CHAPTER V

ULTRA HIGH FREQUENCY CONDUCTIVITY OF POLAR - NONPOLAR
LIQUID MIXTURES.

Introduction

The dipole moment of polar liquids varies
with temperature when the dielectric liquid mixture is
subjected to microwave field or rather to an alternat-
ing high frequency electric field. There are several
methods (Gopala Krishna, 1957, Sen and Ghosh, 1972
and Ghosh et al, 1980) to compute the relaxation times
as well as dipole moment of polar liquids dissolved in
nonpolar solvents under the application of microwave
and radiofrequency electric fields. But most of these
methods suffer from extrapolation difficulties at
infinite dilution i.e. $W_j \longrightarrow 0$. The microwave conduc-
tivity data for nitromethyl acetamide (NMA), have been
computed from the recent studies on dielectric absorption
in the very low concentration region by Dhull et al(1982)
at temperature $25^{\circ}C$, $35^{\circ}C$, $45^{\circ}C$ and $55^{\circ}C$ in two different
nonpolar solvents benzene and dioxane and also in the
high concentration region in benzene at $25^{\circ}C$. Nitrome-
thyl acetamide is supposed to be an important dielect-
ric solute due to its very high values of dielectric
constant and moreover its wide applications in biolo-
gical research. Hence it attracted the attention of a

large number of workers Sato et al (1976) to study its different dielectric parameters.

We too get interested to this system and an attempt has been taken to study the variation of micro-wave conductivity of NMA in very dilute solution of benzene and dioxane at various temperatures, viz. $25^{\circ}C$, $35^{\circ}C$, $45^{\circ}C$ and $55^{\circ}C$ and also at relatively high concent-ration region at $25^{\circ}C$. So it is thought that the calcu-lated data of UHF conductivity of the mixture K_{ij} can be used to show that the low concentration region of this solution the association is solute-solvent type, i.e. monomer which changes into the solute-solute association or dimer at relatively high concentrations. Moreover, the extremely low concentration conductivity data may reveal new information regarding the solvation effect. As the information regarding the various types of interactions of solutes in solution could, however, be inferred from the estimated values of the dipole moments. Hence the dipole moments μ_j's of NMA as well as p-bromonitrobenzene (P-BNB) have been calcu-lated from the concentration variation of UHF conducti-vity of the solution.

Theory:-

The HF conductivity due to Murphy and Morgan (1939) of polar-nonpolar liquid mixture is given by

$$K_{ij} = K'_{ij} + jK''_{ij}$$ where K'_{ij} is the real part

of the conductivity $= \left(\dfrac{\omega \epsilon_{ij}''}{4\pi}\right)$ and K_{ij}'' is the imaginary part $= \left(\omega \epsilon_{ij}' / 4\pi\right)$. The magnitude of total hf conductivity is usually given by

$$K_{ij} = \frac{\omega}{4\pi}\left(\epsilon_{ij}''^2 + \epsilon_{ij}'^2\right)^{1/2} \qquad \ldots 5.1$$

ϵ_{ij}' of solution in the microwave region ($\lambda = 3.004\,cm$) though very small and is equal to optical dielectric constant, but still $\epsilon_{ij}' \gg \epsilon_{ij}''$ where ϵ_{ij}'' is responsible for the absorption of electrical energy to offer resistance to polarization. Hence the real part of K_{ij} of HF conductivity of solution of weight fraction W_j of polar solute at temperature T K is

$$K_{ij}' = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3 M_j kT}\left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2}\right)W_j \qquad \ldots 5.2$$

where μ_j is the dipole moment of polar solute of molecular weight M_j , N the Avogadro's number, k is the Boltzmann constant and $F_{ij} = \left[(\epsilon_{ij} + 2)/3\right]^2$ is the local field. Hence it is evident that, for the microwave electric field, the total conductivity becomes:

$$K_{ij} = \frac{\omega}{4\pi}\epsilon_{ij}' \qquad \ldots 5.3$$

But, for HF region, it can be shown that

$$\epsilon'_{ij} = \epsilon_{ij\infty} + \epsilon''_{ij}/\omega\tau \qquad \text{... 5.4}$$

Using eqn. (5.3) and (5.4) it is shown that

$$K_{ij} = K_\infty + K'_{ij}/\omega\tau_s \qquad \text{... 5.5}$$

where K_∞ is a constant conductivity and τ_s is the relaxation time of the solute molecule in the solvent. Since K_{ij} is a function of W_j from eq. (5.5) we have :

$$\left(\frac{dK'_{ij}}{dW_j}\right)_{W_j \to 0} = \omega\tau_s\left(\frac{dK_{ij}}{dW_j}\right)_{W_j \to 0} = \omega\tau_s\beta \qquad \text{... 5.6}$$

where β is the slope of $K_{ij} - W_j$ curve at $W_j \longrightarrow 0$. When $W_j \longrightarrow 0$ the density of the solution ρ_{ij} becomes ρ_i the density of the solvent and the local field F_{ij} of the solution becomes

$$F_i = \left[(\epsilon_i + 2)/3\right]^2 ,$$

the local field of the solvent.

Under this condition eq. (5.2) on differentiation with respect to W_j and as $W_j \longrightarrow 0$ takes the

form:

$$\left(\frac{dK'_{ij}}{dW_j}\right)_{W_j \to 0} = \frac{M_j^2 N P_j F_j}{3 M_j k T}\left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2}\right) \quad \ldots 5.7$$

Taking

$$b = \beta \Big/ \left(\frac{M_j^2 N P_j F_j \omega}{3 M_j k T}\right) \quad \ldots 5.8$$

and using eqs. (5.6) and (5.7), we can have

$$b = \frac{1}{1 + \omega^2 \tau_s^2}$$

Hence

$$\tau_s = \frac{\lambda}{2\pi c}\left(\frac{1}{b} - 1\right)^{1/2} = \frac{\lambda \times 10^{-10}}{18.84}\left(\frac{1}{b} - 1\right)^{1/2} \quad \ldots 5.9$$

From eq. (5.8) the dipole moment, M_j of polar solute can be evaluated by

$$M_j^{\langle s \rangle} = \left(\frac{3 M_j k T}{N P_j F_j} \cdot \frac{\beta}{b \omega}\right)^{1/2} \quad \ldots 5.10$$

Eq. (5.9) is used to compute 'b' from the reported τ_s data thence the dipole moment $M_j^{\langle s \rangle}$ of polar solute when it is dissolved in solvent, from eq. (5.10).

Müller (1934) gave a relation between $\mu_j^{\langle s \rangle}$ and the corrected μ_j of solute by

$$\mu_j^{\langle s \rangle} = \mu_j \left[1 - c(\epsilon_i - 1)^2 \right] \qquad \text{... 5.11}$$

where c is a constant which is claimed to be 0.038 for a large number of liquids and ϵ_i is the dielectric constant of the solvent.

Results and Discussions:

The eq. (5.2) shows that the real part of K_{ij} of h.f. conductivity of solution of weight fraction W_j of polar solute at temperature T K is function of concentration. So it is observed that the microwave conductivities (K_{ij}) of NMA in e.s.u. in benzene solvent at different temperatures, is a function of concentration and which can be written as :

$$K_{ij} \times 10^{-10} = 1.1415 + 7.0699 W_j \quad \text{, at } 25^\circ C$$

$$K_{ij} \times 10^{-10} = 1.1278 + 8.1738 W_j \quad \text{at } 35^\circ C$$

$$K_{ij} \times 10^{-10} = 1.1178 + 8.4588 W_j \quad \text{at } 45^\circ C$$

and

$$K_{ij} \times 10^{-10} = 1.1062 + 9.1398 W_j \quad \text{at } 55^\circ C$$

Similarly it follows in dioxane solvent also and h.f. conductivity can be represented as:

$$K_{ij} \times 10^{-10} = 1.1107 + 8.1173 W_j \quad \text{at } 25^{\circ}C$$

$$K_{ij} \times 10^{-10} = 1.0943 + 9.5319 W_j \quad \text{at } 35^{\circ}C$$

$$K_{ij} \times 10^{-10} = 1.0922 + 9.2835 W_j \quad \text{at } 45^{\circ}C$$

and

$$K_{ij} \times 10^{-10} = 1.0859 + 9.6132 W_j \quad \text{at } 55^{\circ}c.$$

The results can be shown graphically by the help of fitted curves along with the experimental points on them. The microwave conductivities in e.s.u. are plotted against the weight fractions W_j of the solute shown in fig. (5.1) and (5.2). It is observed from the linear plot that from the region $W_j = 0.0022$ to $W_j = 0.0094$ of the solute in benzene and also from $W_j = 0.0030$ to $W_j = 0.0123$ of the solute in dioxane as the temperature of the systems increases, the UHF conductivity decreases, but maintaining a regular increase in slopes. The h.f. conductivity in the lower concentration region would vary linearly with W_j because ($\rho_{ij} F_{ij} / T$) in eqn. (5.2) assumed to be a constant value in the neighbourhood of 0.006 in
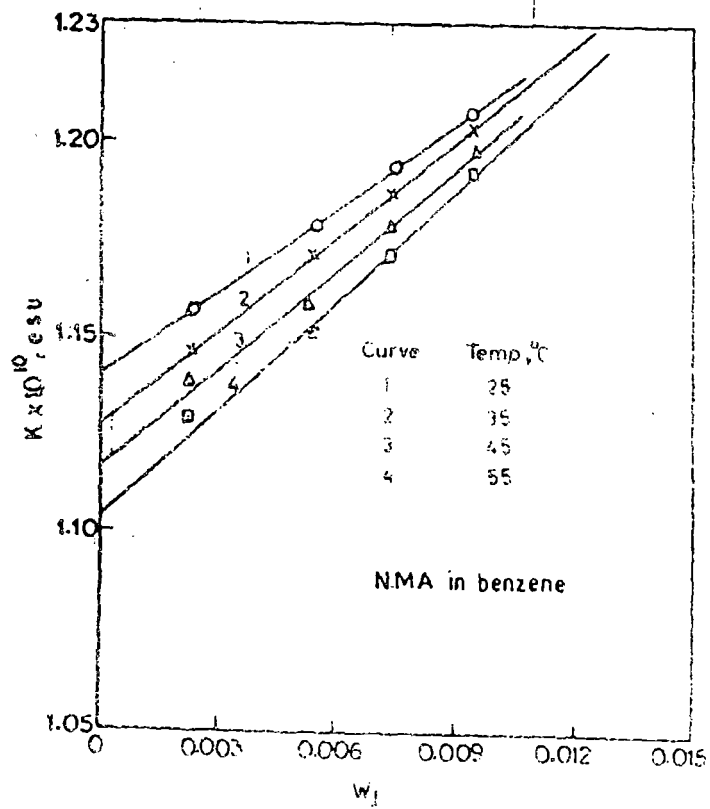
Fig. 5.8—Concentration variation of K of NMA in benzene at different temperatures
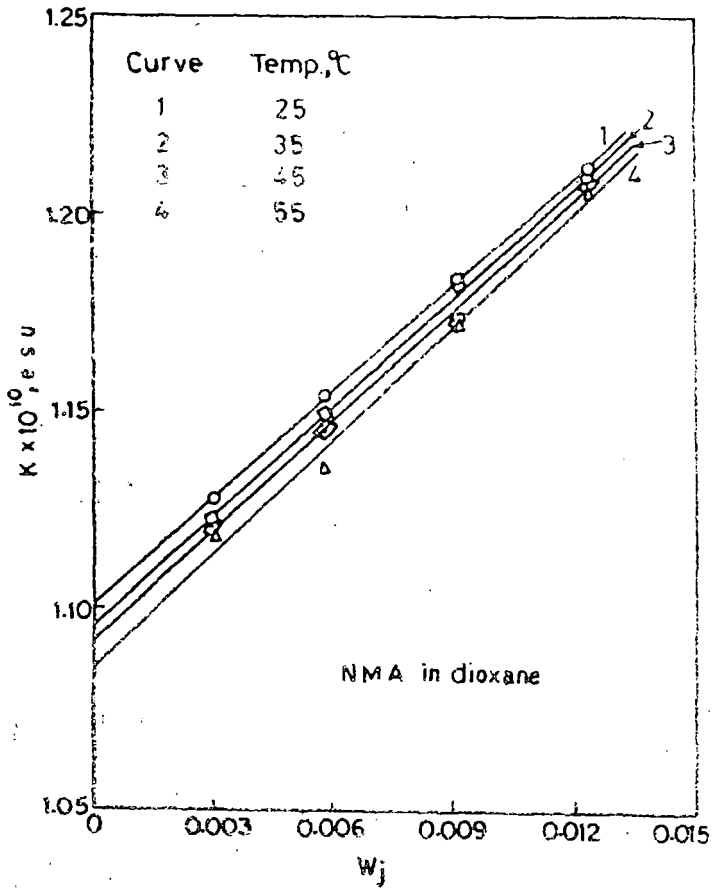
Fig. 5.2-Concentration variation of K of NMA in dioxane at different temperatures

the limit $W_j = 0$, at all the experimental temperatures. But at higher concentration the plot of K_{ij} with W_j will be mostly nonlinear. This is shown in Fig.(5.3) in which the h.f. conductivity of NMA in benzene at $25^{\circ}C$. It has been only plotted with W_j having its range from $W_j = 0.0212$ to $W_j = 0.0520$. This fact is also corroborated by the data of p-bromonitrobenzene in benzene, its nature of concentration variation also is shown in Fig. (5.4).

The nature of variation of conductivity K_{ij} with weight fraction W_j both in benzene and dioxane shown in Figs. (5.1) and (5.2) indicate that the conductivities at different temperature have tending to meet within a certain zone in the higher concentration region, which clearly indicate that higher values of K_{ij} with respect to increasing temperature are expected at higher concentration region. The curves of the high concentration K_{ij} data thus available are found to be temperature dependent quantities, i.e. the elevated temperature of the mixture gives rise to higher value of K_{ij} after a certain concentration zone. Thus for high concentration the conductivity data of mixture of polar-nonpolar liquids forced us to draw the curves of K_{ij} against W_j at all experimental temperatures to meet at a common point on the K_{ij}
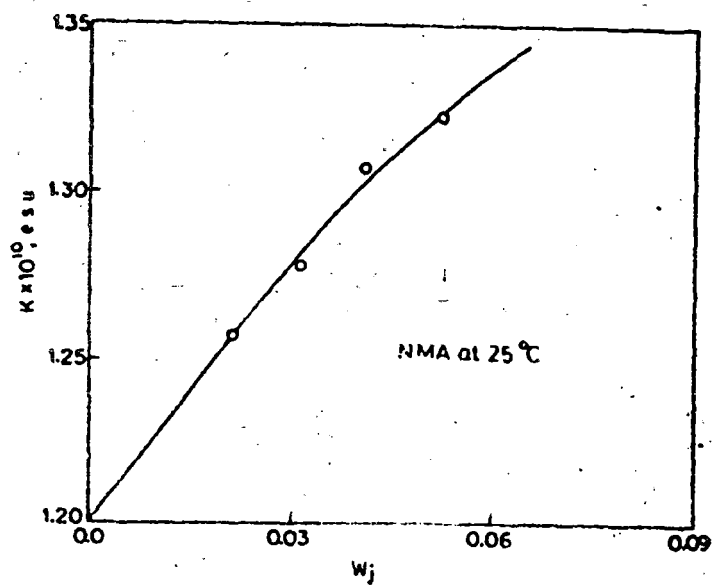
Fig.5.3-Concentration variation of K of NMA in benzene at 25°C

axis in the limit $W_j = 0$ which is apriori deter-
mined value from

$$\left(K_{ij}\right)_{W_j \to 0} = \left(\omega \, \epsilon'_{ij} \, /4\pi\right)_{W_j \to 0}$$

for most of the solute-solvent systems. This is
usually attributed to the solvation effect. When the
conductivity data of P - BNB in benzene are consi-
dered then the curves in Fig. (5.4) presenting the
conductivity data at different temperatures, measured
at relatively higher concentrations from $W_j = 0.0162$
to $W_j = 0.0416$, are found to meet at a common
point on the K_{ij} axis at $W_j = 0$.

In fact, the information regarding the low
concentration conductivities of polar compounds in
nonpolar solvents can no longer be borrowed from high
concentration conductivity data.

The data of K_{ij} (table 5.1a,b, c) for NMA in
benzene and dioxane available from the dielectric absorp-
tion studies by Dhull et al (1982) revealed a new pic-
ture regarding the concentration variation of K_{ij} data
at all stages of dilution, so far as the lower concent-
ration region is concerned. Both in benzene and dioxane
as solvents, the UHF conductivities of the present
system at $W_j \to 0$ gradually decrease as the tempera-
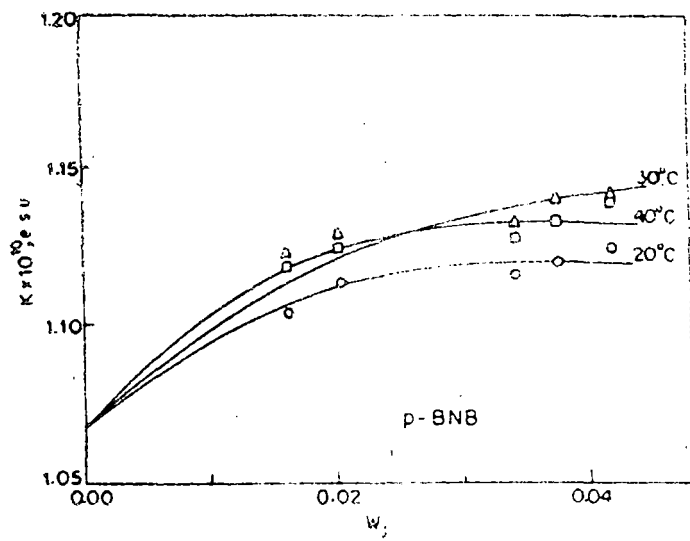ture increases from $25^\circ C$ to $55^\circ C$ shown by the normal

Fig. 5.4 – Concentration variation of K of p-BNB in benzene at different temperatures

equations relating K_{ij} and W_j as derived from the available experimental data and also as illustrated graphically in Figs. 5.1 and 5.2 respectively. But there may exist a certain link between the low and high concentration data of K_{ij} against W_j. In the limit $W_j = 0$, the graphs using lower concentration conductivity data for some suitable system in any solvent like benzene or dioxane, do not meet at a common point, but at different points on the K_{ij} axis as shown is Figs. 5.1 and 5.2. The value of the intercepts for K_{ij} at $W_j = 0$ decreases with increase in temperature. But both these features are not exhibited in case of aromatic compounds like p-BNB in benzene. In the higher concentration region, the experimental curves (Fig. 5.1 and 5.2) have a tendency to meet each other within a certain higher concentration zone, below and above which the system investigated has most probably a different physical nature.

Dipole Moment And Structural Form:

The dipole moments $\mathcal{M}_j$ of NMA and p-BNB at different temperatures were then computed from eq.(5.10) and the equation of fitted curves of the variation of $\mathcal{M}_j$ as function of temperature in $^\circ C$ for the given solute of interest are given below:

$$\mathcal{M}_j = 3.6071 + 0.0112\ t - 8.3 \times 10^{-6} t^2 \text{ for NMA in}$$
benzene

$$\mathcal{M}_j = 3.4294 + 0.0126\ t - 6.7 \times 10^{-5} t^2 \text{ for NMA}$$
in dioxane

and

$$\mathcal{M}_j = 2.114 + 0.0747\ t - 3.8 \times 10^{-4} t^2 \text{ for p-BNB in}$$
benzene

The $\mathcal{M}_j$'s of these systems were found to increase
in a regular fashion with temperature in $^\circ$C. The correc-
ted $\mathcal{M}_j$ values were obtained from eq. (5.11). However,
both the values of dipole moments computed from eq.(5.10)
and (5.11) using the reported values of τ_s are higher
than those of actual values because of the estimated error
(Bhull et al 1982) of the order of 10 percent in the
calculated values of τ_s and hence the computed values
of the dipole moments from these data would naturally be
higher. Both these values of $\mathcal{M}_j$'s are given in table
(5.2), with those of reported $\mathcal{M}_j$, τ_s etc.
The computed $\mathcal{M}_j$ values from eq. (5.10) are finally
shown graphically in fig. 5.5 against temperature. From
table (5.2) it is evident that $\mathcal{M}_j$'s are always higher
when measured from low concentration conductivity data of
NMA in benzene and dioxane, but at 25°C the high concent-
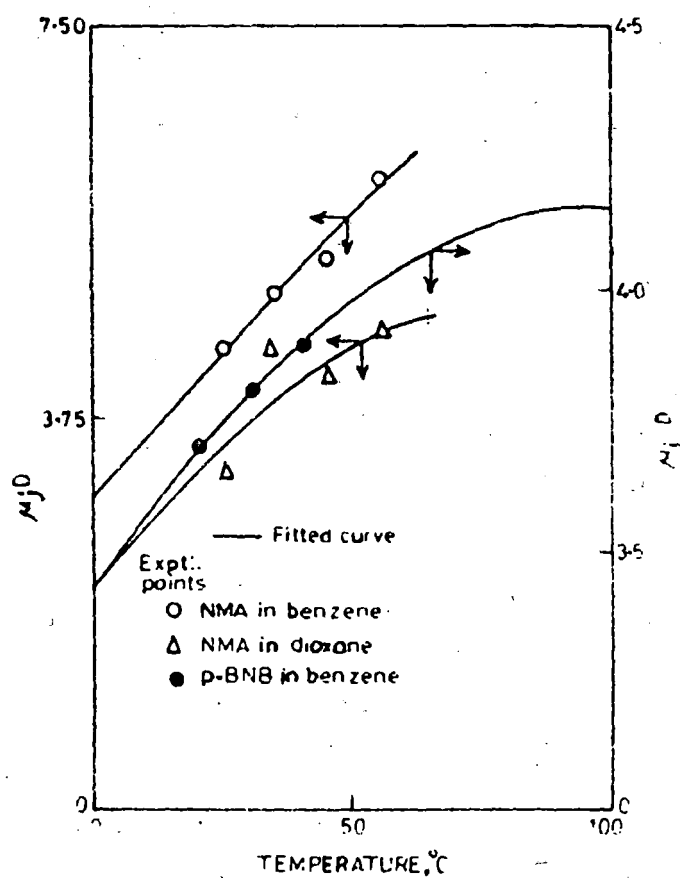ration data (Fig. 5.3) always gives us the low value of

Fig. 5.5-Variation of experimentally observed dipole moment with temperature in °C along with the fitted curves

dipole moment. However, p-BNB in benzene does not fall in this category. As observed by Dhull et al (1982), the high values of dipole moments of NMA in benzene and dioxane are due to monomers, i.e. solute-solvent association which may actually occur in the lower concentration region. This state of affairs changes above a certain concentration zone to dimer, i.e. solute-solute association. The variation in the theoretically computed μ_j values for these molecules, one aliphatic ketonic group and the other substituted benzene might be due to (i) the difference in the values of group moments and (ii) inductive effect. The dipole moments of NMA in solvents at lower concentrations (Table 5.2), shown both by the experimentally computed and theoretically obtained μ_j's due to the solute-solute association, i.e. dimer formation. For p-BNB group moments of $C-NO_2$ and $C-Br$ act at a certain angle, assuming the benzene ring as a planar one (Fig. 5.6). With this conformation in view, the theoretical value of μ_j in terms of bond moments and bond angles gives us only the monomer μ_j value in case of p-BNB as it excellently agrees with the computed μ_j's (Table 5.2). Thus p-BNB gives the dipole moments at higher concentration due to monomer formation. The group moments of $C-CH_3$, $C-N$ and $N-H$ groups act along a common axis as sketched in Fig. 5.6. But the group
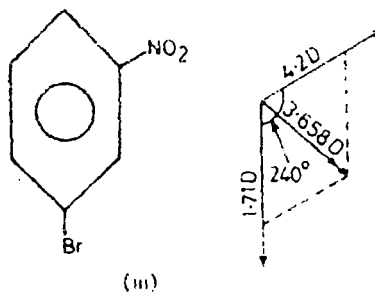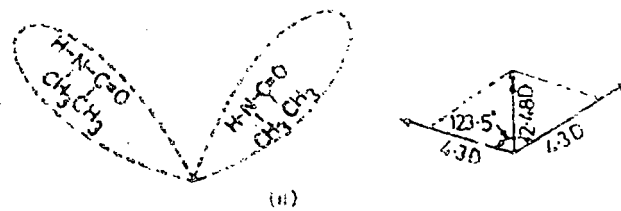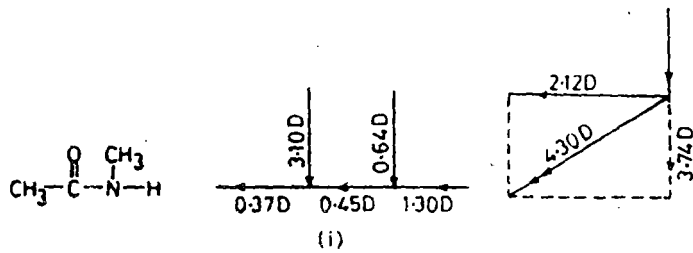
Fig. 5·6—Conformation of the different molecules showing the orientation of the bond axes, bond moments and also the dipole moments [(i) structural form of NMA; (ii), structural form of dimers; and (iii) structural form of p-BNB]

moments of $C = O$ and $N-CH_3$ act along the direction normal
to that of $C-CH_3$. With this preferred conformational
directions for NMA as depicted in Fig. 5.6, the resul-
tant $\mathcal{M}_j$ value was obtained for monomer formation.
These data for $\mathcal{M}_j$'s thus obtained also excellently
agree with the computed $\mathcal{M}_j$'s (Table 5.2). But for
the dimer formation of NMA in benzene the two monomers
attach each other with their most electropositive and
electronegative elements, i.e. $[-H]$ and $[-O-]$
form a certain angle viz. 123.5° as calculated both
from experimental and theoretical $\mathcal{M}_j$ values as
shown in Fig. 5.6, while the electropositive and elect-
ronegative elements project themselves along the dipole
axes. Thus the monomer due to this preferred angle, the
immediate obvious feature in fig. 5.6 (ii). Further the
dipole moment (Fig. 5.5) is a temperature dependent
quantity when the system is subjected to UHF alterna-
ting fields. Hence it is concluded that the high values
of dipole moments are due to formation of monomer and
less value due to formation of dimer in dielectrics,
particularly in the case of NMA in benzene and dioxane.

Table 5.1a

Values of dielectric constant (ϵ'_{ij}), loss factor (ϵ''_{ij}) uhf conductivity (K_{ij}) weight fractions (W_j) at different temperatures (t).

Systems	Temp. t $^\circ C$	W_j	ϵ'_{ij}	ϵ''_{ij}	K_{ij} x 10^{-10} in esu
N-methylaceta-mide in benzene	25	0.0022	2.317	0.0220	1.157
		0.0053	2.361	0.0456	1.179
		0.0073	2.390	0.0700	1.194
		0.0094	2.415	0.0951	1.207
		0.0022	2.295	0.0195	1.146
		0.0053	2.344	0.0414	1.171
	35	0.0073	2.379	0.0684	1.188
		0.0094	2.409	0.0875	1.204
		0.0022	2.281	0.0182	1.139
		0.0053	2.321	0.0364	1.159
	45	0.0073	2.361	0.0620	1.179
		0.0094	2.399	0.0824	1.199
		0.0022	2.261	0.0152	1.129
	55	0.0053	2.305	0.0336	1.151
		0.0073	2.346	0.0593	1.172
		0.0094	2.389	0.0792	1.194
N-methylaceta-mide in benzene in high concent-ration.	25	0.0212	2.512	0.1532	1.257
		0.0310	2.553	0.1866	1.278
		0.0406	2.594	0.2020	1.307
		0.0520	2.638	0.2369	1.323.

Table 5.1b

Values of dielectric constants (ϵ'_{ij}), loss factor (ϵ''_{ij}) uhf conductivity (K_{ij}) and weight fraction (W_j) at different temperatures (t)

Systems	Temp t °C	W_j	ϵ'_{ij}	ϵ''_{ij}	$K_{ij} \times 10^{-10}$ in esu
N-methyl acetamide in dioxane	25	0.0030	2.279	0.0489	1.138
		0.0058	2.310	0.0817	1.154
		0.0091	2.369	0.1188	1.184
		0.0123	2.422	0.1488	1.212
	35	0.0030	2.247	0.0450	1.122
		0.0058	2.303	0.0777	1.150
		0.0091	2.366	0.1151	1.183
		0.0123	2.419	0.1430	1.210
	45	0.0030	2.244	0.0401	1.121
		0.0058	2.291	0.0716	1.144
		0.0091	2.349	0.1072	1.174
		0.0123	2.415	0.1357	1.208
	55	0.0030	2.241	0.0361	1.119
		0.0058	2.274	0.0649	1.136
		0.0091	2.346	0.0994	1.173
		0.0123	2.412	0.1242	1.206

Table 5.1c

Values of dielectric constant (ϵ'_{ij}), loss factor (ϵ''_{ij}) uhf conductivity (K_{ij}) and weight fraction (W_j) at different temperature (t).

System	Temp. $t\ ^oC$	W_J	ϵ'_{ij}	ϵ''_{ij}	K_{ij} $\times 10^{-10}$ in esu
p-Bromonitro-benzene in benzene	20	0.0162	2.21	0.0263	1.104
		0.0202	2.2313	0.0302	1.114
		0.0342	2.2352	0.0346	1.116
		0.0375	2.2423	0.0436	1.120
		0.0416	2.2539	0.0447	1.126
	30	0.0162	2.2483	0.0265	1.123
		0.0202	2.2621	0.0316	1.130
		0.0342	2.2670	0.0346	1.132
		0.0375	2.2739	0.0374	1.140
		0.0416	2.2880	0.0458	1.143
	40	0.0162	2.2394	0.0346	1.118
		0.0202	2.2531	0.0447	1.125
		0.0342	2.2582	0.0583	1.128
		0.0375	2.2691	0.0632	1.134
		0.0416	2.2789	0.0793	1.139

Table 5.2

Values of $(\mu_j)_{compts}$ $(\mu_j)_{rept}$ $(\mu_j)_{theor}$ $(\tau_s)_{rept}$ and b(comput) at different temperatures.

System	Temp. in °C	b(compt)	τ_s (rept.)x 10^{+12} Sec.	μ_j (comp.) [Eq.10] D	μ_j (corr) [Eq.11] D	(μ_j) theor. D	(μ_j) rept. D
N-methyl acetamide in benzene	25	0.6334	12.13	3.882	4.135		3.69
	35	0.7068	10.27	4.008	4.262		3.78
	45	0.7637	8.87	4.064	4.313	4.30	3.80
	55	0.8065	7.81	4.216	4.467		3.82
N-methyl acetamide in dioxane	25	0.7185	9.88	3.647	3.862		3.66
	35	0.7824	8.41	3.886	4.109		3.69
	45	0.8252	7.34	3.830	4.043		3.78
	55	0.8631	6.35	3.907	4.117		3.83
N-methyl acetamide in benzene in high concentration.	25	0.6987	10.47	2.236	2.383	2.48	1.87
p-Bromo-nitrobenzene in benzene	20	0.7905	8.21	3.456	3.687		
	30	0.8259	7.32	4.013	4.272	3.658	
	40	0.8657	6.28	4.494	4.774		

References.

Acharyya S, Chatterjee A K, Acharyya P and Saha I L; Ind.
J Phys 56 (1982) 291.

Acharyya S and Chatterjee A K; Ind J Pure & Appl Phys
23 (1985) 484.

Datta S K, Acharyya C R, Saha I L and Acharyya S;
Ind. J Phys 55 (1981) 140.

Dhull J S, Sharma D R, Gill D S & Lakshiminarayan;
Ind. J Phys 56 (1982) 334.

Ghosh S K, Ghosh A K and Acharyya S; Ind. J Pure &
Appl. Phys. 18 (1980) 629.

Gopala Krishna K V; Trans Faraday Soc (G B) 53
(1957) 767.

Müller F H; Trans Faraday Soc (G B) 30 (1934) 731.

Murphy F J and Morgan S O; Bell Syst Tech J (USA),
18 (1939) 502.

Pant D C, Somevanshi S K S, Mehrotra N K and Saxena M C;
Ind J Phys 51 (1977) 305.

Ras A M and Bordewijk P; Real Trav Chim Phys - Bas
(Netherlands) 90 (1971) 1055.

Sato I K, Takshashi H & Higasi K; Bull Chem Soc Jpn
(Japan) 49 (1976) 329.

Sen S N and Ghosh R; Ind J Pure & Appl Phys 10 (1972) 701.

Ultra High Frequency Conductivity of Polar-Nonpolar Liquid Mixtures

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The variation of UHF conductivity K_{ij} of nitromethylacetamide in benzene and dioxane solvents in the lower as well as higher concentration regions of a polar solute, has been extensively studied to throw light regarding a constant conductivity at infinite dilution due to solvation effect at different temperatures. It is found that the measured data of K_{ij} for the lower concentration region is perfectly linear with W_j, the weight fraction of the solute, but differs radically at $W_j \rightarrow 0$ due to solute-solvent association or monomer formation in dielectrics. This observation, however, escapes detection when the K_{ij} data for higher concentration region are used as found in the case of p-bromonitrobenzene in benzene. The slope of curves showing UHF conductivity data versus concentration of the solution at infinite dilution, is finally used to estimate the temperature dependence of dipole moments for these liquids.

1 Introduction

The dipole moment of polar liquids varies[1,2] with temperature when the dielectric mixture is subjected to an alternating microwave or rather high frequency electric field. There are several methods[3-5] to compute the relaxation times as well as dipole moments of polar liquids dissolved in nonpolar solvents under the application of microwave and radio frequency electric fields. But these methods[3,4], unlike our method[5], suffer from extra-polation difficulties at $W_j \rightarrow 0$. The microwave conductivity data for nitro-methyl acetamide (NMA), have been computed from the recent studies on dielectric absorption in the very low concentration region by Dhull et al.[6] at temperatures 25°C, 35°C, 45°C, and 55°C in two different solvents (benzene and dioxane) and also in the high concentration regions at 25°C in benzene. NMA is an important dielectric solute because of its very high dielectric constant, and its wide biological applications. Hence it attracted the attention of a large number of workers[7].

We, therefore have chosen this system is order to report the microwave conductivity data of NMA in benzene and dioxane at different temperatures, viz. 25°C, 35°C, 45°C and 55°C in the extremely low concentration region as well as those at relatively high concentration region only at 25°C. The data for K_{ij} are then used to show that in the low concentration range of this solution the association is solute-solvent type, i.e. monomer which changes into the solute-solute association or dimer at relatively high concentrations.

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Moreover, the extremely low concentration conductivity data may reveal new information regarding the solvation effect[8].

Finally, the information regarding the various types of interactions of solutes in solution could, however, be inferred from the estimated values of the dipole moments. Hence the dipole moments μ_j's of NMA as well as p-bromonitrobenzene (pBNB) have been calculated from the concentration variation of UHF conductivity of the solution by the method described elsewhere[1]. The μ_j values thus obtained are found to increase with temperature as already shown by Acharyya et al.[1] for other systems. The fitted curves of the variation of μ_j as a function of temperature in °C for the given solutes of interest are

$$\mu_j = 3.6071 + 0.0112t - 8.3 \times 10^{-6}t^2$$

for NMA in benzene

$$\mu_j = 3.4294 + 0.0126t - 6.7 \times 10^{-5}t^2$$

for NMA in dioxane

and

$$\mu_j = 2.114 + 0.0747t - 3.8 \times 10^{-4}t^2$$

for p-BNB in benzene

The μ_j's of these systems were found to increase in a regular fashion with temperature (in °C).

2 Theory

The HF conductivity due to Murphy and Morgan[9] of polar-nonpolar liquid mixture is given by $K_{ij} = K'_{ij} + jK''_{ij}$ where K'_{ij} is the real part of the conductivity $= \omega \varepsilon''_{ij}/4\pi$ and K''_{ij} is the imaginary part $= \omega \varepsilon'_{ij}/4\pi$. The magnitude of total hf conductivity is usually given by

$$K_{ij} = \frac{\omega}{4\pi}(\varepsilon''^2_{ij} + \varepsilon'^2_{ij})^{1/2} \qquad \ldots(1)$$

ε'_{ij} of solution in the microwave region ($\lambda = 3.004$ cm), though very small and is equal to optical dielectric constant, but still $\varepsilon'_{ij} \gg \varepsilon''_{ij}$ where ε''_{ij} is responsible for the absorption of electrical energy to offer resistance to polarization. Hence the real part of K_{ij} of HF conductivity of solution of weight fraction W_j of polar solute at temperature T K is

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3 M_j kT} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) W_j \qquad \ldots(2)$$

where μ_j is the dipole moment of polar solute of molecular weight M_j, N the Avogadro number, k is the Boltzmann constant and $F_{ij} = [(\varepsilon_{ij} + 2)/3]^2$ is the local field. Hence it is evident that, for the microwave electric field, the total conductivity becomes:

$$K_{ij} = \frac{\omega}{4\pi} \varepsilon'_{ij} \qquad \ldots(3)$$

But, for HF region, it can be shown that

$$\varepsilon'_{ij} = \varepsilon_{ij\infty} + \varepsilon''_{ij}/\omega\tau \qquad \ldots(4)$$

Using Eqs (2), (3) and (4) it is shown that

$$K_{ij} = K_\infty + \frac{K'_{ij}}{\omega\tau_s} \qquad \ldots(5)$$

where K_∞ is a constant conductivity and τ_s is the relaxation time of the solute molecule in the solvent. Since K_{ij} is a function of W_j from Eq. (5) we have:

$$\left(\frac{dK'_{ij}}{dW_j} \right)_{W_j \to 0} = \omega\tau_s \left(\frac{dK_{ij}}{dW_j} \right)_{W_j \to 0} = \omega\tau_s \beta \qquad \ldots(6)$$

where β is the slope of $K_{ij} - W_j$ curve at $W_j \to 0$. When $W_j \to 0$ the density of the solution ρ_{ij} becomes ρ_i the density of the solvent and the local field F_{ij} of the solution becomes $F_i = [(\varepsilon_i + 2)/3]^2$ = the local field of the solvent.

Under this condition, Eq. (2) on differentiation with respect to W_j and as $W_j \to 0$ takes the form:

$$\left(\frac{dK'_{ij}}{dW_j} \right)_{W_j \to 0} = \frac{\mu_j^2 N \rho_i F_i}{3 M_j kT} \left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} \right) \qquad \ldots(7)$$

Taking

$$b = \beta \left/ \left(\frac{\mu_j^2 N \rho_i F_i \omega}{3 M_j kT} \right) \right. \qquad \ldots(8)$$

and using Eqs (6) and (7), we can have

$$b = \frac{1}{1 + \omega^2 \tau_s^2}$$

Hence

$$\tau_s = \frac{\lambda}{2\pi c} \left(\frac{1}{b} - 1 \right)^{1/2} = \frac{\lambda \times 10^{-10}}{18.84} \left(\frac{1}{b} - 1 \right)^{1/2} \qquad \ldots(9)$$

From Eq. (8) the dipole moment μ_j of polar solute can be evaluated by

$$\mu_j^{<s>} = \left(\frac{3 M_j kT}{N \rho_i F_i} \cdot \frac{\beta}{b\omega} \right)^{1/2} \qquad \ldots(10)$$

Eq. (9) is used to compute b from the reported τ_s data and thence the dipole moment $\mu_j^{<s>}$ of polar solute when it is dissolved in solvent, from Eq. (10).

Müller[10] gave a relation between $\mu_j^{<s>}$ and the corrected μ_j of solute by

$$\mu_j^{<s>} = \mu_j[1 - C(\varepsilon_i - 1)^2] \qquad \ldots(11)$$

where C is a constant which is claimed to be 0.038 for a large number of liquids and ε_i is the dielectric constant of the solvent.

3 Results and Discussion

The microwave conductivities of NMA in benzene at different temperatures, as a function of concentration, are given by:

$K \times 10^{-10} = 1.1415 + 7.0699\,W_j$ at 25°C

$K \times 10^{-10} = 1.1278 + 8.1738\,W_j$ at 35°C

$K \times 10^{-10} = 1.1178 + 8.4588\,W_j$ at 45°C

and

$K \times 10^{-10} = 1.1062 + 9.1398\,W_j$ at 55°C

while those in dioxane are:

$K \times 10^{-10} = 1.1107 + 8.1173\,W_j$ at 25°C

$K \times 10^{-10} = 1.0943 + 9.5319\,W_j$ at 35°C

$K \times 10^{-10} = 1.0922 + 9.2835\,W_j$ at 45°

and

$K \times 10^{-10} = 1.0859 + 9.6132\,W_j$ at 55°C

and have been shown graphically by the fitted curves along with the experimental points on them in Figs 1 and 2, in which the microwave conductivities in e.s.u. are plotted against the weight fractions W_j of the solute. It is found that from the region $W_j = 0.0022$ to $W_j = 0.0094$ of the solute in benzene and also from $W_j = 0.0030$ to $W_j = 0.0123$ of the solute in dioxane as the temperature of the systems increases, the UHF conductivity decreases, but maintaining a regular increase in slopes. The HF conductivity in the lower concentration region would vary linearly with W_j, because $\rho_{ij}F_{ij}/T$ in Eq. (2) assumes a constant value in the neighbourhood of 0.006 in the limit $W_j = 0$, at all the experimental temperatures, but at higher concentration the plot of K_{ij} with W_j will be mostly nonlinear. This is shown in Fig. 3 in which the HF conductivity of NMA in benzene at 25°C only has been plotted with W_j having its range from $W_j = 0.0212$ to $W_j = 0.0520$. This fact is also corroborated by the data p-bromonitrobenzene[11] in benzene (Fig. 4).

In the variation of K_{ij} with W_j both in benzene and dioxane the K_{ij}'s as shown in Figs 1 and 2 have tendency to meet within a certain zone in the higher concentration region and then they are expected to
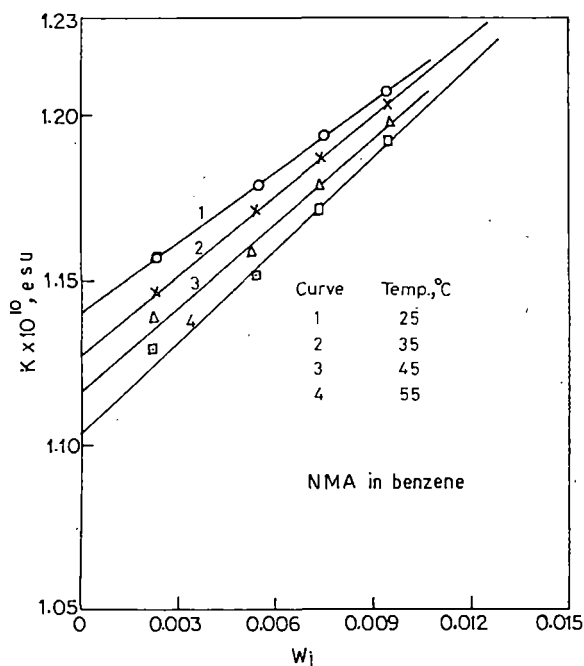
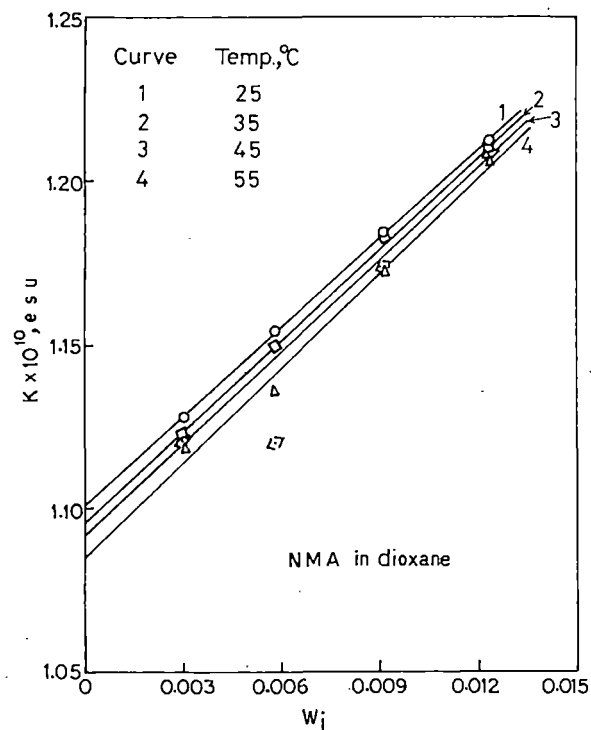Fig. 1—Concentration variation of K of NMA in benzene at different temperatures

Fig. 2—Concentration variation of K of NMA in dioxane at different temperatures

Fig. 3—Concentration variation of K of NMA in benzene at 25°C

Fig. 4—Concentration variation of K of p-BNB in benzene at different temperatures

give the higher values of K_{ij} data with respect to increasing temperatures in the higher concentration region. The curves of the high concentration K_{ij} data thus available are found to be temperature-dependent quantities, i.e.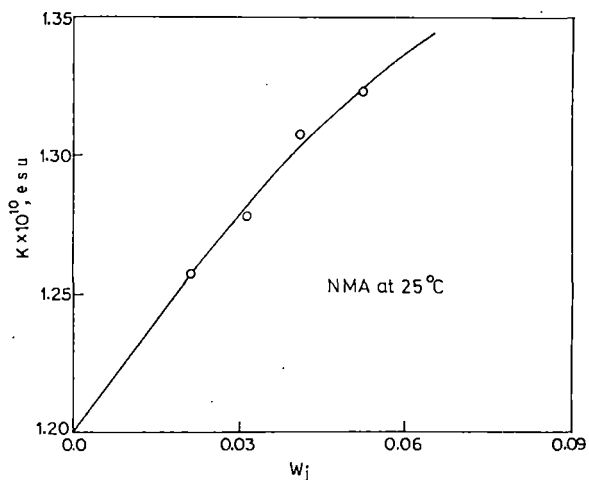 the elevated temperature of the mixture gives rise to higher value of K_{ij} after a certain concentration zone. This had already been demonstrated by Acharyya et al.[1] for a large number of polar compounds in benzene at relatively higher concentrations. Thus, for high concentrations, conductivity data of polar-nonpolar liquid mixture forced the experimentalists to draw curves of K_{ij} against W_j at all experimental temperatures to meet at a common point on the K_{ij} axis in the limit $W_j = 0$ which is apriori determined value from $(K_{ij})_{W_j \to 0}$ $= (\omega \varepsilon'_{ij}/4\pi)_{W_j \to 0}$ for most of the solute-solvent systems. This is usually attributed to the solvation effect[8]. In the case of p-BNB in benzene (Fig. 4), the curves presenting the conductivity data[9] at different temperatures, measured at relatively higher concentrations from W_j $= 0.0162$ to $W_j = 0.0416$, are found to meet at a common point on the K_{ij} axis at $W_j = 0$.

In fact, the information regarding the low-concentration conductivities of polar compounds in nonpolar solvents can no longer be borrowed from

high concentration conductivity data. The high as well as low-concentration data of K_{ij} are very scanty. This is why the data of K_{ij} for NMA in benzene and dioxane available from the dielectric absorption studies by Dhull *et al.*[6] revealed a new picture regarding the concentration variation of K_{ij} data at all stages of dilution so far as the lower-concentration region is concerned. Both in benzene and dioxane as solvents, the UHF conductivities of the present system at $W_j \rightarrow 0$ gradually decrease as the temperature increases from 25°C to 55°C as shown by the normal equations relating K_{ij} and W_j, as derived from the available experimental data and also as illustrated graphically in Figs 1 and 2 respectively. But there may exist a certain link between the low and high concentration data of K_{ij} against W_j. In the limit $W_j = 0$, the graphs using lower-concentration conductivity data for some suitable system in any solvent like benzene or dioxane, do not meet at a common point, but at different points on the K axis as shown in Figs 1 and 2. The value of the intercepts for K_{ij} at $W_j = 0$ decreases with increase in temperature. But both these features are not exhibited in case of aromatic compounds like *p*-BNB in benzene. In the higher-concentration region, the experimental curves (Figs 1 and 2) have a tendency to meet each other within a certain higher-concentration zone, below and above which the system investigated has most probably a different physical nature.

The dipole moments μ_j of NMA and *p*-BNB at different temperatures were then computed from Eq. (10). The corrected μ_j values were obtained from Eq. (11). However both the values of dipole moments computed from Eqs (10) and (11) using the reported values of τ_s are higher than those of the actual values because of the estimated error[6] of the order of 10% in

the calculated values of τ_s and hence the computed values of the dipole moments from these data would naturally be higher. Both these values of μ_j's are given in Table 1, with those of reported μ_j, τ_s etc. The computed μ_j values from Eq. (10) are finally shown graphically in Fig. 5 against temperature. From Table 1 it is evident that μ_j's are always higher when measured from low-concentration conductivity data of NMA in benzene and dioxane, but at 25°C the high concentration data (Fig. 3) always gives us the low value of dipole moment. However, *p*-BNB in benzene does not fall in this category. As observed by Dhull *et al.*[6], the high values of dipole moments of NMA in benzene and dioxane are due to monomers, i.e. solute-solvent association which may actually occur in the lower-concentration region. This state of affairs changes above a certain concentration zone to dimer, i.e. solute-solute association. The variation in the theoretically computed μ_j values for these molecules, one aliphatic ketonic group and the other substituted benzene might be due to (i) the difference in the values of group moments and (ii) the inductive effect[12]. The dipole moments of NMA in solvents at lower concentrations will be greater than those at higher concentrations (Table 1), shown both by the experimentally computed and theoretically obtained μ_j's due to the solute-solute association, i.e. dimer formation. For *p*-BNB the group moments of $C-NO_2$ and $C-Br$ act at a certain angle, assuming the benzene ring as a planar one (Fig. 6). With this conformation in view, the theoretical value of μ_j in terms of bond moments and bond angles gives us only the monomer μ_j value in case of *p*-BNB as it excellently agrees with the computed μ_j's (Table 1). Thus *p*-BNB gives the dipole moments at higher concentration due to

Table 1—Values of $(\mu_j)_{comput}$, $(\mu_j)_{rept}$, $(\mu_j)_{theor}$, $(\tau_s)_{rept}$ and $b(comput)$ at Different Temperatures

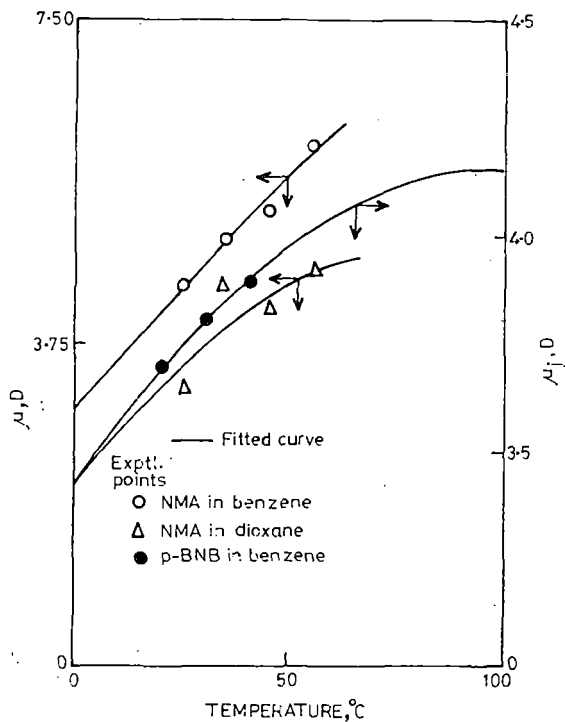| System	Temp. in °C	b(Comput.)	τ_s rept. 10^{-12}s	(μ_j) comput. [Eq. 10]	(μ_j) corr. [Eq. 11]	$(\mu_j)_\lambda$ D	$(\mu_j)_\lambda$ rept D
N-methyl	25	0.6334	12.13	3.882	4.135		3.69
acetamide	35	0.7068	10.27	4.008	4.262		3.78
in benzene	45	0.7637	8.87	4.064	4.313	4.30	3.80
	55	0.8065	7.81	4.216	4.467		3.82
N-methyl	25	0.7185	9.88	3.647	3.862		3.66
acetamide	35	0.7824	8.41	3.886	4.109		3.69
in dioxane	45	0.8252	7.34	3.830	4.043		3.78
	55	0.8631	6.35	3.907	4.117		3.83
N-methyl acetamide in benzene in high concentration	25	0.6987	10.47	2.236	2.383	2.48	1.87
p-Bromonitro-	20	0.7905	8.21	3.456	3.687		
benzene in	30	0.8259	7.32	4.013	4.272	3.658	
benzene	40	0.8657	6.28	4.494	4.774		

Fig. 5—Variation of experimentally observed dipole moment with temperature in °C along with the fitted curves
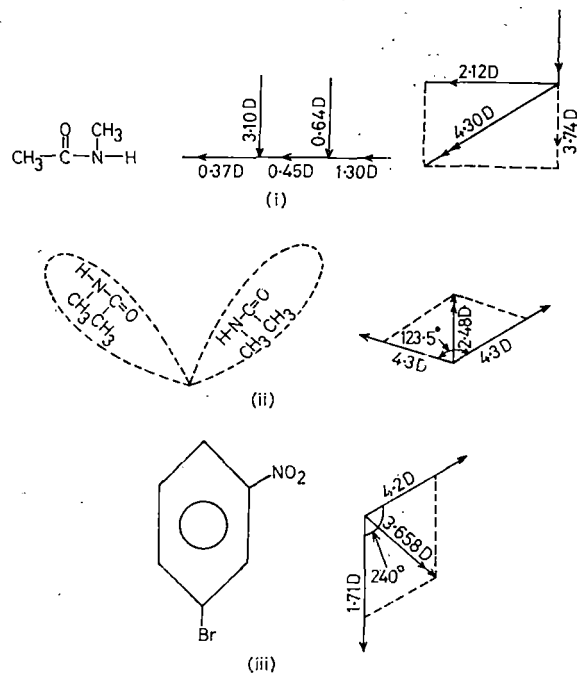

Fig. 6—Conformation of the different molecules showing the orientation of the bond axes, bond moments and also the dipole moments [(i) structural form of NMA; (ii), structural form of dimers; and (iii) structural form of p-BNB]

monomer formation. The group moments of $C-CH_3$, $C-N$ and $N-H$ groups act along a common axis as sketched in Fig. 6. But the group moments of $C=O$ and $N-CH_3$ act along the direction normal to that of $C-CH_3$. With this preferred conformational directions for NMA as depicted in Fig. 6, the resultant μ_j value was obtained for monomer formation. These data for μ_j's thus obtained also excellently agree with the computed μ_j's (Table 1). But for the dimer formation of NMA in benzene the two monomers attach each other with their most electropositive and electronegative elements, i.e. $-H$ and $-O-$ form a certain angle viz. 123.5° as calculated both from experimental and theoretical. μ_j values as shown in Fig. 6, while the electropositive and electronegative elements project themselves along the dipole axes. Thus the dipole moment of dimer formation is less than those of monomer due to this preferred angle — the immediate obvious feature in Fig. 6 (ii). Further, the dipole moment (Fig. 5) is a temperature-dependent quantity when the system is subjected to UHF alternating fields. Hence it is concluded that the high values of dipole moments are due to formation of

monomer and less value due to the formation of dimer in dielectrics, particularly in the case of NMA in benzene and dioxane.

References

1 Acharyya S, Chatterjee A K, Acharyya P & Saha I L, *Indian J Phys*, **56** (1982) 291.

2 Ras A M & Bordewijk P, *Recl Trav Chim Pays-Bas (Netherlands)*, **90** (1971) 1055.

3 Gopala Krishna K V, *Trans Faraday Soc (GB)*, **53** (1957) 767.

4 Sen S N & Ghosh R, *Indian J Pure & Appl Phys*, **10** (1972) 701.

5 Ghosh S K, Ghosh A K & Acharyya S, *Indian J Pure & Appl Phys*, **18** (1980) 629.

6 Dhull J S, Sharma D R, Gill D S & Lakshminarayan, *Indian J Phys*, **56** (1982) 334.

7 Sato I K, Takshashi H & Higasi K, *Bull Chem Soc Jpn (Japan)*, **49** (1976) 329.

8 Datta S K, Acharyya C R, Saha I L & Acharyya S, *Indian J Phys*, **55** (1981) 140.

9 Murphy F J & Morgan S O, *Bell Syst Tech J (USA)*, **18** (1939) 502.

10 Muller F H, *Trans Faraday Soc (GB)*, **30** (1934) 731.

11 Pant D C, Somevanshi S K S, Mehrotra N K & Saxena M C, *Indian J Phys*, **51** (1977) 305.

12 Acharyya S & Chatterjee A K, *Indian J Pure & Appl Phys*, **23** (1985) 484.