

CHAPTER 9

STRUCTURAL ASPECTS AND PHYSICO CHEMICAL PROPERTIES OF BINARY POLAR LIQUIDS IN NONPOLAR SOLVENT UNDER A GIGAHERTZ ELECTRIC FIELD

9. STRUCTURAL ASPECTS AND PHYSICO CHEMICAL PROPERTIES OF BINARY POLAR LIQUIDS IN NONPOLAR SOLVENT UNDER A GIGAHERTZ ELECTRIC FIELD

9. 1 INTRODUCTION

The dielectric relaxation phenomena of two polar liquid mixtures in a nonpolar solvent is gaining much attention from a large number of workers [1,2] for its inherent ability to predict the associational and structural aspects of the dipolar molecules in a suitable solvent. The method is directed to the estimation of dielectric relaxation parameters in terms of real χ'_{ijk} and imaginary χ''_{ijk} parts of high frequency complex dimensionless dielectric orientational susceptibility χ^*_{ijk} along with the static dielectric susceptibility χ_{oijk} which is real. All these parameters are involved only with the orientational polarisations. According to Murphy and Morgan [3], the hf complex conductivity σ^*_{ijk} of binary jk polar mixture in a nonpolar solvent

(i) can be written as
$$\sigma^*_{ijk} = \sigma'_{ijk} + j\sigma''_{ijk} \quad (9.1)$$

where σ'_{ijk} ($= \omega \epsilon_0 \epsilon''_{ijk}$) and σ''_{ijk} ($= \omega \epsilon_0 \epsilon'_{ijk}$) are the real and imaginary parts of hf complex conductivity of a binary solution σ^*_{ijk} . ϵ'_{ijk} and ϵ''_{ijk} are the real and imaginary parts of hf complex relative permittivity ϵ^*_{ijk} which contain all the polarisations including the fast polarisation, ϵ_0 is the permittivity of free space $= 8.854 \times 10^{-12}$ Farad metre⁻¹ and $j = \sqrt{-1}$ is a complex number.

Both σ'_{ijk} and σ''_{ijk} are linearly related by [4]

$$\sigma''_{ijk} = \sigma_{\inftyijk} + (1/\omega\tau_{jk}) \sigma'_{ijk} \quad (9.2)$$

which is a straight line between the variables σ''_{ijk} and σ'_{ijk} . The slope $(1/\omega\tau_{jk})$ has already been used to get τ_{jk} by conductivity measurement as measured elsewhere [5]. Both the static and infinitely hf permittivities ϵ_{oijk} and ϵ_{\inftyijk} are obtained from the following Debye-Pellat equations [6] and known $\omega = (2\pi f)$, where f being the frequency of the applied electric field,

$$\epsilon'_{ijk} = \epsilon_{\inftyijk} + \frac{\epsilon_{oijk} - \epsilon_{\inftyijk}}{1 + \omega^2 \tau_{jk}^2} \quad (9.3)$$

$$\epsilon''_{ijk} = \frac{\epsilon_{oijk} - \epsilon_{\inftyijk}}{1 + \omega^2 \tau_{jk}^2} \omega \tau_{jk} \quad (9.4)$$

In order to get the data χ'_{ijk} ($= \epsilon'_{ijk} - \epsilon_{\inftyijk}$) and χ''_{ijk} ($= \epsilon''_{ijk}$) which are, however, presented in Table 9.1 and displayed graphically in Figs. 9.1 and 9.2 respectively.

The real and imaginary parts hf complex relative permittivity ϵ^*_{ijk} are related by

$$\epsilon'_{ijk} = \epsilon_{\alpha ij k} + \frac{1}{\omega \tau_{jk}} \epsilon''_{ijk} \quad (9.5)$$

Replacing $\epsilon'_{ijk} - \epsilon_{\alpha ij k}$ by χ'_{ijk} and ϵ''_{ijk} by χ''_{ijk} the eq. (9.5) becomes

$$\chi''_{ijk} = (\omega \tau_{jk}) \chi'_{ijk} \quad (9.6)$$

which is a straight line between χ''_{ijk} and χ'_{ijk} . The slope $\omega \tau_{jk}$ is now used to measure τ_{jk} of a polar – polar dimer in which the only orientational polarisation exists.

But for associative liquids like dimethyl formamide (DMF), dimethyl sulphoxide (DMSO) under investigation the variation of χ''_{ijk} with χ'_{ijk} is not strictly linear as claimed elsewhere [7]. The ratio of slopes of individual variations of χ''_{ijk} and χ'_{ijk} against w_{jk} , of Figs. 9.2 and 9.1 the weight fraction of jk polar mixture are found to be a better representation [8] of the slope of eq. (9.6). Thus we have

$$\frac{(d\chi''_{ijk} / dw_{jk})_{w_{jk} \rightarrow 0}}{(d\chi'_{ijk} / dw_{jk})_{w_{jk} \rightarrow 0}} = \omega \tau_{jk} \quad (9.7)$$

τ_{jk} 's so estimated are presented in Table 9.2 to compare them with those of Gopala Krishna's method [9]. Fig. 9.3 shows the variation of relaxation time τ_{jk} of jk polar unit with mole% of DMSO (k). It is evident from the plot that τ_{jk} attains a maximum value showing maximum dimerisation of j and k polar mixtures around 40 mole % of DMSO in benzene (i). The formation of dimer between DMF (j) and DMSO (k) polar unit is supposed to be a physico-chemical aspect of the polar solutes in benzene. The gradual fall of τ_{jk} between 40 to 100 mole % of DMSO in C_6H_6 is probably due to rupture of dimerisation i.e, change over to self association. When $w_{jk} \rightarrow 0$ we get what is known as τ_j of DMF. Similarly, when $w_{jk} \rightarrow 100$ mole%, the plot in Fig. 9.3 reports τ_k of DMSO

The phenomenon of dielectric relaxation is a rotation of the dipolar molecules in response to the hf electric field and it requires an activation energy $(\Delta F\tau)_{jk}$ to overcome the potential energy barrier between the polarised and the free states. The free energy of activation $(\Delta F\tau)_{jk}$ is related to τ_{jk} by the rate process equation of Eyring et al [10] as

$$\tau_{jk} = \frac{A}{T} \exp [(\Delta F\tau)_{jk} / RT] \quad (9.8)$$

$$\text{or, } \ln (\tau_{jk} T) = \ln A' + \frac{(\Delta H\tau)_{jk}}{R} - \frac{1}{T} \quad (9.9)$$

since $[(\Delta F\tau)_{jk}] = (\Delta H\tau)_{jk} - T(\Delta S\tau)_{jk}$ and $A' = Ae^{[-(\Delta S\tau)_{jk} / R]}$

The eq. (9.9) is a straight line of $\ln(\tau_{jk}T)$ against $1/T$ as shown graphically in Fig. 9.4 with the symbols showing the experimental points on them.. The intercepts and slopes of eq. (9.9) are estimated by fit method and are presented in Table 9.3. They are used to get the enthalpy $(\Delta H\tau)_{jk}$, the entropy $(\Delta S\tau)_{jk}$ and free energy $(\Delta F\tau)_{jk}$ of activation due to dielectric relaxation. The enthalpy of activation $\Delta H\eta_i$ due to viscous flow of the solvent was estimated from slope (γ) of the linear equation of $\ln(\tau_{jk}T)$ against $\ln\eta_i$, where η_i is the coefficient of viscosity of the solvent used. The dimensionless parameter δ and $\Delta H\eta_i$ thus obtained are seen in Table 9.3. The Kalman and Debye factors estimated with known τ_{jk} are entered in Table 9.3 to show the applicability of Debye model of dielectric relaxation for such binary polar mixtures.

The μ_{jk} 's of binary polar units are estimated in terms of linear coefficient β 's of χ'_{ijk} vs w_{jk} curves of Fig. 9.1 and dimensionless parameters 'b' where $b=1/(1+\omega^2\tau_{jk}^2)$, from Table 9.2. They are presented in Table 9.2 to compare them with the μ_{theo} estimated in terms of vector addition of bond moments of the substituted polar groups to support their molecular conformations. The disagreement between μ_{jk} 's and μ_{theo} 's suggests the very existence of inductive, mesomeric and electromeric effects suffered by the substituted polar groups attached to the parent molecules under hf electric field in addition to strong hydrogen bonding between DMF and DMSO molecule. The compounds DMF, DMSO are basically amides. They act as building blocks of proteins and enzymes. The barrier to internal rotation around C-N bonds in such compounds falls in the region of magnetic resonance frequency. DMSO, on the other hand, has high penetrating power with its wide application in the field of medicine and industry. Moreover, DMSO is a good constituent of a binary mixture of required characteristic.

9.2 EXPERIMENTAL

Sharma et al [11] estimated the real ϵ'_{ijk} and imaginary ϵ''_{ijk} parts of hf complex dielectric relative permittivity ϵ^*_{ijk} of two polar mixtures in a nonpolar solvent at different mole percentage of the k th polar solute (DMSO) in solvent C_6H_6 in the temperature range of $25^{\circ}C - 40^{\circ}C$ under 9.174 GHz electric field frequency. An X-band microwave bench was used to measure the wavelength in the dielectric and the voltage standing-wave ratio (VSWR) using a short circuiting plunger. The experimental techniques of Arrawatia et al [12] for microwave measurements were used. A range of DMF concentrations was

prepared in C_6H_6 and all the measurements were made at 25,30,35 and 40°C by circulating thermostatted water around the dielectric cell. The temperature control of the thermostat (MLW Baureihe U7⁰) was $\pm 0.05^\circ C$. The precision and equipment was tested by measuring the dipole moments of purified acetone, methanol and pyridine. The dipole moments measured were found to be within $\pm 2\%$, in agreement with the literature values (Pimental and Meclellan 1960, Smyth 1955). The viscosity and density of benzene at various experimental temperatures were measured using an Ubbelohde viscometer and a pycnometer respectively. The analytical grade DMF, DMSO and C_6H_6 were supplied by Central drug Research Institute, Lucknow. They were further purified by repeated fractional distillations and the physical constants like density ρ_i , viscosity η_i and relative permittivity ϵ_i of solvent C_6H_6 were checked in agreement with the literature values [13]. The DMF and DMSO were kept over molecular sieve of mesh 4Å for 48 hours with occasional shaking. They were then distilled through a long vertical fractionating column and the middle fractions were used for the present study. Benzene (BDH Analar) was purified by refluxing over sodium metal for 6 – 8 hours and then distilled through a long vertical fractionating column. The middle fraction of the solvent was used.

9.3 THEORETICAL FORMULATIONS TO ESTIMATE hf DIPOLE MOMENT (μ_{jk}):

The imaginary part χ''_{ijk} of hf complex dielectric orientational susceptibility χ^*_{ijk} is [14,15]

$$\chi''_{ijk} = \frac{N\rho_{ijk}\mu_{jk}^2}{27\epsilon_0 M_{jk} k_B T} \left(\frac{\omega\tau_{jk}}{1+\omega^2\tau_{jk}^2} \right) (\epsilon_{ijk} + 2)^2 w_{jk} \quad (9.10)$$

which on differentiation with respect to w_{jk} and at $w_{jk} \rightarrow 0$ yields that

$$\left(\frac{d\chi''_{ijk}}{dw_{jk}} \right)_{w_{jk} \rightarrow 0} = \frac{N\rho_i \mu_{jk}^2}{27\epsilon_0 M_{jk} k_B T} \left(\frac{\omega\tau_{jk}}{1+\omega^2\tau_{jk}^2} \right) (\epsilon_i + 2)^2 \quad (9.11)$$

From eqs (9.7) and (9.11) one obtains

$$\mu_{jk} = \left[\frac{27\epsilon_0 M_{jk} k_B T \beta}{N\rho_i (\epsilon_i + 2)^2 \omega b} \right]^{1/2} \quad (9.12)$$

where

M_{jk} = Molecular weight of j & k polar mixture in Kilogramme

ϵ_0 = Permittivity of free space = 8.854×10^{-12} Farad metre⁻¹

k_B = Boltzmann constant = 1.38×10^{-23} Joule mole⁻¹ K⁻¹

T = Temperature in absolute scale

β = Linear coefficients of $\chi'_{ijk} - w_{jk}$ curves of Fig. 9.1 at $w_{jk} \rightarrow 0$

N = Avogadro's number = 6.023×10^{23}

ρ_i = Density of solvent C_6H_6 in kg/m^3

ϵ_i = Dielectric relative permittivity of solvent C_6H_6

$b = 1/(1 + \omega^2 \tau_{jk}^2)$, a dimensionless parameter involved with the estimated τ_{jk} .

9.4 RESULTS AND DISCUSSION

The relaxation time τ_{jk} of j and k polar dimer in C_6H_6 at different experimental temperatures in $^{\circ}C$ under 9.174 GHz electric field frequency are worked out from ratio of slopes of individual variation of both χ'_{ijk} and χ''_{ijk} with w_{jk} of polar-polar mixture and are placed in Table 9.2 to compare them with those of Gopala Krishna [9] measured by permittivity measurement of sharma et al [11] The excellent agreement between both the τ_{jk} 's at once reflects the basic soundness of the present method [16] suggested to get τ_{jk} . The real χ'_{ijk} and imaginary χ''_{ijk} parts of hf complex dielectric orientational susceptibility χ^*_{ijk} are derived from estimated relative permittivities ϵ'_{ijk} , ϵ''_{ijk} , $\epsilon_{\infty ij k}$. They are collected in Table 9.1. Correlation coefficients r 's and % of errors of both $\chi'_{ijk} - w_{jk}$ and $\chi''_{ijk} - w_{jk}$ curves are given in Table 9.2 only to show how far both χ'_{ijk} and χ''_{ijk} are correlated with w_{jk} 's. It is seen in Table 9.2 that τ_{jk} 's decrease with temperature. It can be explained on the basis of the fact that at constant temperature, the relaxation time depends upon the energy difference between the activated and normal states. At higher temperature thermal agitation causes an increase in energy loss [15] only due to collision effect to decrease the τ_{jk} . The Fig. 9.3 shows the variation of τ_{jk} with mole% of the k th polar solute, DMSO. τ_{jk} increases upto 40 mole% DMSO yielding both τ_j and τ_k of the respective solutes at $w_{jk \rightarrow 0}$ and $w_{jk \rightarrow 100}$ mole% respectively probably due to polar-polar dimer association and then due to rupture of dimerisation [17] gradually decreases and attains a minimum value at 100 mole% DMSO. Formation of j & k polar-polar dimer and rupture of dimerisation i.e. self association is supposed to be a physico-chemical behaviour [16] of the solutes in a solvent.

Temperature variation of τ_{jk} of jk polar dimer enables one to estimate the thermodynamic energy parameters $(\Delta H\tau)_{jk}$, $(\Delta S\tau)_{jk}$ and $(\Delta F\tau)_{jk}$ from the intercept and slope of fitted linear plots of $\ln(\tau_{jk}T)$ against $1/T$ of Fig. 9.4, due to rate process equation of Eyring et al [10]. The intercepts and slopes, calculated by regression analysis on the measured τ_{jk} at different experimental temperatures in Kelvin are presented in Table 9.3. It is seen that system VI shows negative $\Delta H\tau$ probably for unreliable τ_{jk} at $35^{\circ}C$ which

may be due to experimental error involved in the permittivity measurement. Unlike system I & II all the systems show negative $\Delta S\tau$'s, which suggests that configuration involved in the dipolar rotation has an activated state which is more ordered than the normal state [18]. This fact is further supported by gradual decrease of τ_{jk} with concentration of DMSO beyond 40 mole% as seen in Fig. 9.3. $\Delta F\tau$'s for each system are constant in magnitude at all temperatures, as the activation is accomplished by the rupture of bond of dipolar groups in the same degree of freedom [19]. All the systems except VI show $\gamma > 0.50$, seen in Table 9.3 which indicate solvent environment around jk polar dimer to behave as solid phase rotator [8,15] $\Delta H\eta$, the enthalpy of activation due to viscous flow of the solvent is involved with translational and rotational motions of molecule possess lower values than that of $\Delta H\tau$ due to high value of δ except for system VI. Kalman factor $\tau_{jk}T / \eta^\delta$, and Debye factor $\tau_{jk}T / \eta$ which are proportional to volume of rotating unit are carefully estimated and are entered in the 10th and 11th column of Table 9.3 respectively only to show the applicability of Debye model of dielectric relaxation for such binary polar mixtures in C_6H_6 under GHz electric field.

Dipole moments μ_{jk} estimated from eq.(9.12) are placed in Table 9.2 to compare them with μ_{theo} 's as seen in same Table 9.2. The slope β of $\chi'_{ijk} - w_{jk}$ curves in Fig. 9.1 is used to get the measured dipole moments μ_{jk} . μ_{jk} 's for system VI can not be estimated as it gives negative β owing to the abnormal behaviour of available permittivity data. It is seen in Fig. 9.3 that in analogy with τ_{jk} , μ_{jk} increases gradually with concentration of the k th solute DMSO and attains a maximum value around 40 mole% of DMSO in C_6H_6 showing maximum dimerisation at that concentration and then gradually decreases to attain a minimum value at 80 mole% of DMSO. This gradual fall of τ_{jk} is probably due to rupture of the polar-polar dimerisation and to assume the state of monomer.

The dimerisation or the self association being a physico-chemical property [15] of the solute can also be inferred from μ_{jk} with $t^\circ C$ fitted polynomial plots of Fig. 9.5. It is evident from the plot that unlike systems II & IV all the curves are convex in nature showing minimum μ_{jk} at lower and higher temperatures, probably due to weak symmetry [19] attained at those temperatures, while system II & IV shows maximum μ_{jk} 's at lower and higher temperatures probably due to solute-solute dimer association to have a bigger molecular shape. The nature of variation of μ_{jk} with temperature $t^\circ C$ curves are explained on the basis of symmetric shape and dimerisation of solute molecules. This reflects the internal stability and unstability of the systems which are also confirmed by positive and negative $\Delta S\tau$'s [19,20]. Dimerisation between two polar units of DMF & DMSO can also be explained by the hydrogen bonding between the fractional negative charge δ^- of

oxygen atom which is highly electronegative of DMSO molecule and the fractional positive charge δ^+ of hydrogen atom of DMF molecule. This is also supported by their conformations as sketched in Fig. 9.6.

Theoretical dipole moment μ_{theo} estimated from vector addition of bond moments of the substituted polar groups attached to the parent ones, assuming the molecules to be planar ones provides a deep insight into the geometry of the molecules concerned. The solute-solvent molecular interaction is a physico-chemical behaviour which arises due to interactions of fractional positive charges of 'N' and 'S' atoms of the molecules as δ^+ with the π delocalised electron cloud of C_6H_6 ring. The interactions are sketched in Fig. 9.6 (i) & 9.6 (ii). Fig. 9.6 (iii), however, shows a certain angle ϕ ($=106^\circ$) between monomeric μ_j of DMF and μ_k of DMSO to have $\mu_{\text{theo}} = 15.90 \times 10^{-30}$ Coulomb-metre in close agreement with measured value of μ_{jk} in Table 9.2. The slight deviations of μ_{jk} 's from μ_{theo} 's occur due to inductive, electromeric and mesomeric moments of substituted polar groups attached to such molecules. This can be rectified by the multiplying by $\mu_{\text{theo}} / \mu_{\text{exp}}$ a factor which may account of all these effects mentioned above.

9. 5 CONCLUSION

The structural and associational aspects of DMF and DMSO dimer have been studied in terms of measured parameters with derived theoretical formulations. The interesting equations in terms of χ_{ijk} 's helps one to explore new physical insight about the systems as χ_{ijk} 's are directly linked only with the molecular orientational polarization. Relaxation times τ_{jk} obtained from eq.(9.7) and its excellent agreement with those of Gopala Krishna's method used by Sharma et al [11] at once reflects the validity of our theoretical formulations so far achieved. Now linear variations of τ_{jk} and dipole moment μ_{jk} with mole% of k-th solute (DMSO) reflects strong dimer association between two polar units which is supposed to be a physico-chemical property of the systems. Strong association between the polar units arises due to strong H-bonding (Fig. 9.6 iii) which are also supported by positive and negative $\Delta S\tau$'s giving additional information about unstability and stability of the systems. Higher μ_{jk} 's in comparison to μ_{theo} arises due to solute-solute (dimer) association between DMF & DMSO molecules in addition to inductive, mesomeric and electromeric effects suffered by polar groups attached to the parent polar molecules. All these effects give another information about physico-chemical property of the molecules. Correlation coefficients (r's) and % of errors estimated between different parameters of several curves

establishe the statistical validity of our theoretical formulations based on Debye model to estimate several physical parameters which are more of archival values to study the temperature variation of physico-chemical properties and structural and associational aspects of the aprotic polar liquid of dipolar molecules.

Table 9.1: Temperature variation of the real and imaginary parts of dielectric relative permittivity ϵ^*_{ijk} , infinitely high frequency relative permittivity $\epsilon_{\infty ij k}$, real and imaginary parts of dielectric susceptibilities χ'_{ijk} and χ''_{ijk} of hf complex susceptibility χ^*_{ijk} of binary polar liquids in non polar solvent C_6H_6 at different experimental temperatures under 9.174 GHz electric field.

Systems with Sl. No.	Temp in $^{\circ}C$	Weight fraction	Dielectric permittivities			Dielectric susceptibilities	
			w_{jk}	ϵ'_{ijk}	ϵ''_{ijk}	$\epsilon_{\infty ij k}$	χ'_{ijk}
1. DMF + 0 mole% DMSO	25	0.0036	2.3700	0.0510	2.2532	0.1168	0.0510
		0.0057	2.4000	0.0640	2.2534	0.1466	0.0640
		0.0080	2.4500	0.0820	2.2621	0.1879	0.0820
		0.0101	2.4700	0.0960	2.2501	0.2199	0.0960
	30	0.0036	2.3600	0.0430	2.2599	0.1001	0.0430
		0.0057	2.3700	0.0610	2.2280	0.1420	0.0610
		0.0080	2.4400	0.0760	2.2631	0.1769	0.0760
		0.0101	2.4500	0.0870	2.2475	0.2025	0.0870
	35	0.0036	2.3400	0.0400	2.2280	0.1120	0.0400
		0.0057	2.3700	0.0550	2.2160	0.1540	0.0550
		0.0080	2.4300	0.0700	2.2340	0.1960	0.0700
		0.0101	2.4400	0.0780	2.2217	0.2183	0.0780
	40	0.0036	2.3300	0.0370	2.2246	0.1054	0.0370
		0.0057	2.3700	0.0500	2.2275	0.1425	0.0500
		0.0080	2.4200	0.0650	2.2348	0.1852	0.0650
		0.0101	2.4300	0.0730	2.2220	0.2080	0.0730
2. DMF + 17 mole% DMSO	25	0.0033	2.3600	0.0620	2.2899	0.0701	0.0620
		0.0048	2.4000	0.1040	2.2824	0.1176	0.1040
		0.0067	2.4300	0.1330	2.2795	0.1505	0.1330
		0.0105	2.4600	0.1520	2.2948	0.1652	0.1520
	30	0.0033	2.3500	0.0590	2.2714	0.0786	0.0590
		0.0048	2.3800	0.0940	2.2547	0.1253	0.0940
		0.0067	2.4200	0.1180	2.2627	0.1573	0.1180
		0.0105	2.4500	0.1380	2.2660	0.1840	0.1380
	35	0.0033	2.3400	0.0490	2.2702	0.0698	0.0490
		0.0048	2.3700	0.0810	2.2545	0.1155	0.0810
		0.0067	2.4200	0.1070	2.2675	0.1525	0.1070
		0.0105	2.4500	0.1300	2.2647	0.1853	0.1300
	40	0.0033	2.3100	0.0470	2.2334	0.0766	0.0470
		0.0048	2.3500	0.0710	2.2343	0.1157	0.0710
		0.0067	2.4100	0.1040	2.2406	0.1694	0.1040
		0.0105	2.4400	0.1270	2.2331	0.2069	0.1270

Systems with Sl. No.	Temp in °C	Weight fraction	Dielectric permittivities			Dielectric susceptibilities	
			w_{jk}	ϵ'_{ijk}	ϵ''_{ijk}	$\epsilon_{\infty ij}$	χ'_{ijk}
3. DMF + 50 mole% DMSO	25	0.0036	2.3700	0.0500	2.3146	0.0554	0.0500
		0.0042	2.3800	0.0630	2.3102	0.0698	0.0630
		0.0072	2.4500	0.1320	2.3038	0.1462	0.1320
		0.0100	2.4800	0.1490	2.3150	0.1650	0.1490
	30	0.0036	2.3500	0.0450	2.2957	0.0543	0.0450
		0.0042	2.3600	0.0570	2.2912	0.0688	0.0570
		0.0072	2.4400	0.1240	2.2903	0.1497	0.1240
		0.0100	2.4600	0.1370	2.2946	0.1654	0.1370
	35	0.0036	2.3300	0.0420	2.2734	0.0566	0.0420
		0.0042	2.3500	0.0560	2.2745	0.0755	0.0560
		0.0072	2.4200	0.1110	2.2704	0.1496	0.1110
		0.0100	2.4500	0.1300	2.2748	0.1752	0.1300
	40	0.0036	2.3100	0.0390	2.2550	0.0550	0.0390
		0.0042	2.3400	0.0510	2.2680	0.0720	0.0510
		0.0072	2.4000	0.1030	2.2546	0.1454	0.1030
		0.0100	2.4400	0.1260	2.2622	0.1778	0.1260
4. DMF + 60 mole% DMSO	25	0.0038	2.3600	0.0700	2.2454	0.1146	0.0700
		0.0051	2.3800	0.0810	2.2474	0.1326	0.0810
		0.0072	2.4200	0.1170	2.2285	0.1915	0.1170
		0.0110	2.5000	0.1540	2.2479	0.2521	0.1540
	30	0.0038	2.3500	0.0600	2.2529	0.0971	0.0600
		0.0051	2.3700	0.0720	2.2535	0.1165	0.0720
		0.0072	2.4000	0.1030	2.2334	0.1666	0.1030
		0.0110	2.4800	0.1390	2.2551	0.2249	0.1390
	35	0.0038	2.3100	0.0460	2.2304	0.0796	0.0460
		0.0051	2.3600	0.0670	2.2441	0.1159	0.0670
		0.0072	2.3900	0.0980	2.2205	0.1695	0.0980
		0.0110	2.4600	0.1290	2.2368	0.2232	0.1290
	40	0.0038	2.3000	0.0350	2.2344	0.0656	0.0350
		0.0051	2.3500	0.0660	2.2264	0.1236	0.0660
		0.0072	2.3800	0.0920	2.2076	0.1724	0.0920
		0.0110	2.4400	0.1100	2.2339	0.2061	0.1100

Systems with Sl. No.	Temp in °C	Weight fraction	Dielectric permittivities			Dielectric susceptibilities	
			w_{jk}	ϵ'_{ijk}	ϵ''_{ijk}	$\epsilon_{\infty ij}$	χ'_{ijk}
5. DMF + 80 mole% DMSO	25	0.0042	2.3800	0.0460	2.2769	0.1031	0.0460
		0.0069	2.4400	0.0820	2.2562	0.1838	0.0820
		0.0082	2.4600	0.0960	2.2448	0.2152	0.0960
		0.0120	2.5800	0.1360	2.2752	0.3048	0.1360
	30	0.0042	2.3500	0.0430	2.2442	0.1058	0.0430
		0.0069	2.4200	0.0780	2.2281	0.1919	0.0780
		0.0082	2.4500	0.0920	2.2237	0.2263	0.0920
		0.0120	2.5500	0.1250	2.2425	0.3075	0.1250
	35	0.0042	2.3400	0.0370	2.2442	0.0958	0.0370
		0.0069	2.4100	0.0690	2.2314	0.1786	0.0690
		0.0082	2.4300	0.0870	2.2048	0.2252	0.0870
		0.0120	2.5400	0.1140	2.2449	0.2951	0.1140
	40	0.0042	2.3200	0.0340	2.2310	0.0890	0.0340
		0.0069	2.4000	0.0640	2.2324	0.1676	0.0640
		0.0082	2.4200	0.0750	2.2236	0.1964	0.0750
		0.0120	2.5200	0.1100	2.2319	0.2881	0.1100
6. DMF + 100 mole% DMSO	25	0.0021	2.3100	0.0270	2.2338	0.0762	0.0270
		0.0047	2.3500	0.0440	2.2258	0.1242	0.0440
		0.0084	2.4400	0.0580	2.2763	0.1637	0.0580
		0.0100	2.4800	0.0970	2.2062	0.2738	0.0970
	30	0.0021	2.3000	0.0260	2.2262	0.0738	0.0260
		0.0047	2.3400	0.0400	2.2265	0.1135	0.0400
		0.0084	2.4200	0.0540	2.2668	0.1532	0.0540
		0.0100	2.4700	0.0940	2.2033	0.2667	0.0940
	35	0.0021	2.2800	0.0200	2.2269	0.0531	0.0200
		0.0047	2.3200	0.0320	2.2350	0.0850	0.0320
		0.0084	2.3900	0.0520	2.2518	0.1382	0.0520
		0.0100	2.4500	0.0880	2.2162	0.2338	0.0880
	40	0.0021	2.2700	0.0180	2.2166	0.0534	0.0180
		0.0047	2.3000	0.0250	2.2258	0.0742	0.0250
		0.0084	2.3700	0.0480	2.2275	0.1425	0.0480
		0.0100	2.4400	0.0760	2.2143	0.2257	0.0760

Table-9.2:- Measured τ_{jk} 's from ratio of slopes of individual variations of χ'_{ijk} and χ''_{ijk} with ω_{jk} , reported τ_{jk} in pico second, correlation coefficient and % of error of χ'_{ijk} - ω_{jk} & χ''_{ijk} - ω_{jk} curves of Figs. 9.1 and 9.2, dipole moments (μ_{jk}) using τ_{jk} of eq.(9.7) and theoretical dipole moment μ_{theo} using bond moments in Coulomb - metre of binary polar mixtures in solvent C_6H_6 at different experimental temperatures under 9.174 GHz electric field.

Systems with Sl.no. & molecular weight (M_{jk}) in Kg	Temp. in $^{\circ}C$	Estimated τ_{jk} in psec using eq.(9.7)	Reported τ_{jk} in psec	Correl. coeff. $\chi'_{ijk}-\omega_{jk}$ & $\chi''_{ijk}-\omega_{jk}$ curves	% of error. $\chi'_{ijk}-\omega_{jk}$ & $\chi''_{ijk}-\omega_{jk}$ curves	Estimated hf $\mu_{jk} \times 10^{30}$ in C.m.	$\mu_{theo} \times 10^3$ in C.m.
1.DMF + 0 mole% DMSO $M_{jk} = 0.07300$	25	7.57	7.50	0.9991	0.06	11.30	12.74
	30	7.45	6.90	0.9943	0.38	15.88	
	35	6.20	6.10	0.9921	0.53	16.61	
	40	6.09	5.50	0.9944	0.37	15.55	
2.DMF +17 mole% DMSO $M_{jk} = 0.07385$	25	15.33	16.40	0.9013	6.33	26.48	15.90
	30	13.01	14.10	0.9412	3.85	23.86	
	35	12.17	12.60	0.9570	2.84	23.60	
	40	10.65	11.10	0.9665	2.22	23.53	
3.DMF +50mole% DMSO $M_{jk} = 0.07550$	25	15.66	15.70	0.9673	2.17	28.15	15.90
	30	14.36	13.50	0.9602	2.63	28.76	
	35	12.86	11.20	0.9763	1.58	26.11	
	40	12.29	9.90	0.9853	0.98	24.51	
4.DMF +60 mole% DMSO $M_{jk} = 0.07600$	25	10.59	11.20	0.9925	0.51	17.85	15.90
	30	10.72	10.90	0.9955	0.30	17.05	
	35	10.02	10.00	0.9859	0.95	22.11	
	40	9.26	9.30	0.9393	3.97	27.04	
5.DMF +80 mole% DMSO $M_{jk} = 0.07700$	25	7.74	7.80	0.9977	0.16	18.55	15.90
	30	7.05	7.70	0.9934	0.44	20.46	
	35	6.70	7.40	0.9878	0.82	21.73	
	40	6.62	6.20	0.9984	0.11	18.06	
6.DMF +100 mole% DMSO $M_{jk} = 0.07800$	25	6.14	5.40	0.9286	4.64	—	15.17
	30	6.11	5.00	0.9164	5.41	—	
	35	6.53	4.70	0.9394	3.97	—	
	40	5.84	4.30	0.9492	3.34	—	

Table-9.3 :Intercepts and slopes of $\ln\tau_{jk}T$ against $1/T$ curves of Fig. 9.4, thermodynamic energy parameters like enthalpy of activation ΔH_τ in Kilo Joule mole⁻¹, the entropy of activation ΔS_τ in Joule mole⁻¹ K⁻¹, free energy of activation ΔF_τ in Kilo Joule mole⁻¹, enthalpy of activation ΔH_η in Kilo Joule mole⁻¹ due to viscous flow of solvent, δ (slope of $\ln\tau_{jk}T$ vs. $\ln\eta_i$ equation), Kalman factor ($\tau_{jk}T / \eta^\delta$) and Debye factor ($\tau_{jk}T / \eta$) at different experimental temperatures and the coefficients of $\mu_{jk} - t$ of equations $\mu_{jk} = a + bt + ct^2$ of mixture of liquids in benzene under 9.174 GHz electric field frequency.

Systems with SI.no.	Temp in °C	Intercept & slope of $\ln\tau_{jk}T$ Vs $1/T$ equation		ΔH_τ in KJ mole ⁻¹	ΔS_τ in J mole ⁻¹ K ⁻¹	ΔF_τ in KJ mole ⁻¹	δ =slope of $\ln(\tau_{jk}T)$ vs $\ln\eta_i$ equation	ΔH_η in KJ mole ⁻¹	Kalman factor ($\tau_{jk}T/\eta^\delta$)	Debye factor ($\tau_{jk}T/\eta$) $\times 10^6$	Coefficients of the eqs $\mu_{jk} \times 10^{30} = a + bt + ct^2$ equation		
		Intercept	slope								a	b	c
1.DMF + 0 mole% DMSO	25			10.50	3.10	9.57			6.49x10 ⁻⁴	3.83			
	30	-24.11	1258.40	10.50	2.52	9.73	1.69	6.22	7.04x10 ⁻⁴	4.02	-0.056	3.937	-51.746
	35			10.50	3.36	9.46			6.46x10 ⁻⁴	3.57			
	40			10.50	2.83	9.61			6.69x10 ⁻⁴	3.64			
2.DMF + 17 mole% DMSO	25			15.53	14.10	11.33			2.78x10 ⁻¹	7.76			
	30	-25.47	1861.70	15.53	14.48	11.14	2.41	6.44	2.70x10 ⁻¹	7.03	0.025	-1.840	56.429
	35			15.53	14.07	11.20			2.88x10 ⁻¹	7.01			
	40			15.53	14.24	11.07			2.70x10 ⁻¹	6.37			
3.DMF + 50 mole% DMSO	25			10.49	-2.98	11.38			1.25x10 ⁻³	7.93			
	30	-23.49	1257.60	10.49	-2.98	11.39	1.68	6.26	1.26x10 ⁻³	7.76	-0.022	1.170	12.967
	35			10.49	-2.76	11.34			1.24x10 ⁻³	7.41			
	40			10.49	-3.06	11.45			1.25x10 ⁻³	7.35			
4.DMF + 60 mole% DMSO	25			4.75	-18.99	10.41			4.96x10 ⁻⁷	5.36			
	30	-21.46	569.05	4.75	-19.49	10.65	0.68	6.94	5.28x10 ⁻⁷	5.79	0.057	-3.067	58.458
	35			4.75	-19.33	10.70			5.18x10 ⁻⁷	5.78			
	40			4.75	-19.04	10.71			4.94x10 ⁻⁷	5.54			
5.DMF + 80 mole% DMSO	25			5.55	-13.67	9.63			2.16x10 ⁻⁶	3.92			
	30	-22.23	665.73	5.55	-13.34	9.59	0.92	6.03	2.09x10 ⁻⁶	3.81	-0.056	3.626	-37.420
	35			5.55	-13.35	9.66			2.11x10 ⁻⁶	3.86			
	40			5.55	-13.67	9.83			2.17x10 ⁻⁶	3.96			
6.DMF + 100 mole% DMSO	25			-1.25	-34.58	9.05			2.89x10 ⁻¹⁰	3.51			
	30	-19.69	-150.21	-1.25	-34.61	9.23	-0.31	4.01	1.80x10 ⁻¹⁰	3.26	-	-	-
	35			-1.25	-35.23	9.60			1.79x10 ⁻¹⁰	3.47			
	40			-1.25	-34.37	9.50			1.93x10 ⁻¹⁰	3.84			

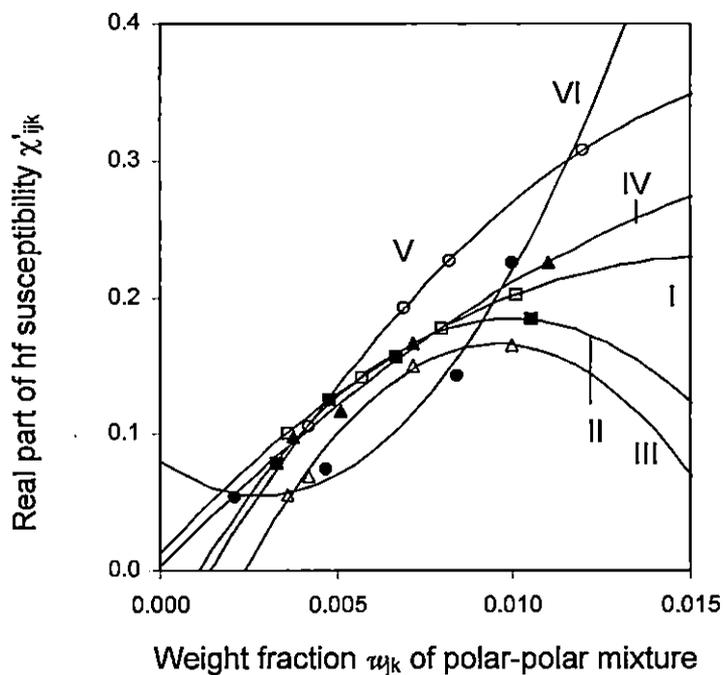


Fig 9.1. Some sample curves showing the variation of imaginary part χ'_{ijk} of hf dielectric susceptibility against weight fraction w_{jk} of polar-polar mixture in solvent C_6H_6 under 9.174 GHz electric field frequency of I. DMF + 0 mole% DMSO (-- □ --) II. DMF + 17 mole% DMSO (-- ■ --) III. DMF + 50 mole% DMSO (-- Δ --) IV. DMF + 60 mole% DMSO (-- ▲ --) V. DMF+ 80 mole% DMSO (-- o --) VI. DMF+ 100 mole% DMSO (-- ● --)

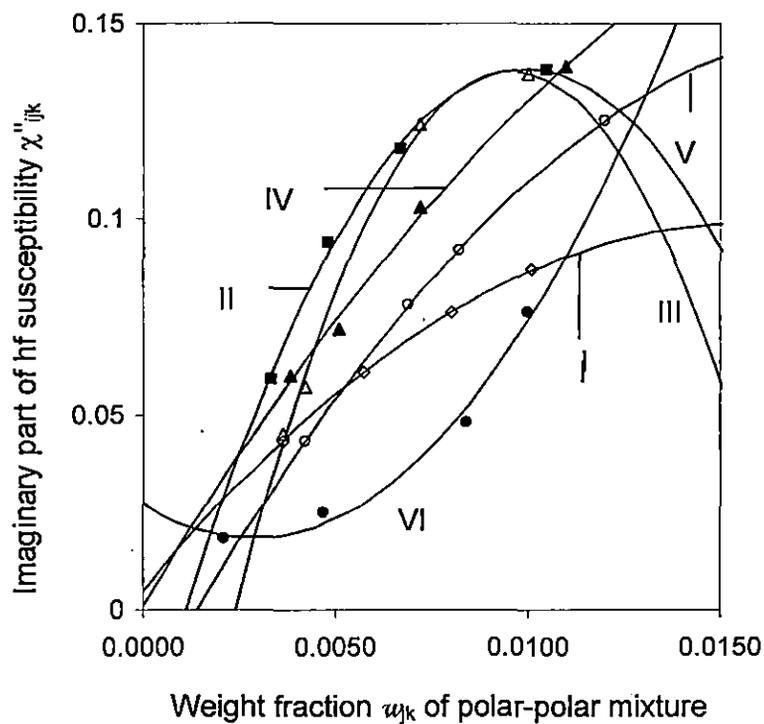


Fig 9.2. Some sample curves showing the variation of imaginary part χ''_{ijk} of hf dielectric susceptibility against weight fraction w_{jk} of polar-polar mixture in solvent C_6H_6 under 9.174 GHz electric field frequency of I. DMF + 0 mole% DMSO (— □ —) II. DMF + 17 mole% DMSO (— ■ —) III. DMF + 50 mole% DMSO (— △ —) IV. DMF + 60 mole% DMSO (— ▲ —) V. DMF + 80 mole% DMSO (— o —) VI. DMF + 100 mole% DMSO (— ● —)

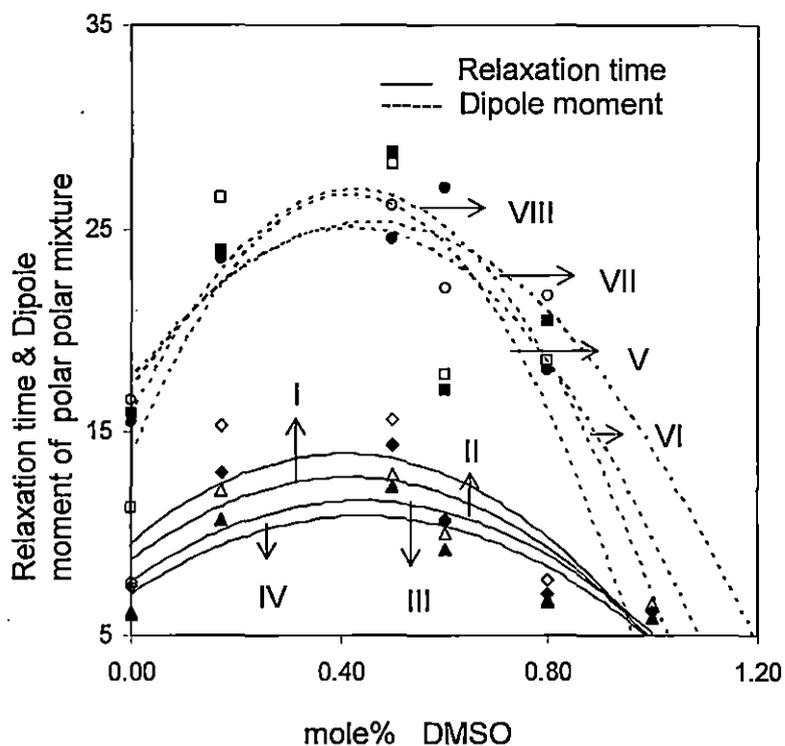


Fig-9.3. Variation of relaxation time τ_{jk} and Dipole moment $\mu_{jk} \times 10^{30}$ in C.m of polar-polar binary mixture against mole% of DMSO in C_6H_6 at different temperature in $^{\circ}C$ under 9.174 GHz electric field frequency I. τ_{jk} (\diamond) at $25^{\circ}C$ II. τ_{jk} (\blacklozenge) at $30^{\circ}C$, III. τ_{jk} (\triangle) at $35^{\circ}C$, IV. τ_{jk} (\blacktriangle) at $40^{\circ}C$, V. μ_{jk} (\square) at $25^{\circ}C$, VI. μ_{jk} (\blacksquare) at $30^{\circ}C$, VII. μ_{jk} (\circ) at $35^{\circ}C$, VIII. μ_{jk} (\bullet) at $40^{\circ}C$

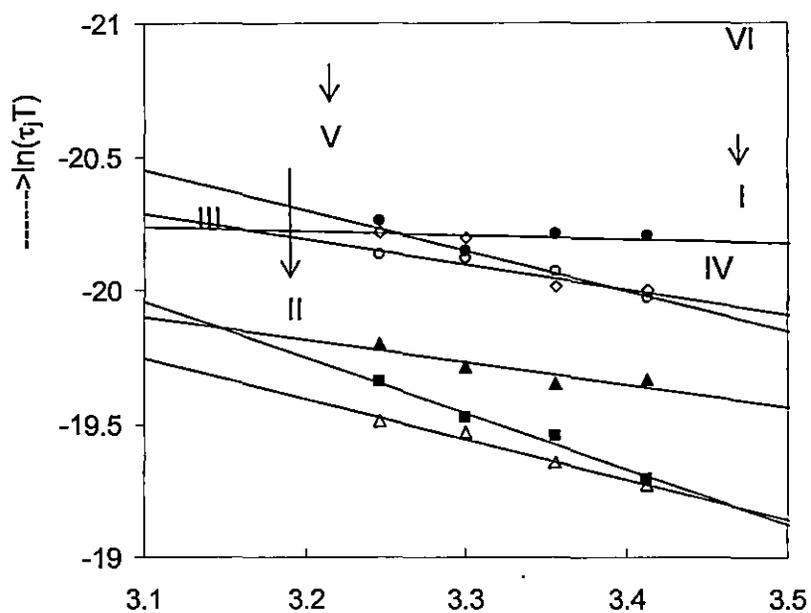


Figure 9.4. Variation of $\ln(\tau_j T)$ against $1/T$ of binary polar mixtures in solvent C_6H_6 under 9.174 GHz electric field frequency I. DMF + 0 mole% DMSO (-- □ --) II. DMF + 17 mole% DMSO (-- ■ --) III. DMF + 50 mole% DMSO(-- △ --) IV. DMF + 60 mole% DMSO (-- ▲ --) V. DMF + 80 mole% DMSO (-- ○ --) VI. DMF + 100 mole% DMSO (-- ● --)

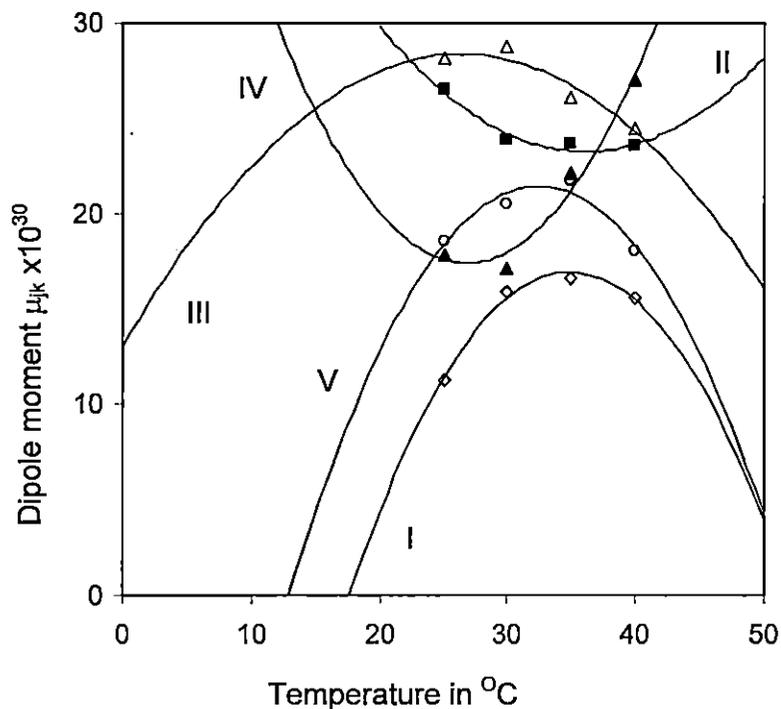
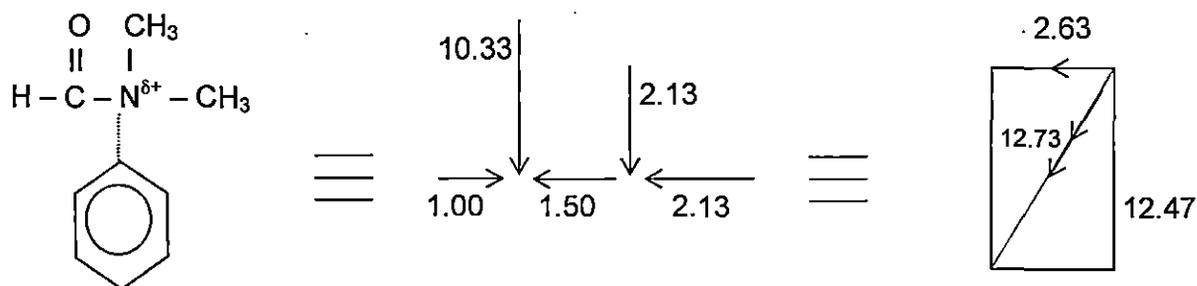
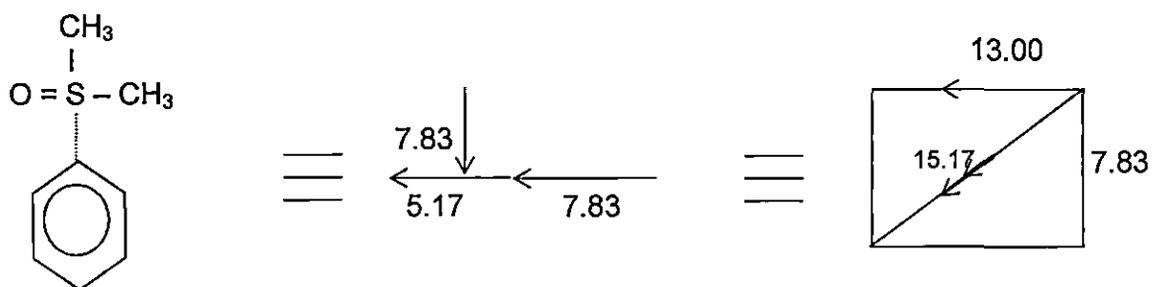


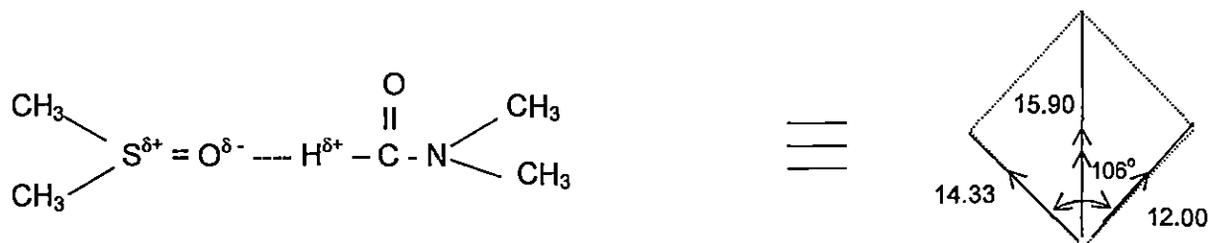
Figure 9.5. Variation of dipole moment $\mu_{jk} \times 10^{30}$ in Coulomb-metre of binary polar - polar mixture against temperature in $^{\circ}\text{C}$ under 9.174 GHz electric field frequency of I. DMF + 0 mole% DMSO (-- \square --) II. DMF + 17 mole% DMSO (-- \blacksquare --) III. DMF + 50 mole% DMSO (-- \triangle --) IV. DMF + 60 mole% DMSO(-- \blacktriangle --) V. DMF + 80 mole% DMSO (-- \circ --) VI. DMF + 100 mole% DMSO (-- \bullet --)



(i)



(ii)



(iii)

Figure 9.6: CONFORMATIONAL STRUCTURES
(Bond moment $\times 10^{30}$ Coulomb metre given in figures)

- (i) DMF in benzene
- (ii) DMSO in benzene
- (iii) DMF - DMSO dimer

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