

## CHAPTER IV

DIPOLE MOMENTS OF ASSOCIATED BINARY SOLUTES IN BENZENE FROM ULTRA  
HIGH FREQUENCY CONDUCTIVITY OF SOLUTIONS.

#### 4.1 Introduction

Now a days, the estimation of dipole moment  $\mu_j$  as well as the relaxation time  $\tau_a$  of a polar solute dissolved in non-polar solvent under ultra-high frequency electric field are really very encouraging (Acharyya and Chatterjee 1985, Acharyya et al 1986, Dhull et al 1982) as they throw much light on the monomer and dimer formations in a liquid mixture. But the measurement of  $\mu_{jk}$  of binary polar mixtures in a given non-polar solvent are, however, very scanty. There are several methods (Gopala Krishna 1957, Sen and Ghosh 1972) to estimate  $\tau_a$  and  $\mu_j$  of polar solute dissolved in non-polar solvent under microwave or radio frequency electric field.

We (Acharyya and Chatterjee 1985), however, devised a method to find out relaxation time and dipole moment of a polar solute in non-polar solvent under uhf electric field. In this paper we thought to extend our method to compute the dipole moment of binary polar mixture in dilute solution of non-polar solvent. The uhf conductivity  $K_{ijk}$  of binary polar solute and non-polar solvent mixture is comparatively easy to measure down to very low concentration by using a Klystron or a r.f. Hartley oscillator in the laboratory. The data of uhf conductivity are, however, very limited (Sen and Ghosh 1972). Recently, Sharma and Sharma (1984, 1985) reported the measured values of  $\epsilon'_{ijk}$  and  $\epsilon''_{ijk}$ , the real and

imaginary parts of complex dielectric constant  $\epsilon_{ijk}^*$  of binary polar mixtures consisting of N,N- dimethyl formamide (DMF) and N,N- tetramethyl urea (TMU) as well as DMF and N,N- dimethyl acetamide (DMA) in benzene under 9.885 GHz electric field. We, therefore, tempted to used these measured values of  $\epsilon'_{ijk}$  and  $\epsilon''_{ijk}$  of the polar mixtures for different mole fractions  $X_j$  of DMF at 15°C to 30°C to obtain uhf conductivities  $K_{ij}$ ,  $K_{ik}$  and  $K_{ijk}$  using Murphy and Morgan relation (1939):

$$k = \frac{\omega(\epsilon'^2 + \epsilon''^2)^{1/2}}{4\pi}$$

The calculated conductivities are presented in Table 4.1. Amides are very important dielectric liquids for their wide biological applications and they form the basic building blocks in proteins. That is why amides attracted the attention of a large number of workers (Sato et al 1976). The  $K_{ijk}$  of DMF+TMU mixtures at 15°C in terms of weight fraction  $W_{jk}$  in benzene were found to be as :

$$K_{ik} \times 10^{-10} = 1.1670 - 1.2030 W_k + 795.72 W_k^2$$

$$K_{ijk} \times 10^{-10} = 1.1455 + 3.9273 W_{jk} - 21.4233 W_{jk}^2$$

$$K_{ijk} \times 10^{-10} = 1.1280 + 6.9023 W_{jk} - 51.4435 W_{jk}^2$$

$$K_{ijk} \times 10^{-10} = 1.1247 + 11.9614 W_{jk} - 249.0353 W_{jk}^2$$

$$K_{ijk} \times 10^{-10} = 1.1286 + 11.5870 W_{jk} - 120.3810 W_{jk}^2$$

**Table 4.1a.** Values of ultra high frequency conductivity  $K_{ijk}$  of polar solute in benzene at various concentration at 15°C

System	Mole fraction Of DMF $X_j$	Weight fraction of polar solute $W_{jk}$	Uhf. Conductivity $K_{ijk} \times 10^{-10}$ , esu
DMF + TMU in benzene	1.0	0.0023	1.1715
		0.0048	1.1941
		0.0063	1.2089
		0.0079	1.2274
	0.9	0.0110	1.2629
		0.0026	1.1607
		0.0046	1.1733
		0.0073	1.2072
	0.7	0.0099	1.2399
		0.0122	1.2467
		0.0025	1.1542
		0.0053	1.1772
0.3	0.0072	1.2006	
	0.0097	1.2148	
	0.0112	1.2264	
	0.0019	1.1418	
	0.0040	1.1537	
	0.0068	1.1714	
	0.0084	1.1859	
	0.0105	1.1935	

Table 4.1a (continued)

System	Mole fraction Of DMF $X_j$	Weight fraction of polar solute $w_{jk}$	Uhf Conductivity $K_{ijk} \times 10^{-10} \text{ esu}$
		0.0020	1.1533
		0.0045	1.1607
	0.1	0.0073	1.1768
		0.0091	1.1780
		0.0120	1.1893
		0.0020	1.1680
		0.0037	1.1715
	0.0	0.0060	1.1866
		0.0078	1.2106
		0.0098	1.2286
		0.0023	1.1715
		0.0048	1.1941
	1.0	0.0063	1.2089
		0.0079	1.2274
		0.0110	1.2629
		0.0020	1.1551
		0.0041	1.1756
	0.9	0.0067	1.2165
		0.0085	1.2320
		0.0104	1.2476

Table 4.1a (continued)

System	Mole fraction of DMF $x_j$	Weight fraction of polar solute $w_{jk}$	Uhf Conductivity $K_{ijk} \times 10^{-10}$ , esu
		0.0027	1.1606
		0.0044	1.1805
	0.7	0.0072	1.2168
		0.0090	1.2300
		0.0117	1.2653
		0.0028	1.1671
		0.0042	1.1806
	0.3	0.0070	1.1983
		0.0094	1.2272
DMF		0.0130	1.2578
+			
DMA		0.0021	1.1546
in		0.0041	1.1677
	0.1	0.0068	1.2050
benzene		0.0086	1.2210
		0.0109	1.2521
		0.0028	1.1645
		0.0039	1.1775
	0.0	0.0068	1.2020
		0.0089	1.2226
		0.0115	1.2470

Table 4.1b. Values of ultra high frequency conductivity  $K_{ijk}$  of (1:1) mixture of binary polar solute in benzene at different temperature

System	Temp. °C	Weight fraction of polar solute $w_{jk}$	UHF Conductivity $K_{ijk} \times 10^{-10}$ esu
		0.0019	1.1546
		0.0052	1.1672
	15	0.0073	1.1775
		0.0098	1.2031
		0.0127	1.2262
DMF		0.0019	1.1462
+		0.0052	1.1563
TMU	20	0.0073	1.1863
in		0.0098	1.1914
benzene		0.0127	1.2197
		0.0019	1.1324
		0.0052	1.1539
	30	0.0073	1.1664
		0.0098	1.1839
		0.0127	1.1970

Table 4.1b (continued)

System	Temp., °C	Weight fraction of polar solute $w_{jk}$	Dhf Conductivity $K_{ijk} \times 10^{-10}$ , esu
		0.0023	1.1690
		0.0039	1.1785
	15	0.0063	1.1991
		0.0105	1.2411
		0.0023	1.1541
		0.0039	1.1733
	20	0.0063	1.2005
DMF		0.0105	1.2357
+			
DMA		0.0023	1.1502
in		0.0039	1.1631
benzene	25	0.0063	1.1960
		0.0105	1.2242
		0.0023	1.1447
		0.0039	1.1611
	30	0.0063	1.1821
		0.0105	1.2187

$$\text{and } K_{ij} \times 10^{-10} = 1.1480 + 9.212 W_j + 109.655 W_j^2$$

respectively for the mole fractions  $W_j = 0.0, 0.1, 0.3, 0.7, 0.9$  and  $1.0$  of DMF in DMF + TMU mixture. They are shown graphically in Fig. 4.1.

The usual behaviour of  $K_{ijk}$  of a ternary solution in the low concentration region is given by

$$K_{ijk} \times 10^{-10} = \alpha + \beta W_{jk} + \gamma W_{jk}^2$$

if the polar solute under consideration have different amount of polarities. When the individual polar solutes like DMF and DMA have almost of the same amount of polarity the  $K_{ijk}$  were found to be linear with  $W_j$  as  $K_{ijk} \times 10^{-10} = \alpha + \beta W_{jk}$

The linear variation of uhf conductivity  $K_{ijk}$  of DMF + DMA mixtures in benzene as a function of  $W_{jk}$  of the solutes of was worked out to be :

$$K_{ij} \times 10^{-10} = 1.1447 + 10.5665 W_j$$

$$K_{ijk} \times 10^{-10} = 1.1326 + 11.4739 W_{jk}$$

$$K_{ijk} \times 10^{-10} = 1.1302 + 11.4907 W_{jk}$$

$$K_{ijk} \times 10^{-10} = 1.1413 + 8.9143 W_{jk}$$

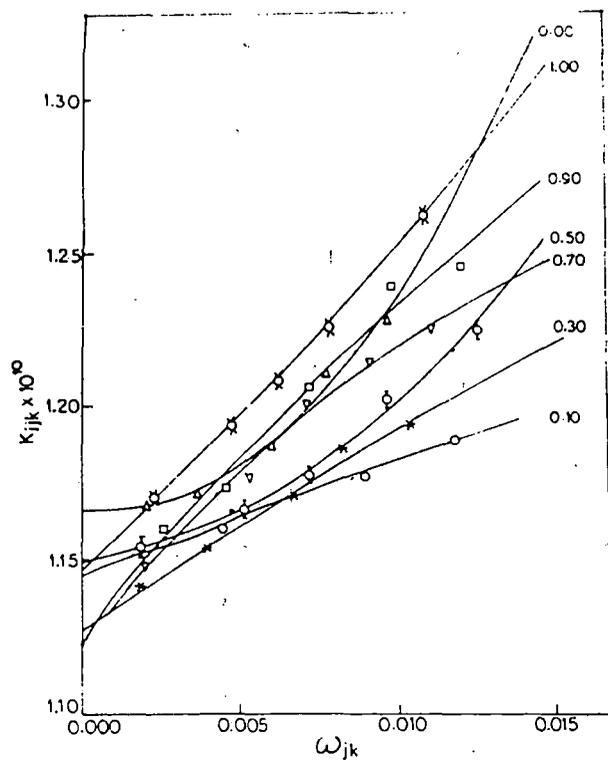


Fig 4.1. Concentration variation of  $K_{ijk}$  of DMF + TMU in benzene at different mole fractions of DMF at 15°C.

of

$$K_{ijk} \times 10^{-10} = 1.1268 + 11.2724 W_{jk}$$

$$\text{and } K_{ik} \times 10^{-10} = 1.1393 + 9.3479 W_k$$

for the mole fraction 1.0, 0.9, 0.7, 0.3, 0.1 and 0.0 of DMF in DMF + DMA at 15°C respectively.

Again  $K_{ijk}$  of 1:1 mixtures of DMF and TMU as well as DMF and DMA in benzene as a function  $W_{jk}$  were also arrived at.:

$$K_{ijk} \times 10^{-10} = 1.1497 + 1.554 W_{jk} + 359.0195 W_{jk}^2 \text{ at } 15^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.1350 + 4.70 W_{jk} + 153.053 W_{jk}^2 \text{ at } 20^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.1180 + 7.532 W_{jk} - 99.625 W_{jk}^2 \text{ at } 30^\circ\text{C}$$

$$\text{and } K_{ijk} \times 10^{-10} = 1.1455 + 8.9409 W_{jk} \text{ at } 15^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.1342 + 9.8777 W_{jk} \text{ at } 20^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.1303 + 9.2387 W_{jk} \text{ at } 25^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.1252 + 8.9482 W_{jk} \text{ at } 30^\circ\text{C}$$

respectively.

The hf conductivity data of 1:1 mixtures of two polar solutes of DMF + TMU and DMF + DMA at different temperatures are shown in Figs. 4.2 and 4.3 respectively. It is found difficult to plot the

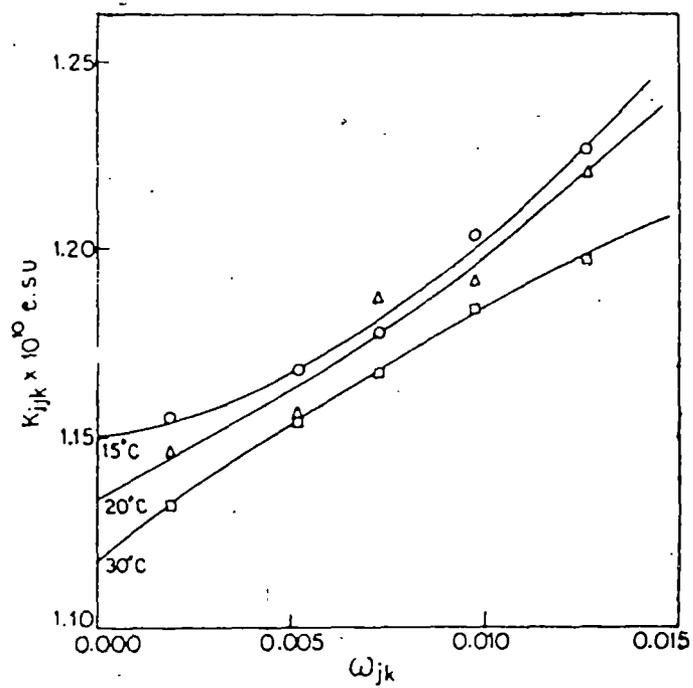


Fig. 4. 2. Concentration variation of  $K_{ijk}$  of DMF + TMU (50% each) in benzene at 15, 20 and 30°C.

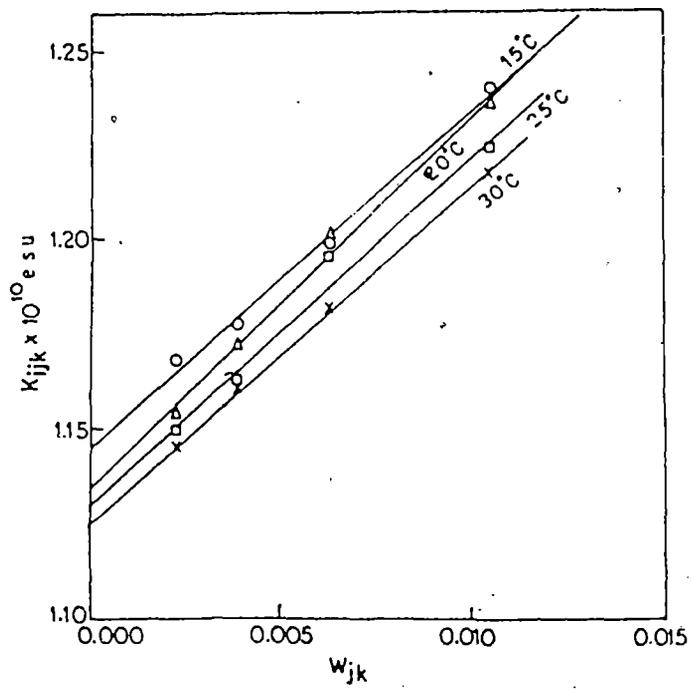


Fig 4.3. Concentration variation of  $K_{ijk}$  of DMF + DMA (50% each) in benzene at 15, 20, 25 and 30°C.

conductivities of DMF + DMA in benzene against  $w_{jk}$  for different mole fractions  $x_{jk}$  at  $15^{\circ}\text{C}$  as their slopes and intercepts are very close probably due to more or less same dipole moments of the two amides. The uhf conductivity data of polar-nonpolar liquid mixture are very sensitive to yield the dipole moment of single or binary polar solute. Hence the information regarding various types of molecular interactions could, however, be inferred from the estimated values of dipole moments. The variation of dipole moment with temperature is not a new concept, but it actually occurs when the polar-nonpolar liquid mixture is subjected to the high frequency electric field (Acharyya et al 1982, 1986, Ras and Bordewijk 1971), probably due to stretching of the bond lengths of molecules. The dipole moment  $\mu_{jk}$  of (1:1) polar mixtures of DMF + TMU and DMF + DMA have been calculate from the concentration variation of uhf conductivity at different temperatures. The most probable variation of  $\mu_{jk}$  of 50% DMF and 50% TMU mixture in benzene with respect to the temperature in  $^{\circ}\text{C}$  is given by

$$\mu_{jk} = -4.393 + 0.6248 t - 1.157 \times 10^{-2} t^2$$

Showing the zero value of  $\mu_{jk}$  at  $8.31^{\circ}\text{C}$  and  $45.69^{\circ}\text{C}$  due to orientation of the monomer dipole moments  $\mu_j$  and  $\mu_k$  of the individual solutes. The temperature variation of  $\mu_{jk}$  of 1:1 mixture of DMF and DMA in benzene was also worked out to be :

$$\mu_{jk} = 2.97 + 0.133 t - 3 \times 10^{-3} t^2$$

showing a maximum value of  $\mu_{jk}$  at  $22.5^{\circ}\text{C}$ . The temperature variation

of  $\mu_{jk}$  for both the systems are displayed graphically in Fig 4.5

#### 4.2 Theoretical Formulation

According to Murphy and Morgan (1939) the magnitude of total uhf conductivity  $K_{ijk}$  for weight fraction  $W_{jk}$  of a binary solute (j and K) dissolved in a non-polar solvent (i) is given by

$$K_{ijk} = \frac{\omega}{4\pi} \left( \epsilon'_{ijk}{}^2 + \epsilon''_{ijk}{}^2 \right)^{1/2} \dots\dots\dots(4.1)$$

Where  $\omega = 2\pi f$ , f being the frequency of the applied electric field. The values of  $\epsilon'_{ijk}$  of the solution in the uhf electric field is very small and is often equal to optical dielectric constant, but still  $\epsilon'_{ijk} \gg \epsilon''_{ijk}$ , where  $\epsilon''_{ijk}$  is the dielectric loss which is responsible for the absorption of electrical energy to offer resistance to the polarisation. Hence it is evident that in the electric field of microwave region, the magnitude of total conductivity become

$$K_{ijk} = \frac{\omega}{4\pi} \epsilon'_{ijk} \dots\dots\dots(4.2)$$

It can be shown that the real part  $K'_{ijk} = \omega \epsilon''_{ijk} / 4\pi$

of uhf conductivity of solution of concentration  $W_{jk}$  of binary polar solute in non-polar solvent at temperature  $T^{\circ}K$  is

$$K'_{ijk} = \frac{\mu_{jk}^2 N \rho_{ijk}}{3M_{jk} kT} \frac{\omega^2 \tau_a}{1 + \omega^2 \tau_a^2} W_{jk} \quad \dots (4.3)$$

where  $\mu_{jk}$  is the dipole moment of polar solute of molecular weight

$$M_{jk} = x_j M_j + x_k M_k, \quad x_j \text{ and } x_k \text{ being the mole fractions of}$$

individual solutes of molecular weights  $M_j$  and  $M_k$  respectively in the binary polar mixture,  $N$  is the Avogadro number and  $k$  is the Boltzmann constant.

But for hf region

$$\epsilon'_{ijk} = \epsilon_\alpha + \frac{\epsilon''_{ijk}}{\omega \tau_a} \quad \dots (4.4)$$

and hence with eq.(4.2) we get

$$K_{ijk} = K_\alpha + K'_{ijk} / \omega \tau_a \quad \dots (4.5)$$

Where  $K_\alpha = \omega \epsilon_\alpha / 4\pi$  is a constant conductivity and  $\tau_a$  is the relaxation time of the associated solute.

Since  $K_{ijk}$  is a function of  $W_{jk}$ , we have from eq (4.5)

$$\left[ \frac{dK'_{ijk}}{dW_{jk}} \right]_{W_{jk} \rightarrow 0} = \omega \tau_a \left[ \frac{dK_{ijk}}{dW_{jk}} \right]_{W_{jk} \rightarrow 0} = \omega \tau_a \beta \quad \dots (4.6)$$

Where  $\beta$  is the slope of  $K_{ijk} - W_{jk}$  curve at  $W_{jk} \rightarrow 0$ .

When  $W_{jk} \rightarrow 0$ ,  $\rho_{ijk}$  the density of the solution becomes  $\rho_i$  the

density of the solvent and local field  $F_{ijk}$  of the solution

becomes  $F_i = \left[ (\epsilon_i + 2) / 3 \right]^2$ , the local field of the solvent.

Under this condition eq. (4.3) on differentiation with respect to  $W_{jk}$  takes the form

$$\left[ \frac{dk'_{ijk}}{dW_{jk}} \right]_{W_{jk} \rightarrow 0} = \frac{\mu_{jk}^2 N \rho_j F_j}{3 M_{jk} k T} \left[ \frac{\omega^2 \tau_a^2}{1 + \omega^2 \tau_a^2} \right] \dots\dots\dots(4.7)$$

From eqs. (4.6) and (4.7) the dipole moment of binary polar mixture becomes

$$\mu_{jk} = \left[ \frac{3 M_{jk} k T}{N \rho_i F_i} \frac{\beta}{\omega b} \right]^{1/2} \dots\dots\dots(4.8)$$

Where  $b = 1 / \left[ 1 + \omega^2 \tau_a^2 \right] \dots\dots\dots(4.9)$

Now b could, however, be estimated from eq.(4.9) in terms of the available relaxation time  $\tau_a$  to obtain the dipole moment of associated solute from eq.(4.8) in a solvent.

### 4.3 Results and Discussion

The estimated uhf conductivity of DMF + TMU and DMF + DMA in benzene are given in Table 4.1. The equations of  $K_{ijk}$  against  $W_{jk}$  are already presented in the previous section. The variation of  $K_{ijk}$  with  $W_{jk}$  of DMF + TMU at different  $X_j$  at 15°C are shown in

Fig. 4.1 and that of (1:1) Mixtures of DMF + TMU and DMF + DMA at various temperatures are shown in Figs.4.2 and 4.3 respectively. The weight fraction  $W_{jk}$  of the binary solute changes in the solutions, the curves of  $K_{ijk}$  against  $W_{jk}$  have different intercepts and slopes (Figs. 4.2 and 4.3). This sort of behaviour of  $K_{ijk} - W_{jk}$  curves does not occur for different  $X_j$  and for different temperatures, if we measure the conductivities in comparatively high concentration region (Acharyya et al 1982). The curves at all the experimental temperatures for a wide range of concentration when are drawn, are expected to meet at a common point on the  $K_{ijk}$  - axis because the term  $\left[ \rho_{ijk} F_{ijk} / T \right]$  in eq. (4.3) assumes a constant value 0.006 at  $W_{jk} \rightarrow 0$  for benzene as solvent. At  $W_{jk} \rightarrow 0$  the intercepts of  $K_{ijk} - W_{jk}$  curves are incidentally different at different temperatures and decrease with the rise of temperature, as observed in Figs. 4.2 and 4.3, due to solvation effect (Datta et al 1981).

When the mole fraction  $X_j$  of DMF in the mixtures are in the limit of  $X_j = 0.0$  and  $X_j = 1.0$  we get what are known as concentration variation of uhf conductivities  $K_{ik}$  and  $K_{lj}$  of TMU or DMA and DMF respectively at 15°C. The estimated slopes  $\beta$  of this concentration variation of uhf conductivity are very important to yield the dipole moments. The computed dipole moments are tabulated in Table 4.2 along with the slopes  $\beta$ . When  $X_j = 0.0$  and 1.0 we get monomer dipole moments  $\mu_k$  for TMU or DMA and  $\mu_j$  for DMF respectively. The values of  $\mu$ , computed from eq. (4.8) in terms of

Table 4.2- Dipole moments of N, N-dimethyl formamide (DMF) in DMF + N,N-tetramethyl urea (TMU) and in DMF + N, N-dimethyl acetamide (DMA) mixtures in benzene as a function of mole fraction  $x_j$  of DMF at 15°C as well as those of (1:1) DMF + TMU and (1:1) DMF + DMA mixtures in benzene at different experimental temperature in °C

System	temp t in °C	Mole Fraction DMF $x_j$	Slope of $K_{ijk} - \omega_{jk}$ curve $\beta \times 10^{-10}$	Assumed molecular wt. $M_{jk}$ of solute	$b = 1/(1+\omega_{jk}^2 r_{jk}^2)$	Computed $\mu_j, \mu_k$ and $\mu_{jk}$ in D (Expt.)	Calculated $\mu_j, \mu_k$ and $\mu_{jk}$ in D from the values of bond moments and bond axes
DMF and TMU in benzene	15	1.00	9.2120	73.0920	0.8406	3.76	3.82
		0.90	11.5870	77.3986	0.6853	4.80	3.63
		0.70	11.9614	86.0118	0.6433	5.31	3.24
		0.30	6.9023	103.2362	0.5120	4.95	2.48
		0.10	3.9273	111.8514	0.6402	3.48	2.10
		0.00	1.2030	116.1580	0.6909	1.89	1.90
DMF and DMA in benzene	15	1.00	10.5665	73.0944	0.8406	4.02	3.82
		0.90	11.4739	74.4971	0.8193	4.29	3.84
		0.70	11.4907	77.3024	0.7543	4.56	3.88
		0.30	8.9143	82.9132	0.6929	4.23	3.96
		0.10	11.2724	85.7185	0.7575	4.74	4.00
		0.00	9.3479	87.1212	0.7660	4.33	4.02
DMF and TMU in benzene	15	0.50	1.5540	94.6250	0.4520	2.39	2.40
	20	0.50	4.7000	94.6250	0.6684	3.42	
	30	0.50	7.5320	94.6250	0.8770	3.94	
DMF and DMA in benzene	15	0.50	8.9409	80.1078	0.6929	4.27	4.27
	20	0.50	9.8777	80.1078	0.7120	4.49	
	25	0.50	9.2387	80.1078	0.7248	4.36	
	30	0.50	8.9482	80.1078	0.7470	4.28	

reported (Sharma and Sharma 1984, 1985)  $\tau_{jk}$ , for TMU and DMF were thus found to be 1.89 D and 3.76 D respectively. The values of the dipole moment of the associated solutes (solute - solute molecular association) at 15°C, presented in Table 4.2, can, however, be fitted by a polynomial equation as a function of  $X_j$  of DMF:

$$\mu_{jk} = 2.5145 + 10.7785 X_j - 9.42 X_j^2$$

The graph of  $\mu_{jk}$  against  $X_j$  satisfying the above equation is shown in Fig 4.4 with experimentally estimated  $\mu_{jk}$ . The fitted curve, however, excludes two values of dipole moments : one  $\mu_k = 1.89$ -D For TMU and the other  $\mu_{jk} = 2.39$  D at  $X_j = 0.0$  and 0.5 respectively. As  $X_j$  of DMF changes  $\mu_{jk}$  gradually increase in a regular manner and then suddenly drops to a very low value at  $X_j = 0.5$  (Fig. 4.4), after  $X_j > 0.5$ ,  $\mu_{jk}$  slowly decreases thus resembling the convex nature to terminate to  $\mu_j = 3.76$  D of solute - solvent associated monomers of DMF at  $X_j = 1.0$ . This nature of variation of  $\mu_{jk}$  against  $X_j$  may be due to formation of dimers in the liquid mixture of DMF and TMU. The sudden drop in the value of  $\mu_{jk}$  from its regular behaviour is probable due to the maximum dimerisation in the liquid mixture having mole fraction nearly 0.5 of DMF. In case of DMF and DMA mixture in benzene the monomer for DMA and DMF were found to be  $\mu_k = 4.33$  D and  $\mu_j = 4.02$  D respectively. The curves in Fig.4.4 for DMF + DMA mixtures drawn with all experimental points shows two peaks : one at  $X_j = 0.1$  and other at  $X_j = 0.7$  and in the range  $0.1 \leq X_j \leq 0.7$  it is simply a concave curve suggesting the formation of dimers in this region.

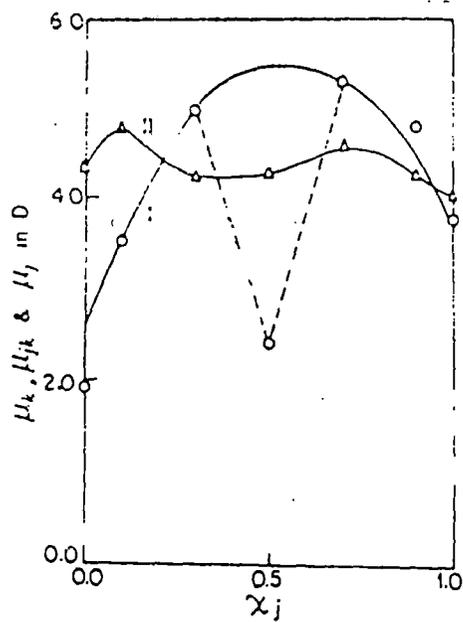


Fig. 4.4. Variation of experimentally observed dipole moments  $\mu_k$ ,  $\mu_{jk}$  and  $\mu_j$  with mole fraction of DMF in DMF + TMU and DMF + DMA mixtures at 15°C (-O-O- of DMF + TMU and - $\Delta$ - $\Delta$ - for DMF + DMA).

But the dipole moment  $\mu_{jk}$  is to be minimum at  $x_j = 0.3$  (Fig.4.4) and hence the dimerisation of this mixture may be maximum near  $x_j = 0.3$  unlike the observation made by Sharma and Sharma (1984).

The nature of behaviour of  $\mu_{jk}$  against temperature in  $^{\circ}\text{C}$  are plotted in Fig. 4.5 with the experimentally measured values upon them. The curve of  $\mu_{jk}$  for the 1st. mixture shows that the monomer solutes orient along their dipole axes such that the resultant dipole moments are zero at  $8.31^{\circ}\text{C}$  and  $45.69^{\circ}\text{C}$ . As shown in Fig.4.5 the  $\mu_{jk}$  of the expected associate solute for (1.1) DMF + DMA mixture in benzene increases slowly from 2.97 D at  $0^{\circ}\text{C}$  to the maximum 4.49 D at  $22.5^{\circ}\text{C}$  and then slowly decrease to 3.49 D at  $40^{\circ}\text{C}$ . All these data show that the dipole moments of (1.1) binary polar mixtures in non-polar solvent do change with temperature in the hf region of alternating electric field.

Finally. to interpret the experimental monomer dipole moments of the solute, we calculated the theoretical  $\mu_j$  and  $\mu_k$  in terms of bond moments, bond axes and bond angles as sketched in Fig.4.5 for DMF, TMU and DMA respectively. In DMF the bond moments of C = O and  $\text{CH}_3$ -N act along same direction making resultant moment of 3.74 D while those of  $\text{CH}_3$ -N, H-C and N-C act along a common axis with a resultant dipole moment of 0.79 D and perpendicular to C-O [ Fig.4.6(i) ]. They thus gives rise to the monomer dipole moment 3.82 D of DMF in benzene. But the Table 4.2 shows 3.76 D and 4.02 D as the experimental dipole moments of DMF in the two mixtures respectively probably due to the effect of trace presence of TMU

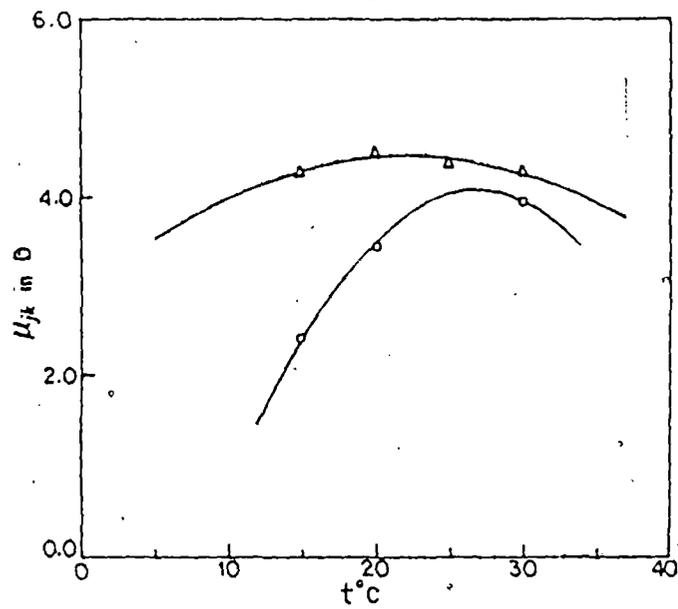


Fig 4.5. Variation of experimentally observed dipole moments with temperatures in °C for DMF + TMU and DMF + DMA in 1:1 mixtures (-O-O- for DMF and TMU and -Δ-Δ- for DMF + DMA).

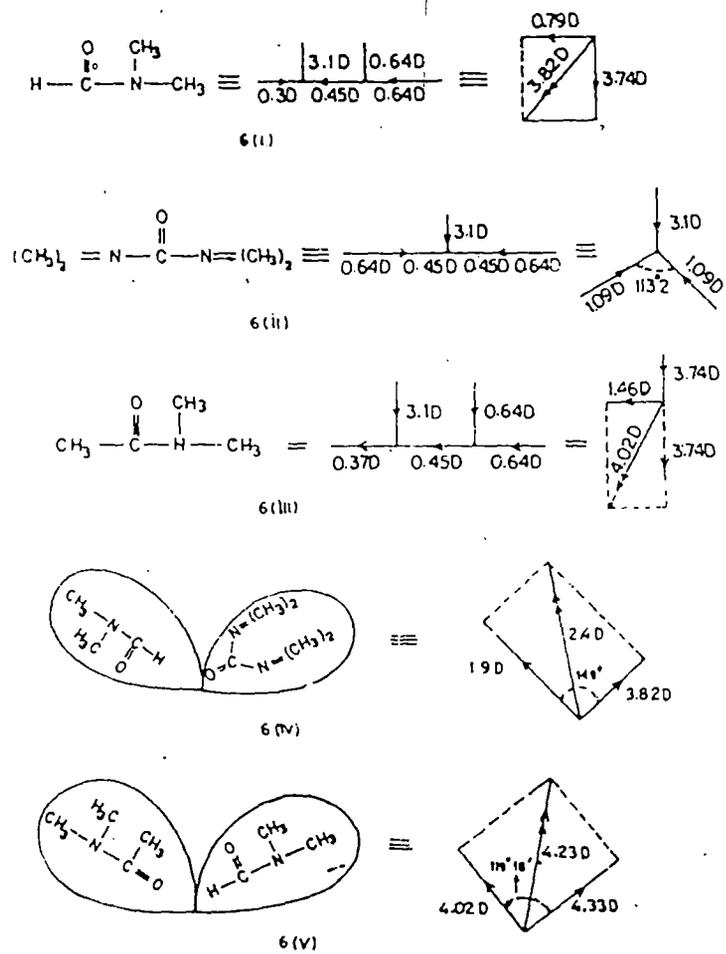


Fig 4.6. (i) Structural form of DMF, (ii) Structural form of TMU, (iii) Structural form of DMA, (iv) Structural form of dimer (DMF + TMU) and (v) Structural form of dimer (DMF + DMA)

and DMA in benzene at  $W_{jk} \rightarrow 0$ . Both the arms in TMU contain  $(\text{CH}_3)_2 = \text{N}$  about a carbon atom in  $\text{C} = \text{O}$  forming an angle  $113.2^\circ$  to give a resultant moment of nearly 1.2 D. This in its turn reduces the bond moment of 3.1D of  $\text{C} = \text{O}$  to give rise to 1.9D as the monomer dipole moment of TMU [ Fig. 4.6 (ii) ]. Similarly in case of DMA the group moments of  $\text{CH}_3\text{-N}$  and  $\text{C} = \text{O}$  act along the same direction while the moments  $\text{C-CH}_3$ ,  $\text{C-N}$ ,  $\text{N-CH}_3$  are in the perpendicular direction [ Fig. 4.6 (iii) ] giving 4.02 D as the monomer dipole moment of DMA. With this preferred conformational directions for DMF, TMU and DMA the calculate values of dipole moments from vector model, assuming molecules to be planer ones, are in close agreement with the experimental values as evident in Table 4.2. The smaller values of  $\mu_{jk}$  for 50:50 mixtures of DMF + TMU and DMF + DMA in benzene are due to dimer formation. For dimerisation between DMF and TMU [ Fig. 4.6 (iv) ] and between DMF and DMA [ Fig. 4.6 (v) ] in benzene the two monomers attach each other with there most electropositive (-H) and electronegative (-O) elements forming angles  $149^\circ$  and  $119.18^\circ$  in the two mixtures respectively as calculated from the experimental  $\mu_j$ ,  $\mu_k$  and  $\mu_{jk}$  values. The values of  $\mu_{jk}$  of dimers change strongly with temperature probably due to the change of preferred conformational directional angle with temperature. The is more pronounced in the case of maximum dimerisation (Fig.4.5). This may be the reason that  $\mu_{jk}$  of 50% of DMF in the mixture exhibit zero value at  $8.31^\circ\text{C}$  and  $45.69^\circ\text{C}$  where as in the 2nd mixture the  $\mu_{jk}$  changes very

slowly as the maximum dimerisation occurs for 30% of DMF in this mixture.

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