

APPENDIX

LIST OF PUBLISHED AND COMMUNICATED PAPERS

1. Dielectric Relaxation Parameters From Ultra-High Frequency Electric Conductivity of Polar-Nonpolar Liquid Mixtures - U.Saha and S.Acharyya, Ind. J.Pure & Appl. Physics

(Accepted)
2. Dipole Moments of Associated Binary Solutes in Benzene From Ultra - High Frequency conductivities of Solutions - A.K.Chatterjee, U.Saha, N.Nandi, R.C.Basak and S.Acharyya, Indian J.Physics 66B (1992) 291-302.
3. Dipole Moments of Binary Polar Solutes From Ultra - High Frequency conductivities of Solutions - in Non-Polar Solvents - U.Saha, and S.Acharyya, Ind. J.Pure & Appl. Phys 31 (1993) 181-186.
4. Theoretical Relaxation Time of Associated Binary Polar Mixture in Non-Polar Solvent - U. Saha and S. Acharyya, J. Phys D: Appl Phys (G.B)(communicated)
5. Double Relaxation Times of Nonspherical Polar Liquids in Non-Polar Solvents - A New Approach Based on Single Frequency Measurement - U.Saha, S.K.Sit, R.C. Basak, and S.Acharyya, J.Phys D: Appl Phys (G.B.) (in Press).

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**Dipole moments of associated binary solutes
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Abstract : The dipole moments of the binary polar mixtures in benzene of NN-dimethyl-formamide (DMF) with NN-tetramethyl-urea (TMU) and NN-dimethyl-acetamide (DMA) respectively for different mole fractions of DMF as well as those of their (1 : 1) mixtures in benzene in the temperature range of 15°C to 30°C are measured from the concentration variation of ultra high frequency 9.885 GHz electric conductivity K_{ijk} of the solutions. The method used here is an extension of our previous work for a polar-nonpolar liquid mixture. The mole fraction and temperature variations of dipole moments thus obtained when compared with the theoretical values from the bond moments and bond axes indicate the very existence of solute-solvent i.e. monomer and solute-solute i.e. dimer formations which occur in the liquid mixtures when subjected to the ultra high frequency alternating electric fields.

Keywords : Uhf conductivity, dipole moment, monomer and dimer.

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1. Introduction

Now a days, the estimation of dipole moment μ_j as well as the relaxation time τ_s 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 a 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-tetramethyl 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 their 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_{ijks} '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 *h-f* 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 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.

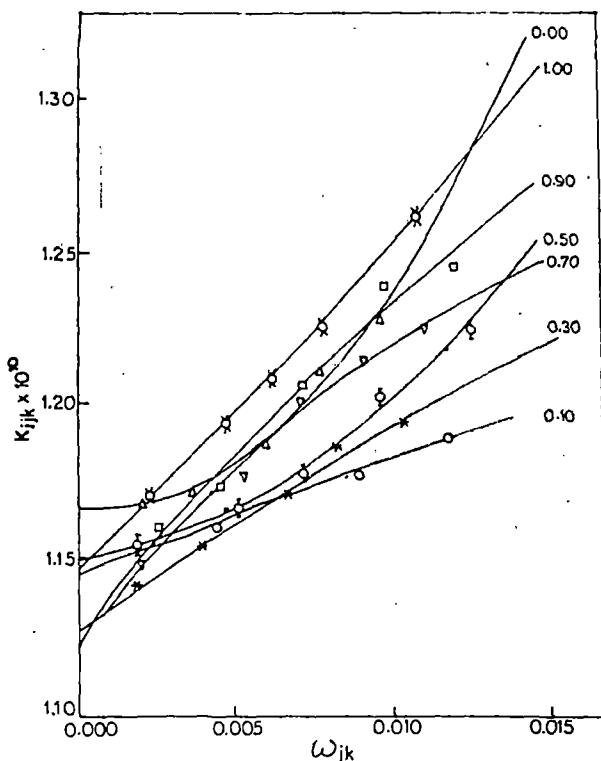


Figure 1. Concentration variation of K_{ijk} of DMF + TMU in benzene at different mole fractions of DMF at 15°C.

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 $K_{ijk} \times 10^{-10} = 1.1455 + 8.9409\omega_{jk}$ at 15°C,

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

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

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

The $h\text{-}f$ 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

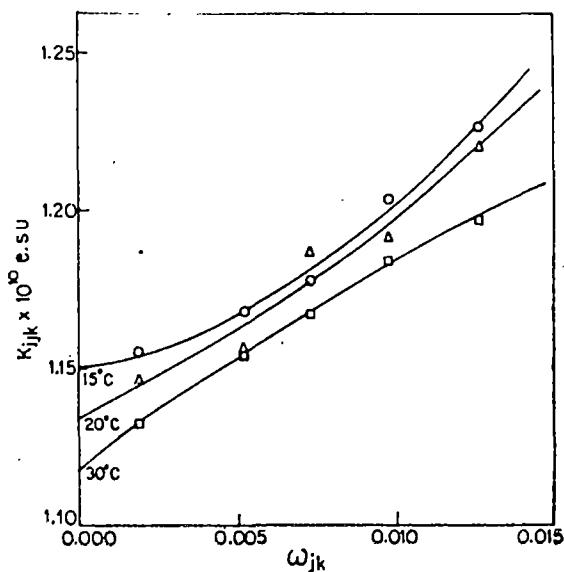


Figure 2. Concentration variation of K_{ijk} of DMF + TMU (50% each) in benzene at 15, 20 and 30°C.

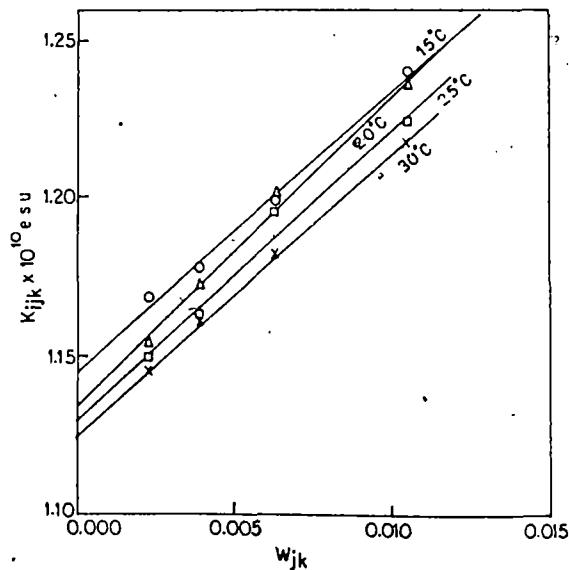


Figure 3. Concentration variation of K_{ijk} of DMF + DMA (50% each) in benzene at 15, 20, 25 and 30°C.

difficult to plot the estimated *h-f* 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 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 °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 of the individual solutes. The temperature variation of μ_{jk} of 1 : 1 mixture of DMF and DMA in Benzene was also worked out to be :

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

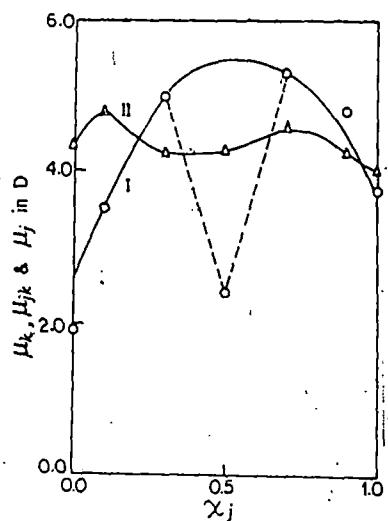


Figure 4. Variation of experimentally observed dipole moments μ_k , μ_{jk} and μ_j with mole fraction of DMF in DMF + TMU and DMF + DMA mixtures at 15°C (-O-O- for DMF + TMU and -Δ-Δ- for DMF + DMA).

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

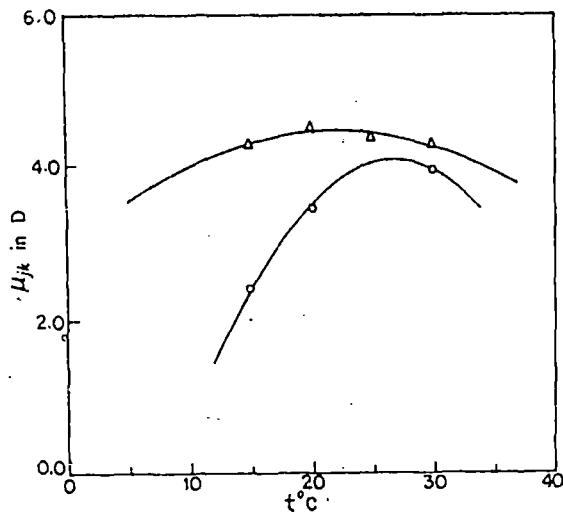


Figure 5. Variation of experimentally observed dipole moments with temperatures in °C for DMF + TMU and DMF + DMA in 1 : 1 mixtures (-O-O- for DMF and TMU and -Δ-Δ- for DMF + DMA).

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

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

where $\omega = 2\pi f$; $f = 9.885$ GHz being the frequency of the applied h-f 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

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

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	$b = 1/(1 + \omega^2 \tau_s^2)$	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 T MU 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 T MU 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	

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

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

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.

$$\text{But for hf region } \epsilon'_{ijk} = \epsilon''_{ijk} + \epsilon''_{ijk} / \omega \tau_s \quad (4)$$

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

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

where $K''_{ijk} = \omega\epsilon''_{ijk}/4\pi$ is a constant conductivity and τ_s is the relaxation time of the associated solutes. Since K_{ijk} is a function of ω_{jk} from eq. (5) we have

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

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 :

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

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

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

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

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 :

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 fractions 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 :

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

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 $\mu_k = 1.89$ D for TMU alone and the other $\mu_{jk} = 2.39$ 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 $\mu_j = 3.76$ 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 $\mu_k = 4.33$ D and $\mu_j = 4.02$ 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 °C respectively.

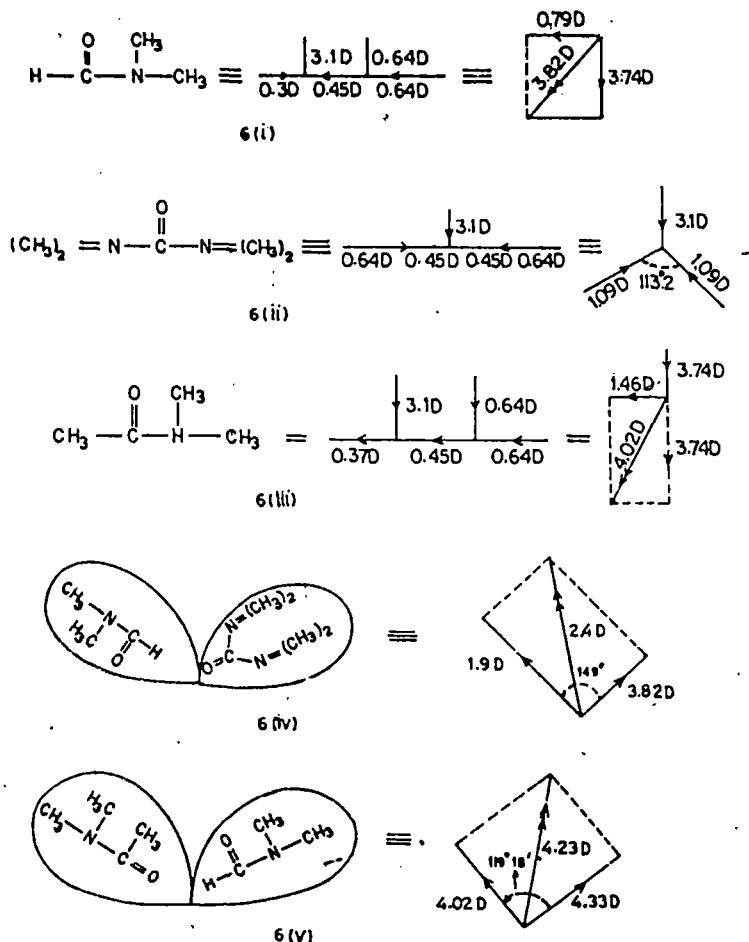


Figure 6. (i) Structural form of DMF, (ii) Structural form of TMU, (iii) Structural form of DMA, (iv) Structural form of dimer (DMF + TMU) and (v) Structural form of dimer (DMF + DMA)

The nature of behaviour of μ_{jk} against the temperature t °C are plotted in Figure with the experimentally measured values upon them. The curve of μ_{jk} for the 1st mixtur

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 $\mu = 1.89$ D (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 C—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 planer 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 formation between DMF and TMU (Figure (6 iv)) and DMF and DMA (Figure (6 v)) in benzene, the two monomers attach each other with their most electropositive (—H) and electronegative (—O—) elements forming angles 149° and 119°.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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Dipole moments of binary polar solutes from ultra high frequency conductivities of solutions in non-polar solvent

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The dipole moments μ_j and μ_k of the respective monomers and μ_{jk} of dimer of binary polar solutes like N,N-dimethyl formamide (DMF) with (I) methyl alcohol (MeOH), (II) acetonitrile (AN) and (III) acetone (AC) at different mole fractions X_j of DMF are computed from the concentration variation of ultra high frequency conductivities of solutions in benzene at 15°C under 3.035 cm wavelength electric field only to locate the maximum solute-solute molecular associations at $X_j = 0.5$, 0.9 and 0.5 in DMF+ MeOH, DMF+ AN and DMF+ AC respectively. The μ_{jk} of 1 : 1 binary polar mixtures at 15, 20, 25 and 30°C are also estimated only to support the above facts by showing that the dimer moments μ_{jk} 's decrease with temperature for all the mixtures except for DMF+ AN where μ_{jk} remains almost constant.

1 Introduction

Now a days the study of dielectric relaxation mechanism of polar liquids dissolved in non-polar solvents from the concentration variation of the ultra high frequency (uhf) conductivity¹⁻⁴ of solutions is widely used in comparison to the pure liquids because of the absence of dipole-dipole interactions and low viscosity coefficients. The concentration variation of uhf conductivity in a microwave or radio-frequency electric field for the polar-non-polar liquid mixtures is very much sensitive to yield the molecular parameters such as relaxation times τ_s , dipole moment μ_j , thermodynamic relaxation parameters ΔH_r , ΔS_r and ΔF_r etc. They also provide one with the information regarding the solute-solvent and solute-solute type of molecular associations^{2,4}. But the study of dielectric relaxation behaviour of binary polar liquid mixtures in a non-polar solvent is of great interest although the data of such mixtures are very scanty. Schallamach⁵, however, studied the temperature dependence of a few mixtures of relatively complex non-rigid molecules under a constant radio-frequency electric field and revealed that the mixtures of both associated or non-associated polar molecules correspond to a single relaxation process. The above conclusion was also arrived at by Madan⁶ and, Vyas and Vashisth⁷ on binary polar mixtures of alcohols, amides and ketones. In contrast, the results of other workers^{8,9} suggest the possibility of two dispersion regions to describe the dielectric behaviour of binary polar mix-

tures. But still a few systems have been examined so far and even less information is available for polar mixtures in non-polar solvents. The binary polar mixtures of N,N-dimethyl formamide (DMF) with (I) methyl alcohol (MeOH) or (II) acetonitrile (AN) or (III) acetone (AC) respectively in benzene from our recently developed method¹⁰ are studied. The present investigation is, however, concerned with the estimation of dipole moment of these polar mixtures from the slopes of uhf conductivity at infinite dilution. Sharma *et al.*¹¹⁻¹³ showed the probable solute-solute type of molecular association in the polar mixtures in terms of relaxation times τ_s . We further studied these systems for understanding the molecular association from our theoretical formulation in terms of dipole moment of the systems and the molecular behaviour in the binary polar mixtures because of the possibility of having optimum binary system corresponding to desired physical properties. Moreover in addition to other liquids under the present investigation formamide is a very important non-aqueous dielectric liquid for its wide biological applications. Hence it attracted the attention of a large number of workers^{7,14-16}. Thus, the extensive study of the ternary mixtures of suitable dielectric liquids should be needed to throw much light on the solute-solute type of molecular associations which is quite uncommon feature of liquids. The solute-solute molecular formations, are, however, interpreted as a result of weak hydrogen bonding of the dipole-dipole interactions between the different solutes.

2 Theoretical Formulations

The uhf conductivity due to Murphy and Morgan¹⁷ of binary solutes in a non-polar solvent is given by

$$K_{ijk}^* = K'_{ijk} + jK''_{ijk} \quad \dots (1)$$

where $K'_{ijk} = \omega \epsilon'_{ijk} / 4\pi$ and $K''_{ijk} = \omega \epsilon''_{ijk} / 4\pi$. The magnitude of total uhf conductivity is usually computed from the relation

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

The real part ϵ'_{ijk} of the complex dielectric constant ϵ_{ijk}^* of the solution in the microwave region although very small and equals the 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 total uhf conductivity becomes

$$K_{ijk} = \frac{\omega}{4\pi} \epsilon'_{ijk} \quad \dots (3)$$

The real part of uhf conductivity of solution having weight fraction ω_{jk} of binary polar solute in a non-polar solvent at T K is given by

$$K'_{ijk} = \frac{\mu_{jk}^2 N \rho_{ijk} F_{ijk}}{3 M_{jk} kT} \left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} \right) \omega_{jk} \quad \dots (4)$$

where τ_s and μ_{jk} are the relaxation time and the dipole moment of binary polar solute respectively having molecular weight $M_{jk} = (X_j M_j + X_k M_k)$, X_j being the mole fraction of polar liquid j in polar mixture of j and k and $X_k = 1 - X_j$.

It can be shown in the hf region that $\epsilon'_{ijk} = \epsilon_\infty + \epsilon''_{ijk} / \omega \tau_s$ and hence with the help of Eq. (3) we get

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

where K_∞ = the constant conductivity = $\omega \epsilon_\infty / 4\pi$.

Since K_{ijk} is a function of ω_{jk} we have

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

where β is the slope of K_{ijk} versus ω_{jk} curve at $\omega_{jk} \rightarrow 0$. At $\omega_{jk} \rightarrow 0$, ρ_{ijk} and F_{ijk} the density and local field of the solution become ρ_i and F_i of the solvent respectively, where $F_i = [(\epsilon_i + 2)/3]^2$. Differentiating Eq. (4) w.r. to ω_{jk} and using Eq. (6) at $\omega_{jk} \rightarrow 0$, we ultimately get

$$\mu_{jk} = \left(\frac{3 M_{jk} kT}{N \rho_i F_i} \frac{\beta}{\omega b} \right)^{1/2} \quad \dots (7)$$

where $b = 1/(1 + \omega^2 \tau_s^2)$ is a dimensionless parameter. Eq. (7) can be used to measure the dipole moment of binary polar solute. When $k=0$ or $j=0$ the uhf conductivity becomes K_{ij} or K_{ik} to yield the dipole moment μ_j or μ_k of the j th or the k th polar solute respectively from Eq. (7) with the reported τ_s .

3 Result and Discussion

The K_{ijk} of polar mixtures (I) DMF+MeOH, (II) DMF+AN and (III) DMF+AC in benzene at mole fractions $X_j = 1.0, 0.9, 0.7, 0.3, 0.1$ and 0.0 of DMF in the polar mixtures at 15°C and those of 1:1 polar mixtures in benzene at 15, 20, 25 and 30°C were estimated using Murphy and Morgan¹⁷ relation (Eq. 2) from the available measured data of ϵ_{ijk} and ϵ'_{ijk} of Sharma *et al.*¹¹⁻¹³ under 3.035 cm wavelength electric field. The hf conductivity in the range $0 < X_j < 1$ are K_{ijk} of solution having binary polar mixture, and for $X_j = 1.0$ and 0.0 we get K_{ij} and K_{ik} of solutions containing single polar solute. The variation of K_{ijk} , K_{ij} and K_{ik} with the respective weight fractions was found to be linear. The intercepts α and slopes β of the linear variations of K_{ij} , K_{ik} and K_{ijk} are presented in Table 1. The K_{ijk} of 1:1 mixtures as a function of ω_{jk} are shown graphically in Fig. 1 at 15, 20, 25 and 30°C which showed that the value of K_{ijk} decreases as the temperature increases. The constancy of the factor $(\rho_{ijk} F_{ijk})/T$ at $\omega_{jk} \rightarrow 0$ in Eq. (4) suggests that at all the experimental temperatures K_{ijk} should meet at a common point on the K_{ijk} -axis at $\omega_{jk} = 0$. But in practice the intercepts are all different (Fig. 1) and decrease with temperature. This is perhaps due to the solvation effect¹⁸. The slopes of $K_{ij} - \omega_j$ and $K_{ik} - \omega_k$ curves, are however, used to compute dipole moments of single polar solutes from Eq. (7). The measured values, $\mu = 4.02, 1.65, 3.78$ and 2.95 D for DMF, MeOH, AN and AC respectively (Table 1) are very close to the literature values^{16,19}. The μ_j and μ_k 's may be considered as monomer dipole moments due to solute-solvent molecular associations. The solute-solvent molecular associations can arise due to the interactions of π -electron cloud of the benzene ring with the fractional positive charges on the nitrogen atom ($-\text{C}-\text{N}^{\delta+}-$), the hydrogen atom ($-\text{O}-\text{H}^{\delta+}$) the nitrogen atom ($-\text{C}\equiv\text{N}^{\delta+}$) and the carbon atom ($>\text{C}^{\delta+}=\text{O}$) of DMF, MeOH, AN and AC respectively.

The slopes β of $K_{ijk} - \omega_{jk}$ curves at $\omega_{jk} \rightarrow 0$ in the mole fraction range $0 < X_j < 1$ give us μ_{jk} , the dipole moment of binary polar solute (Table 1). For a mixture of two polar molecules j and k in

Table 1—Reports the values of experimental intercepts (α) and slopes (β) of conductivity versus concentration linear plots, reported τ_s , computed b , computed experimental dipole moments (μ_j , μ_k and μ_{jk} 's) with theoretical μ_j and μ_k

System	t in °C	Mol. fraction X_j of DMF	$\alpha \times 10^{-10}$ in esu	$\beta \times 10^{-10}$ in esu	Mol. Wt $M_{jk} = (X_j M_j + X_k M_k)$	τ_s (Rept) in ps	b 1 $= \frac{1}{1 + \omega^2 \tau_s^2}$	μ_j , μ_k & μ_{jk} (Comt) in D	Average dipole moment μ_{jk} (av) in D $(= X_j \mu_j + X_k \mu_k)$	μ_j & μ_k (Theo) in D
DMF + MeOH in benzene	15	1.0	1.1447	10.5666	73.0944	7.01	0.8406	4.02	4.02	3.82
		0.9	1.1310	11.3857	68.9892	7.87	0.8072	4.14	3.78	
		0.7	1.1344	10.0244	60.7787	9.83	0.7285	3.84	3.31	
	20	0.3	1.1354	7.0783	44.3577	11.70	0.6544	2.91	2.36	
		0.1	1.1374	5.7261	36.1472	8.96	0.7643	2.18	1.89	
		0.0	1.1388	4.2240	32.0420	6.00	0.8781	1.65	1.65	1.64
DMF + AN in benzene	15	0.5	1.1337	9.0717		12.87	0.6101	3.71	2.84	
		0.5	1.1324	8.1091		11.26	0.6716	3.39		
		0.5	1.1251	8.2537	52.5682	9.73	0.7325	3.32		
	20	0.5	1.1218	8.4359		7.35	0.8275	3.20		
		1.0	1.1447	10.5666	73.0944	7.01	0.8406	4.02	4.02	3.82
		0.9	1.1302	11.3961	69.8902	10.78	0.6905	4.51	4.00	
benzene	25	0.7	1.1333	12.2275	63.4818	8.94	0.7643	4.23	3.95	
		0.3	1.1372	13.7086	50.6650	8.23	0.7928	3.93	3.85	
		0.1	1.1430	13.9588	44.2566	7.78	0.8107	3.66	3.80	
	30	0.0	1.1231	17.2720	41.0524	6.04	0.8766	3.78	3.78	3.67
		0.5	1.1286	14.0757		8.74	0.7832	4.25	3.90	
		0.5	1.1179	14.1762		7.60	0.8178	4.23		
benzene	15	0.5	1.1174	13.2377	57.0734	7.23	0.8322	4.11		
		0.5	1.1169	12.4521		6.94	0.8433	4.01		
		1.0	1.1447	10.5666	73.0944	7.01	0.8406	4.02	4.02	3.82
	20	0.9	1.1419	10.6848	71.5929	7.94	0.8044	4.09	3.91	
		0.7	1.1409	9.9640	68.5900	10.73	0.6925	4.17	3.70	
		0.3	1.1559	7.0894	62.5842	8.76	0.7716	3.18	3.27	
benzene	25	0.1	1.1473	7.3437	59.5813	5.17	0.9065	2.92	3.06	
		0.0	1.1372	8.1709	58.0798	3.35	0.9585	2.95	2.95	2.75
		0.5	1.1383	10.8577		13.34	0.5930	4.60	3.49	
	30	0.5	1.1370	10.0415		11.85	0.6486	4.29		
		0.5	1.1312	9.3474	65.5871	9.12	0.7571	3.88		
		0.5	1.1209	9.8827		8.10	0.7860	3.97		

Refs 11-13

dilute solution in a non-polar solvent there may appear two dispersion regions characterised by relaxation times τ_j and τ_k . Davidson²⁰ has shown that, even in the case of two independent polarisation, the resolution of different dispersion regions is difficult unless the relaxation time of one component should be at least 5 times that of the

other. Therefore, the binary polar mixtures with τ_s 's which are not considerably different from one another, as in the present investigation, exhibit a broad dispersion-absorption behaviour in which separate loss peaks do not occur^{6,21}. The relaxation of the mixture is thus the resultant of the relaxations of the individual molecule which is of

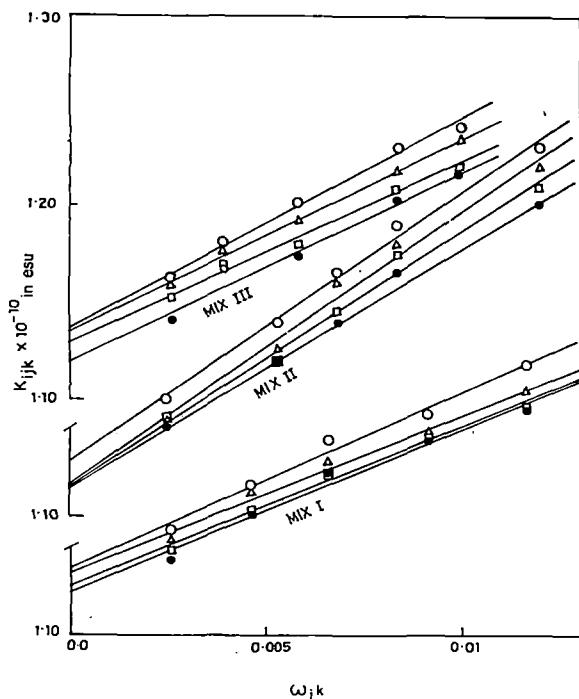


Fig. 1—uhf Conductivity K_{ijk} of (1:1) mixtures of (I) DMF+MeOH, (II) DMF+AN and (III) DMF+AC in benzene against weight fraction ω_{jk} at different temperatures ($-O-$ 15°C, $-\Delta-$ 20°C, $-\square-$ 25°C and $-\bullet-$ 30°C)

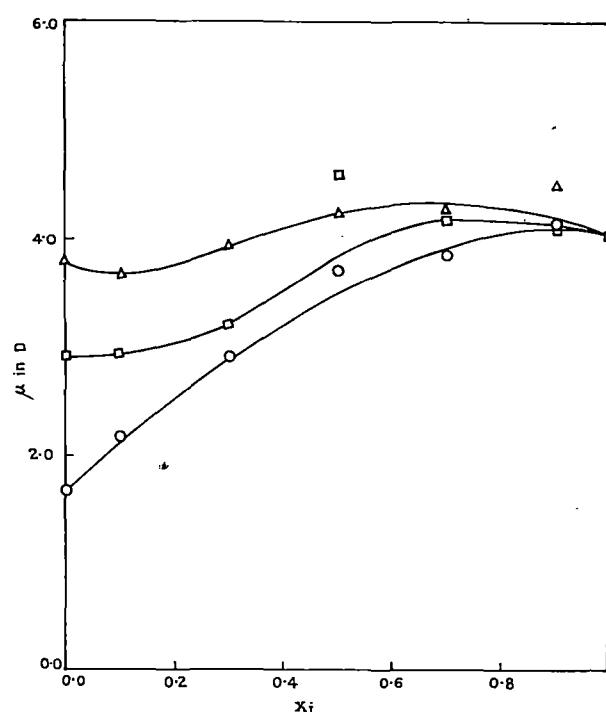


Fig. 2—Variation of dipole moment μ against the mole fraction X_j of DMF in the binary polar mixtures of DMF with (I) MeOH ($-O-$), (II) AN ($-\Delta-$) and (III) AC ($-\square-$) in benzene at 15°C

course, strongly influenced by the variety of the molecular environments encountered in rotation as well as by the other factors such as size, shape, solute-solvent, solute-solute interactions etc. When a polar mixture is studied in a non-polar solvent, its ϵ_{ijk}^* is represented by the weighted sum of complex dielectric constants of individual components²². Obviously if there is no solute-solute association in the mixture, the τ_s as well as μ_{jk} , measured by our method, should vary linearly with the concentration of the components. The formation of dimer leads to τ_s considerably larger than the average value of the individual relaxation times^{23,24}. In such a case, the dielectric behaviour of polar mixture is mainly governed by the resulting molecular species.

The measured dipole moments (Table 1) of the mixtures are plotted against X_j of DMF at 15°C and shown in Fig. 2. The curves drawn through the experimental points are not the average values between two monomeric dipole moments. These sort of deviation at once indicate the existence of solute-solute molecular association in solutions. The deviations are found to be maximum at $X_j = 0.5$, 0.9 and 0.5 for DMF+MeOH, DMF+AN and DMF+AC respectively, suggesting the maximum dimerisation at those X_j for the mixtures, in agreement with the observation made

by Sharma *et al*¹¹⁻¹³. There may be also jj and kk dimers in the solutions. But the τ_s as well as μ_j and μ_k values as shown in Table 1 exhibit no self-association for DMF, MeOH, AN and AC up to $\omega_j = 0.0110$ and $\omega_k = 0.0103$, 0.0100 and 0.0103 in benzene respectively. These ω_j and ω_k are considerably higher than the concentration of j and k in solution of jk in benzene. This rules out the possibility of jj or kk dimer formation in the solutions of polar mixtures. The single relaxation times, measured by Sharma *et al*¹¹⁻¹³ of these polar mixtures investigated, are found to follow the rate process equation. McDuffie and Litovitz²⁵ have pointed out that if a single relaxation time is assumed, the degree of polarisation order in the polar mixtures should decay exponentially. Therefore, the relaxation behaviour of these mixtures in dilute solutions may be assumed to be mainly governed by the resulting relaxing units of jk dimers, as an approximation to the true behaviour of the systems. Hence it is reasonable to consider the reported τ_s and measured μ_{jk} of Table 1 as those for jk dimers.

The experimentally computed μ_j and μ_k are compared with theoretically calculated values in terms of bond moments and bond angles as sketched in Fig. 3. The moments of C—H, C—N and N—CH₃ groups of DMF act along a com-

mon axis, but the group moments $C=O$ and $N-CH_3$ act \perp to that of $C-N$ (Fig. 3a). In MeOH, $O-CH_3$ and $O-H$ make an angle 105° (Fig. 3b). In case of AN, $C-CH_3$ and $C\equiv N$ not along the same axis (Fig. 3c) while in AC one of the two $C-CH_3$ acts along $C=O$ and the other is \perp to $C=O$ (Fig. 3d). With these preferred conformations, the calculated values of μ_j and μ_k 's, from vector model, assuming molecules to be planar ones, are 3.82, 1.54, 3.67 and 2.75 D respectively for DMF, MeOH, AN and AC in close agreement with the experimental values of Table 1.

For dimer formation between DMF and MeOH the two monomers attach each other with their highly electropositive ($-H$) and highly electronegative ($-O-$) elements forming certain angle viz. 112.7° at $15^\circ C$, as calculated from experimental μ_j , μ_k and μ_{jk} values (Fig. 3e). In case of DMF+AN, the molecules attach themselves by the interaction of fractional positive charge on N-atom of DMF with π -electron cloud of triple bond of AN molecule. But for DMF+AC frac-

tional positive charge on ($-H$) of DMF interacts with fractional negative charge on ($-O-$) of AC to form dimer. The angle between two dipolar axes for mixtures II and III are found to be 114.05° and 98.98° respectively (Figs 3f and 3g).

The measured μ_{jk} for 1 : 1 mixtures are plotted against temperature in Fig. 4. The variations are, however, represented by the following equations:

$$DMF + MeOH \quad \mu_{jk}$$

$$= 5.075 - 0.122 t + 2.0 \times 10^{-3} t^2,$$

$$DMF + AN \quad \mu_{jk} = 4.148 + 0.019 t - 8.0 \times 10^{-4} t^2$$

and

$$DMF + AC \quad \mu_{jk} = 7.120 - 0.226 t + 4.0 \times 10^{-3} t^2.$$

As observed earlier^{2,26} the μ_j of a single polar solute in a non-polar solvent increases with temperature under uhf electric field. But in the present investigation the μ_{jk} of dimer decreases as the temperatures rises (Fig. 4) and shows a tendency to yield the average value at a certain temperature. The result may be interpreted as an indication of the breaking of weak solute-solute molecular associations due to thermal agitation. Therefore, we may conclude that for such binary mix-

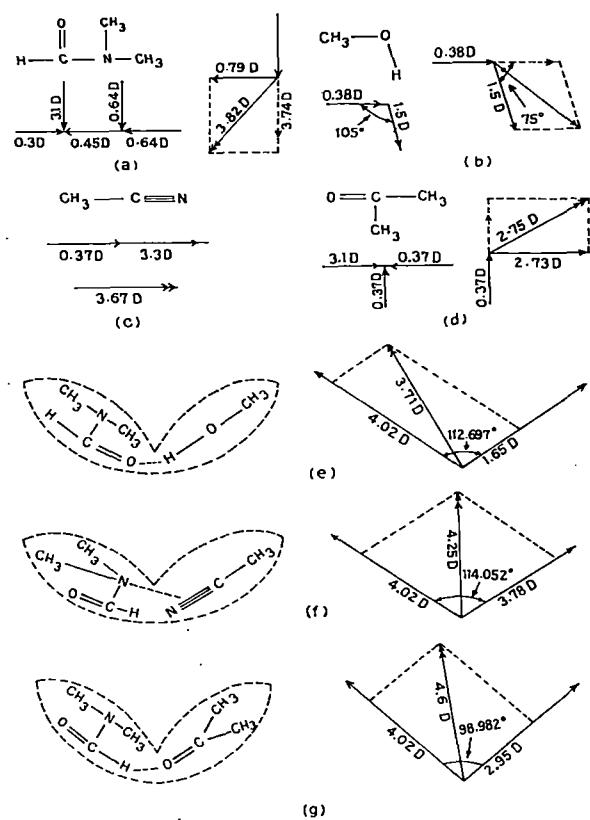


Fig. 3—Conformations of different molecules showing orientations of the bond axes, bond moments and also dipole moments [Structural form of (a) DMF, (b) MeOH, (c) AN and (d) AC; structural form of dimers (e) DMF+MeOH, (f) DMF+AN and (g) DMF+AC in $15^\circ C$]

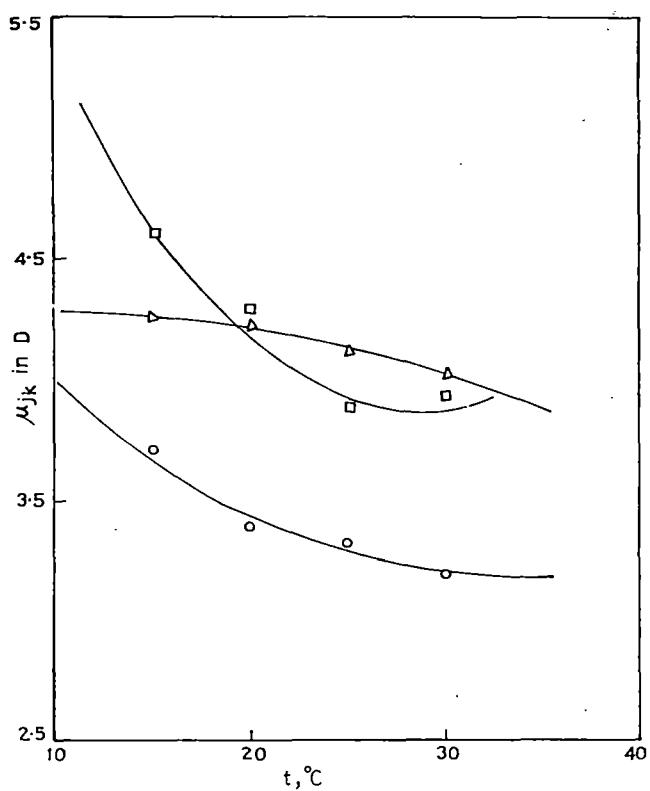


Fig. 4—Temperature variation of dipole moment μ_{jk} of (1 : 1) mixtures of DMF with (I) MeOH ($-O-$) (II) AN ($-\Delta-$) and (III) AC ($-\square-$) in benzene

tures there will be only j and k monomers in benzene at higher temperatures giving the average value of μ_{jk} .

In case of (1 : 1) DMF + AN mixture dimer dipole moment decreases very slowly so that the μ_{jk} remains almost constant in the studied temperature range (Fig. 4). In this mixture the maximum dimerisation does not occur at $X_j=0.5$ and the interaction of fractional positive charge on N-Atom of DMF with π -electron cloud of triple bond of AN results in greater bond energy compared to the interactions of other two dimers. This may be the reason that the breaking of molecular association for this (1 : 1) mixture is comparatively low causing small change in μ_{jk} with temperature unlike other two polar mixtures.

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