited as, increase in the freedom of activation. Further it is observed that due to the positive value of $\Delta S_{\tau_{\infty}}$ the calculated values of $\Delta F_{\tau_{\infty}}$ becomes relatively small compared to ΔH_{η} .

Debye (1929) equation $\tau = 4\pi\eta a^3/kT$ has been used here to calculate the radius of the molecule. All the radii values thus calculated are placed in the Table (6.4). It is found that the values are nearly equal to the actual values. This suggest that the Debye equation is not adequately represented the relation between relaxation time (τ), molecular radius (a) and the macroscopic viscosity (η) of the medium.

All most uniform values of radius of the molecules given in table (6.4), further suggest that the relaxation time τ_{∞} at infinite dilution of alcohol molecule in nonpolar solvent, is relatively low in comparison to the time of relaxation of pure solute (Böttcher, 1952) and also depend very little upon the size of the molecules and temperatures. Therefore, we may conclude that, the dipole relaxation at infinite dilution in nonpolar solvent is due to the rotational orientation of the (-OH) group of a molecule.

Table 6.1a, b, c

Values of r.f. conductivity K'_{ij} in e.s.u., weight fraction (W_j), constants of the fitting equations and dielectric parameters i.e. static dielectric constant (ϵ_0) dielectric constant at infinite frequency (ϵ_∞) and dipole moment (μ) of the different systems at different temperatures.

Table 6.1a

System - Methanol + Benzene at temperature 30°C.

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-3}$ in esu	Weight fraction W_j^2	Weight fraction W_j^3	Weight fraction W_j^4	$K'_{ij} \times W_j \times 10^{-3}$	$K'_{ij} \times W_j^2 \times 10^{-3}$	Fitting equation constants	Dielectric parameters		
								ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	1.81	1.00	1.00	1.00	1.81	1.81				
0.95	1.67	0.9025	0.8574	0.8145	1.5865	1.5072	$\alpha = 0.552$			
0.89	1.48	0.7921	0.7049	0.6274	1.3172	1.1723				
0.83	1.21	0.6889	0.5718	0.4746	1.0043	0.8336	$\beta = -1.499$	31.55	3.30	1.69
0.76	1.02	0.5776	0.4390	0.3336	0.7752	0.5892				
0.69	0.82	0.4761	0.3285	0.2266	0.5658	0.3904	$\gamma = 2.792$			
0.55	0.59	0.3025	0.1664	0.0915	0.3239	0.1782				
0.48	0.47	0.2304	0.1106	0.0531	0.2270	0.1089				

Table 6.1b

System - Methanol + Benzene at temperature 40°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-3}$ in esu	Fitting eq. constants.	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	2.32				
0.95	1.96	$\alpha = 1.269$			
0.89	1.74				
0.83	1.37	$\beta = -3.91$	31.53	3.45	1.69
0.76	1.15				
0.69	0.94	$\gamma = 4.93$			
0.55	0.63				
0.48	0.51				

Table 6.1c

System - Methanol + Benzene at temperature 50°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-3}$ in esu	Fitting equation constants.	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	2.69				
0.95	2.32	$\alpha = 1.192$			
0.89	2.05				
0.83	1.57	$\beta = -3.986$	31.50	3.62	1.69
0.76	1.34				
0.69	1.04	$\gamma = 5.471$			
0.55	0.67				
0.48	0.54				

Table 6.2a

System - Ethanol + Benzene at Temp. 30°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-2}$ in esu	Weight fraction W_j^2	Weight fraction W_j^3	Weight fraction W_j^4	$K'_{ij} \times W_j \times 10^{-2}$	$K'_{ij} \times W_j^2 \times 10^{-2}$	Fitting Equation constant	Dielectric parameters		
								ϵ_0 in esu	ϵ_∞ in esu	μ in D ^{cm}
1.00	4.46	1.00	1.00	1.00	4.46	4.46				
0.93	3.47	0.8649	0.8044	0.7480	3.2271	3.0012				
0.85	2.68	0.7225	0.6141	0.5220	2.278	1.9363	$\alpha = 2.178$			
0.78	1.96	0.6084	0.4746	0.3702	1.5288	1.1925				
0.69	1.51	0.4761	0.3285	0.2267	1.0419	0.7189	$\beta = -8.321$	23.52	2.23	1.67
0.59	0.99	0.3481	0.2054	0.1212	0.5841	0.3446				
0.49	0.69	0.2401	0.1176	0.0576	0.3381	0.1656	$\gamma = 10.515$			
0.39	0.46	0.1521	0.0593	0.0231	0.1794	0.0699				

Table 6.2b

System - Ethanol + Benzene at temperature 40°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-2}$ in esu	Fitting Equation constants	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	6.64				
0.93	4.93	$\alpha = 3.922$			
0.85	3.89				
0.78	2.75	$\beta = -14.37$	23.50	2.30	1.67
0.69	2.13				
0.59	1.48				
0.49	1.04	$\gamma = 16.87$			
0.39	0.74				

Table 6.2c

System - Ethanol + Benzene at temperature 50°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-2}$ in esu	Fitting Equation constants	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	7.80				
0.93	5.72	$\alpha = 4.356$			
0.85	4.62				
0.78	3.36	$\beta = -15.404$	23.48	2.40	1.67
0.69	2.71				
0.59	1.91	$\gamma = 18.527$			
0.49	1.34				
0.39	1.02				

Table 6.2d

System - Ethanol + Benzene at Temperature 60°C.

Weight fraction W_j	RF. conduc- tivity ₋₂ $K'_{ij} \times 10^2$ in esu	Fitting Equation constants.	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ 'in esu'	μ in D
1.00	8.64				
0.93	6.99	$\alpha = 3.624$			
0.85	5.44				
0.78	4.24	$\beta = -12.195$	23.46	2.55	1.67
0.69	3.56				
0.59	2.45				
0.49	1.84	$\gamma = 17.059$			
0.39	1.34				

Table 6.3a

System - 1 Propanol + Benzene at temperature 30°C.

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-2}$ in esu	Weight fraction W_j^2	Weight fraction W_j^3	Weight fraction W_j^4	$K'_{ij} \times W_j \times 10^{-2}$	$K'_{ij} \times W_j^2 \times 10^{-2}$	Fitting Equation constants	Dielectric parameters		
								ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	2.4	1.00	1.00	1.00	2.4	2.4				
0.921	2.0	0.8482	0.7812	0.7195	1.842	1.6965	$\alpha = 4.851$			
0.823	1.9	0.6773	0.5574	0.4588	1.5637	1.2869		17.30	2.10	1.66
0.730	1.9	0.5329	0.3890	0.2839	1.387	1.0125	$\beta = -8.624$			
0.635	1.8	0.4032	0.2560	0.1626	1.143	0.7258	$\gamma = 6.119$			

Table 6.3b

System - 1 Propanol + Benzene at temperature 40°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-2}$ in esu	Fitting Equation constants	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	3.1				
0.921	2.8	$\alpha = 4.39$			
0.823	2.4	$\beta = -7.065$	17.28	2.12	1.66
0.730	2.4				
0.635	2.2	$\gamma = 5.771$			

Table 6.3c

System - 1 Propanol + Benzene at Temp. 50°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-2}$ in esu	Fitting Equation constants	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	4.50				
0.921	3.72	$\alpha = 3.684$			
0.823	3.42	$\beta = -5.539$	17.26	2.15	1.66
0.730	3.07				
0.635	2.64	$\gamma = 6.266$			

Table 6.4

Values of relaxation times for solution (τ_s), for infinite dilution (τ_∞), molecular relaxation times (τ'_∞) and due to solvent effect (τ_∞^*), thermodynamical parameters [Heat activation energy (ΔH_{τ_∞}), entropy of activation (ΔS_{τ_∞}), free energy of activation (ΔF_{τ_∞}) for dipole relaxation and heat activation energy (ΔH_η), entropy of activation (ΔS_η), free energy of activation (ΔF_η) for viscous flow], viscosity coefficient (η) and radius of the molecule (a).

System	Temp. in K	Relaxation times in secs.				ΔH_{τ_∞} KCal/ mole	ΔS_{τ_∞} Cal/ mole	ΔF_{τ_∞} KCal/ mole	η in CP	ΔH_η Kcal/ mole	ΔS_η cal/mole	ΔF_η KCal/ mole	Radius (a) in A
		$\tau_s \times 10^{11}$	$\tau_\infty \times 10^{11}$	$\tau'_\infty \times 10^{11}$	$\tau_\infty^* \times 10^{11}$								
1. Methanol	303	0.515	0.45	0.343	0.51		1.173	2.026	0.53	-0.984	2.898	1.48	
	313	1.365	1.09	0.91	1.23	2.381	-0.9126	2.095	0.48	2.60	-1.087	2.940	2.14
	323	1.407	0.94	0.938	1.06		-0.9149	2.085	0.40		-1.002	2.924	2.32
2. Ethanol	303	0.696	0.61	0.464	0.69		0.6898	2.210	0.53	-0.984	2.898	1.63	
	313	1.234	0.99	0.823	1.12	2.419	-0.5987	2.606	0.48	2.60	-1.087	2.940	2.07
	323	1.348	0.899	0.899	1.01		-0.7081	2.648	0.40		-1.002	2.924	2.29
	333	1.076	0.65	0.717	0.73		-0.3453	2.534	0.36		-1.056	2.952	2.22
3. 1-Propanol	303	1.299	1.11	0.866	1.26		5.2614	2.573	0.53	-0.984	2.898	2.01	
	313	1.104	0.85	0.736	0.96	4.167	5.2909	2.511	0.48	2.60	-1.087	2.940	1.992
	323	0.897	0.58	0.589	0.65		5.5802	2.365	0.40		-1.002	2.924	1.996

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