

Chapter 8

**DIPOLE MOMENTS OF
ASSOCIATED BINARY SOLUTES IN
BENZENE FROM ULTRA HIGH
FREQUENCY CONDUCTIVITIES
OF SOLUTIONS**

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1. INTRODUCTION

Now a days, the estimation of dipole moment μ_j as well as the relaxation time τ_j of a single polar solute dissolved in a nonpolar solvent like benzene or dioxane or carbontetrachloride etc. under the application of 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 structures of monomer and dimer formations in a liquid mixture. But the measurements of μ_{jk} of binary polar mixtures in a given nonpolar solvent are, however, very scanty. There are several methods (Gopala Krishna 1957, Sen and Ghosh 1972) to estimate μ_j of a polar solute dissolved in a nonpolar solvent under an alternating microwave or radio frequency electric field.

We (Acharyya and Chatterjee 1985), however, devised a method to find out the relaxation time and the dipole moment of a polar solute in a nonpolar solvent under the *uhf* electric field. In this paper we thought to extend our previous method to obtain the dipole moment of binary polar solutes in a nonpolar solvent. The *uhf* conductivity K_{ijk} of binary polar solutes dissolved in a nonpolar solvent is comparatively easy to measure down to very low concentration by using a klystron or a radiofrequency Hartley oscillator in the laboratory. The data of *uhf* conductivity under the radiofrequency or the microwave electric field is very limited (Sen and Ghosh 1972). Recently, Sharma and Sharma (1984, 1985) reported the measured values of ϵ'_{ijk} and ϵ''_{ijk} the real and the imaginary parts of the complex dielectric constant ϵ^*_{ijk} of binary polar mixtures consisting of N,N-dimethyl formamide (DMF) and N, N-tetra methyl urea (TMU) as well as N, N-dimethyl formamide (DMF) and N,N-dimethyl acetamide (DMA) in benzene solution using microwave absorption technique at a frequency of 9.885

GHz electric field, in order to collect information regarding the solute-solvent and solute-solute molecular association in the liquid mixtures. we, therefore, tempted to use these measured values of ϵ'_{ijk} and ϵ''_{ijk} of the two binary polar mixtures for different mole fractions x_j of DMF at 15°C to 30°C to obtain *hf* conductivities K'_{ij} , K'_{ik} and K'_{ijk} 's for different weight fractions of single and binary polar solutes using Murphy-Morgan (1939) relation :

$$K_{ijk} = K'_{ijk} + jK''_{ijk}, \text{ where } K'_{ijk} = \frac{\omega \epsilon''_{ijk}}{4\pi} \text{ is the real part and } K''_{ijk} = \frac{\omega \epsilon'_{ijk}}{4\pi} \text{ is the}$$

imaginary part of the *hf* conductivity. Amides are very important dielectric solutes for thier wide biological applications and they form the basic building blocks in proteins. That is why amides attracted much attention of a large number of workers (Sato *et al* 1976). The K'_{ijk} 's of DMF + TMU mixtures at 15°C in terms of the weight fractions ω_{jk} in benzene were found to be of the following equations :

$$K'_{ik} \times 10^{-10} = 1.167 - 1.203\omega_k + 795.72\omega_k^2$$

$$K'_{ijk} \times 10^{-10} = 1.1455 + 3.9273\omega_{jk} - 21.4223\omega_{jk}^2$$

$$K'_{ijk} \times 10^{-10} = 1.128 + 6.9023\omega_{jk} - 51.4435\omega_{jk}^2$$

$$K'_{ijk} \times 10^{-10} = 1.1247 + 11.9614\omega_{jk} - 249.0353\omega_{jk}^2$$

$$K'_{ijk} \times 10^{-10} = 1.1286 + 11.587\omega_{jk} - 120.381\omega_{jk}^2$$

$K'_{ij} \times 10^{-10} = 1.148 + 9.212\omega_j + 109.655\omega_j^2$ respectively for the mole fractions 0.0, 0.1, 0.3, 0.7, 0.9 and 1.0 of DMF in TMU and benzene solutions. They are shown graphically in Figure 1 with the measured values of K'_{ijk} upon the fitted lines.

The usual behaviour of K'_{ijk} of a ternary solution in the low concentration region is thus given by $K'_{ijk} \times 10^{-10} = \alpha + \beta\omega_{jk} + \gamma\omega_{jk}^2$ if the polar solutes 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 *hf* conductivity K'_{ijk} were found to be linear like $K'_{ijk} \times 10^{-10} = \alpha + \beta\omega_{jk}$. The linear variation of *uhf* conductivities K'_{ijk} of DMF + DMA mixtures in benzene as a

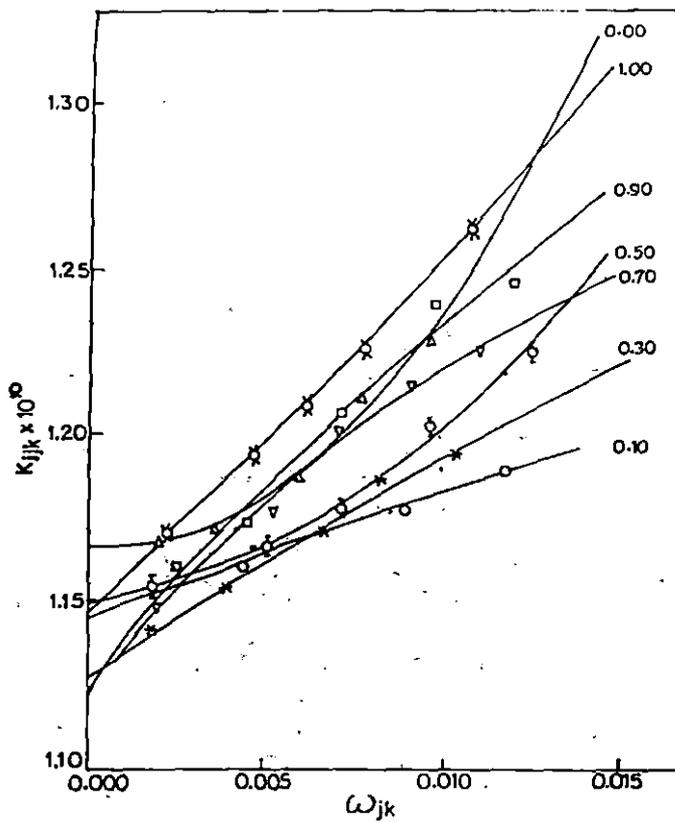


Figure 1. Concentration variation of K_{ijk} of DMF + TMU in benzene at different mole fractions of DMF at 15°C.

function of weight fraction ω_{jk} of the solutes was worked out to be :

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

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

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

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

$$K_{ijk} \times 10^{-10} = 1.1268 + 11.2724\omega_{jk} \text{ and}$$

$K_{ik} \times 10^{-10} = 1.1393 + 9.3479\omega_k$ for the given mole fractions 1.0, 0.9, 0.7, 0.3, 0.1 and 0.0 of DMF in DMA and benzene solution at 15°C.

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

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

$$K_{ijk} \times 10^{-10} = 1.135 + 4.70\omega_{jk} + 153.053\omega_{jk}^2 \text{ at } 20^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.118 + 7.532\omega_{jk} - 99.625\omega_{jk}^2 \text{ at } 30^\circ\text{C}$$

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

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

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

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

The *hf* conductivity data of 1 : 1 mixtures of two polar solutes consisting of DMF + TMU and DMF + DMA respectively at different experimental temperatures are graphically shown in Figures 2 and 3 along with the experimentally measured K_{ijk} 's upon them. It is found difficult to plot the estimated *hf* conductivities of DMF and DMA as a function of weight fraction ω_{jk} for different mole fractions of DMF at 15°C as their slopes and intercepts are very close probably due to the more or less same dipole moments of the two amides under investigation. The ultra high frequency conductivity data of polar-nonpolar liquid mixture are very much sensitive to yield the dipole moment of single or binary polar solutes. Hence the information regarding the various

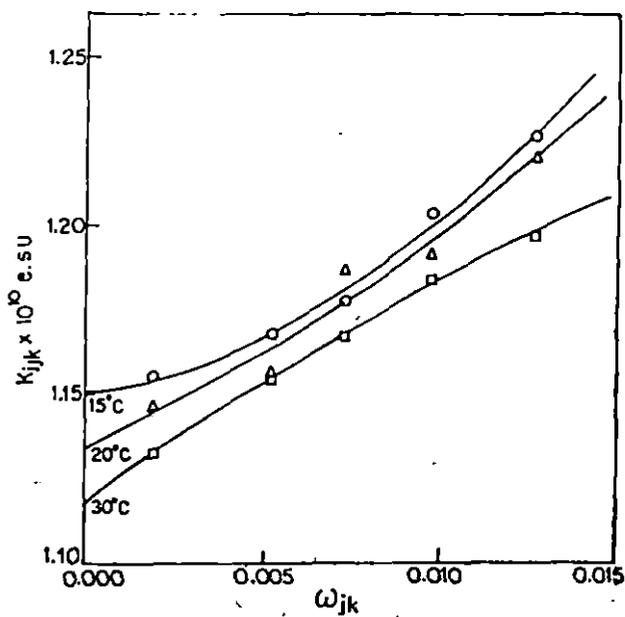


Figure 2. Concentration variation of K_{ijk} of DMF + TMU (50% each) in benzene at 15, 20 and 30°C.

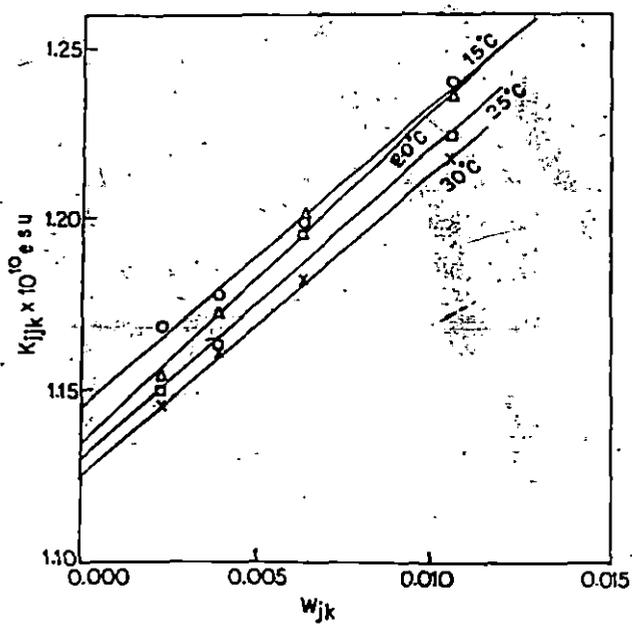


Figure 3. Concentration variation of K_{ijk} of DMF + DMA (50% each) in benzene at 15, 20, 25 and 30°C.

types of molecular interactions of solute-solute and solute-solvent could, however, be inferred from the estimated values of the 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 of GHz region (Acharyya *et al* 1982, 1986, Ras and Bordewijk 1971), probably due to stretching of the bond lengths of the molecules at an elevated temperature. The dipole moments μ_{jk} 's of the associated polar solutes of 50% DMF and 50% TMU as well as 50% DMF and 50% DMA dissolved in benzene have been calculated from the concentration variation of *uhf* conductivity K_{ijk} at different experimental temperatures $t^{\circ}\text{C}$. The most probable variation of μ_{jk} with respect to the temperature change in $^{\circ}\text{C}$ is given by :

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

for DMF and TMU mixtures in benzene showing the zero value of μ_{jk} at 8.31°C and 45.69°C respectively due to orientation of the monomer dipole moments μ_j and μ_k and of the individual solutes. The temperature variation of μ_{jk} of 1 : 1 mixture of DMF and DMA in Benzene was worked out to be :

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

showing a maximum value of μ_{jk} at 22.5°C . Both the μ_{jk} 's thus obtained are displayed graphically in Figure 5.

As evident from Table 1, when the mole fractions of DMF are 0% and 100% respectively at 15°C indicate $\mu_j = 3.82\text{D}$ for DMF, $\mu_k = 1.90\text{D}$ for TMU and $\mu_k = 4.02\text{D}$ for DMA (Figure 4) as their individual theoretical dipole moments whereas the experimentally measured values are $\mu_j = 3.76\text{D}$ and 4.02D for DMF in two mixtures, $\mu_k = 1.89\text{D}$ for TMU and $\mu_k = 4.33\text{D}$ for DMA respectively.

2. THEORETICAL FORMULATIONS

According to Murphy and Morgan (1939) relation the magnitude of the total *h-f* conductivity K_{ijk} for a given weight fraction ω_{jk} of a binary solute (*j* and *k*)

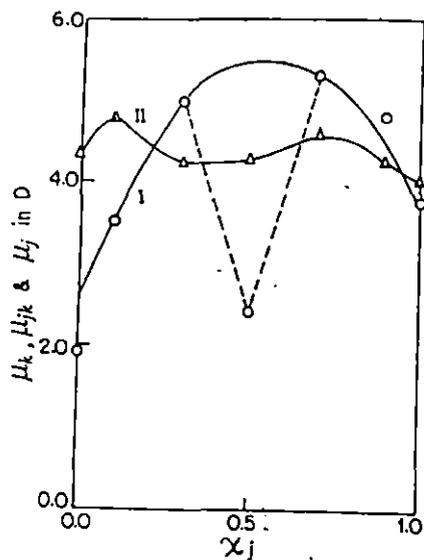


Figure 4. Variation of experimentally observed dipole moments μ_k , μ_{jk} and μ_j with mole fraction of DMF in DMF + TMU and DMF + DMA mixtures at 15°C (—O—O— of DMF + TMU and — Δ — Δ — for DMF + DMA).

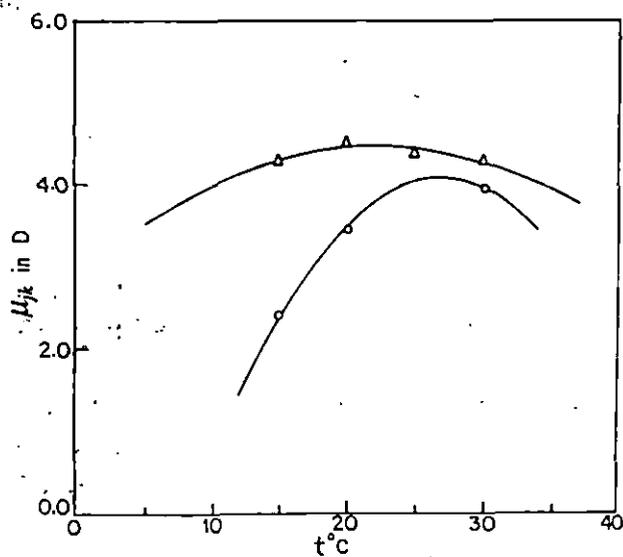


Figure 5. Variation of experimentally observed dipole moments with temperatures in °C for DMF + TMU and DMF + DMA in 1 : 1 mixtures (—O—O— for DMF and TMU and — Δ — Δ — for DMF + DMA).

dissolved in a nonpolar solvent (i) is usually given by

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

where $\omega = 2\pi f$; $f = 9.885$ GHz being the frequency of the applied *hf* electric field in the present work. The value of real part of the dielectric constant ϵ'_{ijk} of the solution in the microwave electric field is very small and is often equal to optical dielectric constant, but still $\epsilon'_{ijk} \gg \epsilon''_{ijk}$ where ϵ''_{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 the total conductivity becomes

$$K_{ijk} = \frac{\omega}{4\pi} \epsilon'_{ijk} \dots\dots\dots (2)$$

It can be shown that the real part $K'_{ijk} = \omega \epsilon''_{ijk} / 4\pi$ of *hf* conductivity of solution of weight fraction ω_{jk} of binary polar solute in non-polar solvent at temperature $T^\circ\text{K}$ is

$$K'_{ijk} = \frac{\mu_{jk}{}^2 N \rho_{ijk} F_{ijk}}{3M_{jk} kT} \frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} \omega_{jk} \dots\dots\dots (3)$$

where μ_{jk} is the dipole moment of polar solutes of molecular weight $M_{jk} = x_j M_j + x_k M_k$, x_j and x_k being the mole fraction of individual solutes in binary mixtures of polar solute having molecular weights M_j and M_k respectively, N is the Avogadro number, k is the Boltzmann constant and $F_{ijk} = [(\epsilon_{ijk} + 2)/3]^2$ is the local field.

But for *hf* region $\epsilon'_{ijk} = \epsilon^\infty_{ijk} + \epsilon''_{ijk} / \omega \tau_s$ \dots\dots\dots (4)

and from eqs. (2) and (4) we get

$$K_{ijk} = K^\infty_{ijk} + K'_{ijk} / \omega \tau_s \dots\dots\dots (5)$$

where $K^\infty_{ijk} = \omega \epsilon^\infty_{ijk} / 4\pi$ is a constant conductivity and τ_s is the relaxation time of

Table 1. 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 temperatures in °C.

System	temp. t in °C	Mole fractions of DMF x_j	Slope of $K_{ijk} - \omega_{jk}$ curve $\beta \times 10^{-10}$	Assumed molecular wt. M_{jk} of solutes	$b = 1/(1 + \omega^2 \tau^2)$	Computed μ_j, μ_k and μ_{jk} in D (Expt.)	Calculated μ_j, μ_k and μ_{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	103.2382	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	

the associated solutes. Since K_{ijk} is a function of ω_{jk} from eq. (5) we have

$$\left(\frac{dK'_{ijk}}{d\omega_{jk}}\right)_{\omega_{jk} \rightarrow 0} = \omega \tau_s \left(\frac{dK_{ijk}}{d\omega_{jk}}\right)_{\omega_{jk} \rightarrow 0} = \omega \tau_s \beta \quad \dots\dots\dots (6)$$

where β is the slope of $K_{ijk}-\omega_{jk}$ curve at $\omega_{jk} \rightarrow 0$. When $\omega_{jk} \rightarrow 0$ ρ_{ijk} the density of the solution becomes ρ_i the density of the solvent and local field F_{ijk} of the solution becomes $F_i = [(\epsilon_i + 2)/3]^2$, local field of the solvent. Under this condition eq. (3) on the differentiation with respect to ω_{jk} takes the form :

$$\left(\frac{dK'_{ijk}}{d\omega_{jk}}\right)_{\omega_{jk} \rightarrow 0} = \frac{\mu_{jk}^2 N \rho_i F_i}{3M_{jk} kT} \left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2}\right) \quad \dots\dots\dots (7)$$

From eqs. (6) and (7) the dipole moment of associated polar solutes μ_{jk} is

$$\mu_{jk} = \left(\frac{3M_{jk} kT}{N \rho_i F_i} \frac{\beta}{\omega b}\right)^{1/2} \quad \dots\dots\dots (8)$$

where $b = \frac{1}{(1 + \omega^2 \tau_s^2)}$ (9)

Now b could, however, be estimated from eq. (9) in terms of the available relaxation time τ_s to obtain the dipole moment of associated solutes from eq. (8) in a suitable solvent.

3. RESULTS AND DISCUSSION

The estimated uhf conductivity of DMF + TMU and DMF + DMA in benzene respectively at 15°C are already presented by the fitted polynomial equations in terms of the weight fractions ω_{jk} of the respective binary solutes for different mole fractions of DMF in Section 1. The K_{ijk} 's of DMF + TMU mixtures for different mole fractions of DMF are shown graphically in Figure 1, with respect

to ω_{jk} of the solutes. Similarly those of 1 : 1 mixtures of DMF in TMU and DMF in DMA with benzene as solvent in terms of ω_{jk} at different experimental temperatures in the range of 15°C to 30°C respectively are also shown graphically in Figures 2 and 3. The weight fractions ω_{jk} of the binary solutes as changes in the mixtures, the curves of K_{ijk} against ω_{jk} have different intercepts and slopes. This sort of behaviour of $K_{ijk} - \omega_{jk}$ curves do not occur for different x_j and for different experimental temperatures if we measure the conductivities in comparatively higher concentration region (Acharyya *et al* 1982). The K_{ijk} 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 $(\rho_{ijk} F_{ijk}/T)$ in eq. (3) assumes a constant value 0.006 at $\omega_{jk} \rightarrow 0$ for benzene as solvent. At $\omega_{jk} \rightarrow 0$, the intercepts of $K_{ijk} - \omega_{jk}$ curves at different temperatures are incidentally different and decrease with increase of temperature as observed in Figures 2 and 3, due to solvation effect (Datta *et al* 1981).

When the mole fraction x_j of DMF in the two mixtures are in the limit of $x_j=0.0$ and $x_j=1.0$ we get what are known as the concentration variation of hf conductivities K_{ik} and K_{ij} of TMU or DMA and DMF respectively in benzene against weight fractions ω_k and ω_j of the solutes (Figure 1) at 15°C. The estimated slopes β as obtained from fitted equations of the K_{ijk} against ω_{jk} are very important to yield the dipole moments. When $x_j = 0.0$ and 1.0 we get monomer dipole moments μ_k for TMU or DMA and μ_j for DMF respectively. The slope β of $K_{ijk} - \omega_{jk}$ curves are placed in Table 1. The dipole moments thus obtained are considered as monomer because the concentration of solutes in the solution is very low and lies within the range of about 0.0023 to 0.0110 weight fraction. The values of μ_k for TMU and μ_j for DMF were thus found out to be 1.89D and 3.76D respectively. The values of μ_{jk} the dipole moments of the associated solutes (solute-solute molecular association) at 15°C, presented in Table 1, can, however, be fitted by a polynomial equation of μ_{jk} as a function of x_j of DMF :

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

The graph of μ_{jk} against x_j satisfying the above equation is shown in Figure 4, with the experimentally estimated values of μ_k , μ_{jk} and μ_j respectively from eq. (8) with the knowledge of the reported τ_s (Sharma and Sharma 1985). The fitted curve, however, excludes two values of the dipole moments: one $\mu_k = 1.89\text{D}$ for TMU alone and the other $\mu_{jk} = 2.39\text{D}$ for dimer at $x_j = 0$ and $x_j = 0.5$ respectively. As x_j of DMF changes μ_{jk} gradually increases in a regular manner and then suddenly drops to a very low value at $x_j = 0.5$ (Figure 4). After $x_j > 0.5$, μ_{jk} slowly decreases thus resembling the convex nature to terminate to $\mu_j = 3.76\text{D}$ of the solute-solvent associated monomer of DMF at $x_j = 1.0$. The sudden drop in the value of μ_{jk} from its regular behaviour with x_j is probably due to the formation of dimer in the liquid mixture having mole fraction nearly 0.5 of DMF. In the case of DMF and DMA mixture in benzene the monomer dipole moments for DMA and DMF are $\mu_k = 4.33\text{D}$ and $\mu_j = 4.02\text{D}$ respectively from eq. (8) in terms of reported τ_s (Sharma and Sharma 1984). From Figure 4, as x_j of DMF is $0.0 < x_j < 1.0$, we get μ_{jk} 's at 15°C using the slopes of $K_{ijk} - \omega_{jk}$ linear equations presented in Section 1. The curve in Figure 4 drawn with all μ_k , μ_{jk} 's and μ_j at 15°C as a function of x_j shows two peaks: one at $x_j = 0.1$ and the other at $x_j = 0.7$ and in the range of $0.1 \leq x_j \leq 0.7$ it is simply a concave curve suggesting the formation of dimer in this region. But the dipole moment μ_{jk} is to be minimum at $x_j = 0.3$ (Figure 4) and hence the dimerisation of this mixture may be yet to be maximum near $x_j = 0.3$ unlike the observation made by Sharma and Sharma (1984). The data of μ_j , μ_k and μ_{jk} 's of DMF, TMU or DMA and their respective binary solutes at 15°C as well as μ_{jk} 's of 1:1 mixtures of DMF + TMU and DMF + DMA in benzene at different experimental temperatures which are listed in the seventh column of Table 1, are plotted in Figures 4 and 5 as the functions of x_j of DMF and temperature t in $^\circ\text{C}$ respectively.

The nature of behaviour of μ_{jk} against the temperature $t^\circ\text{C}$ are plotted in Figure 5 with the experimentally measured values upon them. The curve of μ_{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°C and 45.69°C respectively.

As shown in Figure 5, the μ_{jk} 's of the expected associated solutes for 1 : 1 mixture of DMF and DMA in benzene increases slowly from 2.97D at 0°C to the maximum 4.49D at 22.5°C and then slowly decreases to 3.49D at 40°C. All these data show that the dipole moments of the 1 : 1 binary polar solute mixture in benzene do change with temperature in the *hf* region of alternating electric field.

Finally, to interpret the experimental monomer dipole moments of the solutes we calculated the theoretical μ_j and μ_k as sketched in Figure 6, for DMF, TMU and DMA in terms of bond moments, bond axes and bond angles respectively. In DMF, the bond moments of C = O and CH₃—N act along a common axis, being sketched in Figure 6(i), with a resultant dipole moment of 3.74D while those of CH₃—N, H—C and N—C make the resultant moment 0.79D acting in other direction. They, thus give rise to the monomer dipole moment 3.82D of pure DMF in benzene. But the Table 1 shows 3.76D and 4.02D respectively as the experimental dipole moments of DMF in the two mixtures under consideration probably due to the effect of trace presence of TMU and DMA in benzene at $\omega_{jk} \rightarrow 0$. Both the arms in TMU contain (CH₃)=N about a carbon atom in C=O form an angle 113°.2 to give the resultant moment of nearly 1.2D. This in its turn reduces the bond moment of 3.1D of C = O to give rise to 1.9D as the monomer dipole moment of TMU [Figure 6 (ii)] in close agreement with the experimental $\mu = 1.89D$ (Table 1). Similarly in case of DMA, the group moments of CH₃—N and C=O act along the same direction having the resultant moment 3.74D which with the resultant moment of 1.46D for G—CH₃, C—N and N—CH₃ (Figure 6 (iii)) yields 4.02D (Table 1) as the monomer dipole moment of DMA. With these preferred conformational directions for DMF and TMU and DMA as sketched in Figure 6, the calculated values of dipole moments from the vector model, assuming molecules to be planar are in close agreement with the experimental values as evident in Table 1 in which all the data are placed for comparison. The smaller values of μ_{jk} for 50 : 50 and 30 : 70 mixtures of DMF + TMU and DMF + DMA in benzene are due to dimer formation. For dimer

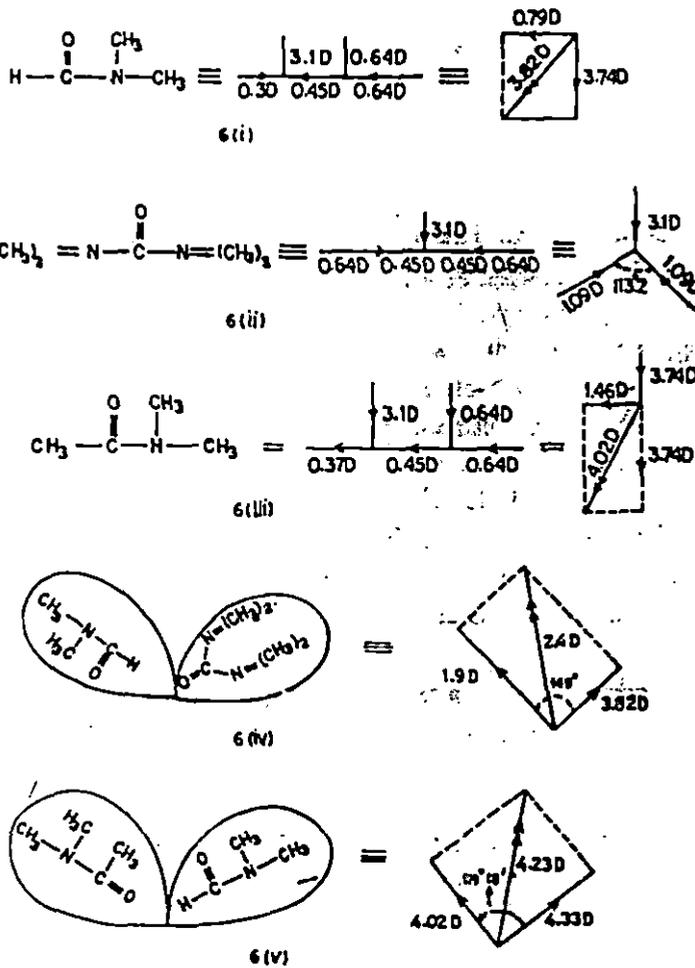


Figure 6. (i) Structural form of DMF, (ii) Structural form of TMU, (iii) Structural form of DMA, (iv) Structural form of dimer (DMF + TMU) and (v) Structural form of dimer (DMF + DMA)

formation between DMF and TMU (Figure (6 iv)) and DMF and DMA (Figure (6v) in benzene, the two monomers attach each other with their most electropositive (-H) and electronegative (-O-) elements forming angles 149° and $119^\circ.18$ at mole fractions $x_j = 0.5$ and $x_j = 0.3$ for DMF in the two mixtures respectively as calculated from the experimental μ_j , μ_k and μ_{jk} values. The values of μ_{jk} 's of dimers change strongly with temperature probably due to this preferred conformational directional angle which changes with temperature. The change is more pronounced in the case of maximum dimerisation (Figure 5). This is the reason that μ_{jk} of 50% of DMF in the mixture exhibit zero value at 8.31°C and 45.69°C whereas in the 2nd mixture the μ_{jk} changes very slowly as the maximum dimerisation occurs for 30% of DMF in this mixture.

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