

Dielectric behaviour of some amides and formamides dissolved in nonpolar solvents under static electric field

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Abstract. Structural and associational aspects of polar amides (j) like formamide, acetamide, N-methyl acetamide (NMA), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMA) and acetanilide dissolved in the nonpolar solvent (i) benzene or 1,4-dioxan have been estimated from the measured static relative permittivity ϵ_{0ij} and high-frequency permittivity $\epsilon_{\infty ij}$ at different weight fractions w_{js} of polar solute at 35°C under static electric field using Debye model of polar liquid molecule. The static dipole moments μ_{ss} are compared with μ_{js} reported from conductivity method and theoretical $\mu_{\text{theo}S}$ to get exact μ_{cal} . $\mu_{\text{theo}S}$ of the molecules are predicted from the available bond angles and bond moments where difference in electron affinity exists between two adjacent atoms of a polar group due to inductive, mesomeric and electromeric effects in them. Solute–solute molecular association for NMA in benzene and solute–solvent association for other amides are ascertained to arrive at their conformational structures.

Keywords. Dielectric behaviour; dipole moment; monomer; dimer.

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1. Introduction

Amides, the main constituents of proteins and enzymes, have attracted the attention of researchers because of their wide biological applications [1, 2]. It is important to understand the mutual interaction of amides with nonpolar solvents to shed light on the conformational stability of protein molecules [3]. It is also very much essential to determine μ_{ss} , the dipole moments of formamides and amides under static or low-frequency electric field to understand the solute–solvent (monomer) and solute–solute (dimer) molecular associations. Malathi *et al* [4] measured the static relative permittivity ϵ_{0ij} and high-frequency permittivity $\epsilon_{\infty ij}$ of several amide liquid molecules (j) dissolved in nonpolar solvents (i) benzene or 1,4-dioxan for several mole fractions x_{js} of amides at 35°C. They intended to

Table 1. The measured static relative permittivity ϵ_{0ij} , high-frequency relative permittivity $\epsilon_{\infty ij}$ and static experimental parameter X_{ij} of different amides dissolved in nonpolar solvents at 35°C.

System	Weight fraction w_j of the solute	Static relative permittivity ϵ_{0ij}	High-frequency relative permittivity $\epsilon_{\infty ij}$	Static experimental parameter $X_{ij} = \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{(\epsilon_{0ij} + 2)(\epsilon_{\infty ij} + 2)}$
(I) Formamide in 1,4-dioxan	0.00876	2.479	2.006	0.026361
	0.01294	2.663	2.008	0.035047
	0.01715	2.831	2.008	0.042505
	0.02139	3.021	2.008	0.05034
	0.02567	3.221	2.008	0.057967
	0.02998	3.435	2.009	0.06545
	0.03378	3.662	2.009	0.07282
	0.03815	3.864	2.011	0.07878
(II) Acetamide in 1,4-dioxan	0.01690	2.655	1.911	0.04087
	0.02237	2.786	1.911	0.04675
	0.02786	2.923	1.913	0.05243
	0.03339	3.050	1.915	0.05741
	0.03895	3.173	1.915	0.06212
	0.04384	3.315	1.915	0.06728
	0.04945	3.426	1.917	0.07110
	0.05438	3.577	1.918	0.07592
(III) N-methyl acetamide in C ₆ H ₆ (NMA+C ₆ H ₆)	0.00843	2.410	2.217	0.01038
	0.01030	2.476	2.216	0.01378
	0.01780	2.819	2.216	0.02968
	0.02061	3.052	2.215	0.03931
	0.03470	4.042	2.211	0.07197
(IV) N,N-dimethyl formamide in C ₆ H ₆ (DMF+C ₆ H ₆)	0.00842	2.421	2.222	0.01066
	0.01029	2.456	2.222	0.012438
	0.01684	2.602	2.222	0.01956
	0.01965	2.673	2.221	0.02292
	0.02434	2.778	2.219	0.02773
	0.03279	2.963	2.217	0.03564
	0.04782	3.252	2.214	0.04690
	0.06289	3.654	2.211	0.06061
	0.0780	4.148	2.207	0.07504
0.0780	4.290	2.205	0.07883	
(V) N,N-dimethyl formamide in 1,4-dioxan (DMF+dioxan)	0.0143	2.535	1.910	0.03525
	0.02080	2.721	1.910	0.04393
	0.02750	2.868	1.910	0.05033
	0.03421	3.032	1.910	0.05703
	0.04095	3.186	1.911	0.06286
	0.0477	3.376	1.913	0.06955
	0.05362	3.570	1.914	0.07596
	0.06040	3.723	1.914	0.08076

Dielectric behaviour of some amides and formamides

Table 1. *Continued.*

System	Weight fraction w_j of the solute	Static relative permittivity ϵ_{0ij}	High-frequency relative permittivity $\epsilon_{\infty ij}$	Static experimental parameter $X_{ij} = \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{(\epsilon_{0ij} + 2)(\epsilon_{\infty ij} + 2)}$
(VI) N,N-dimethyl acetamide + C ₆ H ₆ (DMA + C ₆ H ₆)	0.00557	2.320	2.223	0.00532
	0.01113	2.414	2.223	0.01025
	0.02112	2.591	2.222	0.01904
	0.04104	2.982	2.219	0.03630
	0.06088	3.383	2.215	0.05148
	0.07845	3.783	2.213	0.06444
(VII) N,N-dimethyl acetamide in 1,4-dioxan (DMA+dioxan)	0.09704	4.119	2.208	0.07422
	0.01580	2.476	1.996	0.02684
	0.03458	2.858	1.998	0.04428
	0.05138	3.260	2.001	0.05982
	0.06721	3.699	2.002	0.07441
	0.07512	3.947	2.002	0.08172
(VIII) Acetanilide in 1,4-dioxan	0.08304	4.178	2.003	0.08795
	0.006124	2.298	2.000	0.017334
	0.019807	2.474	2.007	0.0260496
	0.02585	2.577	2.009	0.030955
	0.03186	2.678	2.012	0.035486

estimate Kirkwood correlation factor g with the change of concentration of the polar amide molecules in nonpolar solvents. The measured g gives an idea of cyclic or linear multimerization of amide molecules. The estimation of g is based on the measurement of μ of polar molecules from the available bond angle and bond moment [5] data. The Kirkwood correlation factor g also reflects solute–solute and solute–solvent associational behaviours of polar–nonpolar liquid mixture [4].

We thought to study further the dielectric behaviour of eight amides dissolved in benzene or 1,4-dioxan under static or low-frequency electric field at 35°C in terms of static relative permittivity ϵ_{0ij} and high-frequency permittivity $\epsilon_{\infty ij}$ for several weight fractions w_j of the solutes. The dipole moments μ_s under static and low-frequency electric fields were estimated in terms of slope a_1 of static experimental parameter $X_{ij} [= (\epsilon_{0ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} + 2)(\epsilon_{\infty ij} + 2)]$ against w_j within the framework of Debye model of polar–nonpolar liquid mixture. The purpose of the present paper is to throw light on solute–solvent and solute–solute associational aspects of amides dissolved in benzene or 1,4-dioxan in terms of the measured μ_s based on Debye theory. The μ_s under static electric field may be compared with μ_{js} , the high-frequency conductivity dipole moment of amides, to judge how much the frequency of the electric field affects the dipole moment of the molecule. Investigations have already been carried out on amides dissolved in nonpolar solvent to study the relaxation behaviour in high-frequency electric field using conductivity technique [6]. The existence of double relaxation times under single high-frequency electric field has been studied to ascertain structural and associational behaviour of the

molecule [7]. However, the dielectric behaviours of several primary, secondary and tertiary amides dissolved in nonpolar solvent under static or low-frequency electric field have not been studied so far. The formamides and amides are excellent donors and acceptors of protons [3] which associate themselves by hydrogen bonding. The conformational structures of the polar molecules in terms of μ_{theo} s were also ascertained from the available bond angle and bond moment data [8] to get exact estimated μ_{cal} s where inductive, mesomeric and electromeric effects play vital roles. The systems under study are interesting because the estimated μ_{s} s vary from solvent to solvent. The solvent benzene with a π -delocalized electron cloud having six p electrons may easily interact with the polar molecule. The hydrogen bonding solvent 1,4-dioxan, on the other hand, facilitates alignment of the polar molecule to enhance orientational polarization. It is also a carcinogenic compound miscible in water in all proportions and an important co-solvent for reactions.

The polar liquid amides and formamides as well as the nonpolar solvents benzene and 1,4-dioxan are all good-quality samples and used after purification [4]. The static relative permittivities ϵ_{0ij} s of polar–nonpolar liquid mixture were measured by WTWM dipolemeter DM 01 at 2 kHz frequency. The high-frequency relative permittivities $\epsilon_{\infty ij}$ ($= n_{Dij}^2$) were measured by Abbe's refractometer [4]. The percentage of accuracy in the measurement for both the ϵ_{0ij} s and $\epsilon_{\infty ij}$ s was within $\pm 1\%$. The mole fractions x_j s were transformed

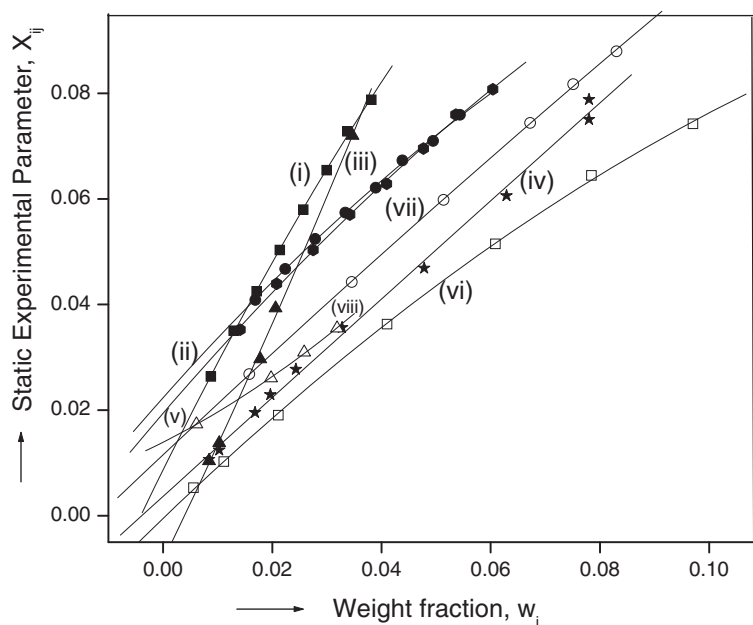


Figure 1. The nonlinear plot of static experimental parameter X_{ij} against w_j of different amides dissolved in nonpolar solvents at 35°C under static electric field. (i) formamide in 1,4-dioxan (—■—), (ii) acetamide in 1,4-dioxan (—●—), (iii) N-methyl acetamide in C_6H_6 (—▲—), (iv) N,N-dimethyl formamide in C_6H_6 (—★—), (v) N,N-dimethyl formamide in 1,4-dioxan (—●—), (vi) N,N-dimethyl acetamide + C_6H_6 (—□—), (vii) N,N-dimethyl acetamide in 1,4-dioxan (—○—), (viii) acetanilide in 1,4-dioxan (—△—).

Table 2. Coefficients a_0 , a_1 and a_2 of $X_{ij} = a_0 + a_1 w_j + a_2 w_j^2$ curve, estimated dipole moment $\mu_s \times 10^{30}$ C.m, reported $\mu_j \times 10^{30}$ C.m in the high-frequency electric field, theoretical dipole moment μ_{theo} from available bond angle and bond moments and calculated theoretical dipole moment $\mu_{\text{cal}} \times 10^{30}$ C.m under static or low-frequency electric field of some amides in different nonpolar solvents at 35°C.

System	Coefficients a_0 , a_1 and a_2 of $X_{ij} = w_j$ curve			Estimated dipole moment $\mu_s \times 10^{30}$ C.m	Reported dipole moment $\mu_j \times 10^{30}$ C.m (HF method)	Theoretical dipole moment $\mu_{\text{theo}} \times 10^{30}$ C.m	Calculated theoretical dipole moment $\mu_{\text{cal}} \times 10^{30}$ C.m
	a_0	a_1	a_2				
(I) Formamide in 1,4-dioxan	0.00866	2.09234	-6.39895	12.56	12.50 [12]	10.43	12.54
(II) Acetamide in 1,4-dioxan	0.02236	1.16229	-3.37094	10.70	12.10 [12]	10.36	10.70
(III) N-methyl acetamide in C_6H_6 (NMA + C_6H_6)	-0.00845	2.13133	5.46872	17.43	13.27 [6]	15.44	17.43
(IV) N,N-dimethyl formamide in C_6H_6 (DMF + C_6H_6)	0.00365	0.93808	-0.0837	11.56	12.90 [6]	12.73	11.56
(V) N,N-dimethyl formamide in 1,4-dioxan (DMF + dioxan)	0.0194	1.20332	-3.04671	12.10	12.87 [6]	12.73	12.10
(VI) N,N-dimethyl acetamide in C_6H_6 (DMA + C_6H_6)	-5.16794×10^{-4}	0.9942	-2.26004	12.99	12.27 [6]	13.37	13.00
(VII) N,N-dimethyl acetamide in 1,4-dioxan (DMA + dioxan)	0.01152	0.97199	-0.57102	11.87	12.44 [6]	13.37	11.87
(VIII) Acetamide in 1,4-dioxan	0.01392	0.524	4.88689	10.86	11.04 [12]	14.71	10.87

into weight fractions w_j s of the solute by mixing the solute and solvent in appropriate proportions of weights according to the formula [9]

$$w_j = \frac{x_j M_j}{x_j M_j + x_i M_i}, \quad (1)$$

where x_i and x_j are the mole fractions of the solvent and solute of molecular weight M_i and M_j respectively, such that $x_i + x_j = 1$.

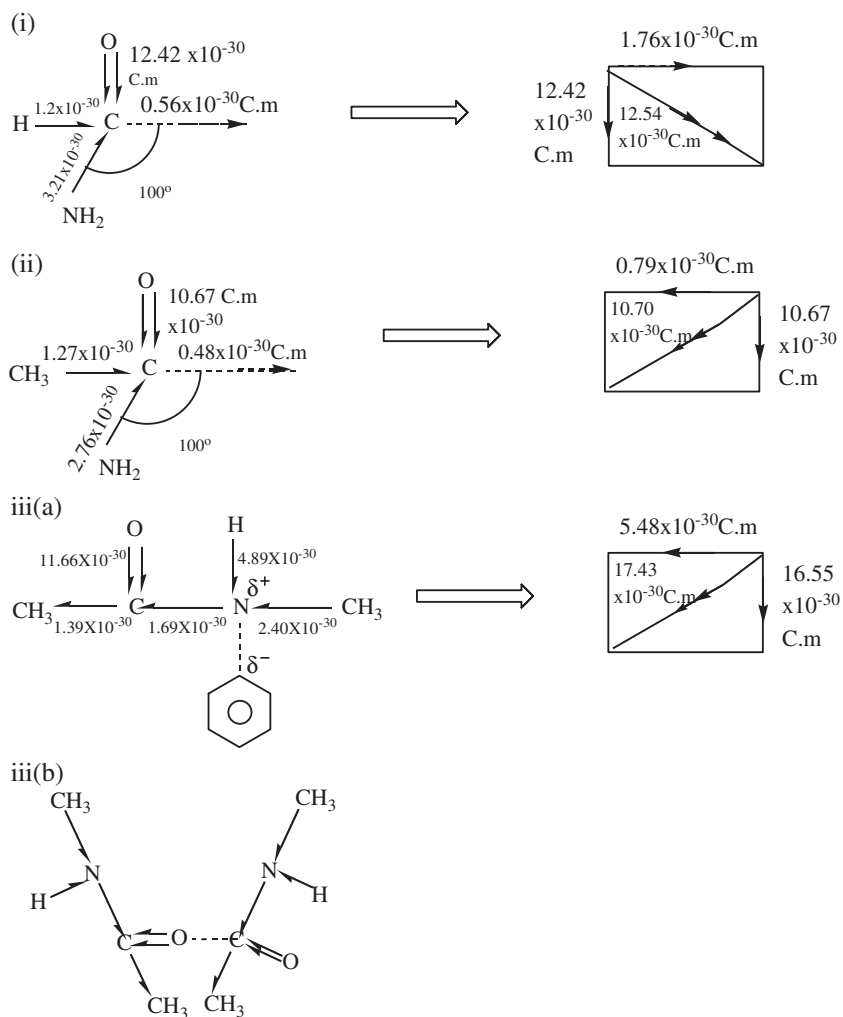


Figure 2. Theoretical dipole moment μ_{theo} to get exact $\mu_{\text{cal}} \times 10^{30}$ C-m from available bond angles and bond moments (multiples of 10^{-30} C-m) of some amides and formamides: (i) Formamide, (ii) acetamide, [iii(a)] solute–solvent association of NMA in benzene, [iii(b)] solute–solute association of NMA, (iv) N,N-dimethyl formamide (DMF) in C_6H_6 , (v) N,N-dimethyl acetamide (DMA) in C_6H_6 and (vi) acetanilide.

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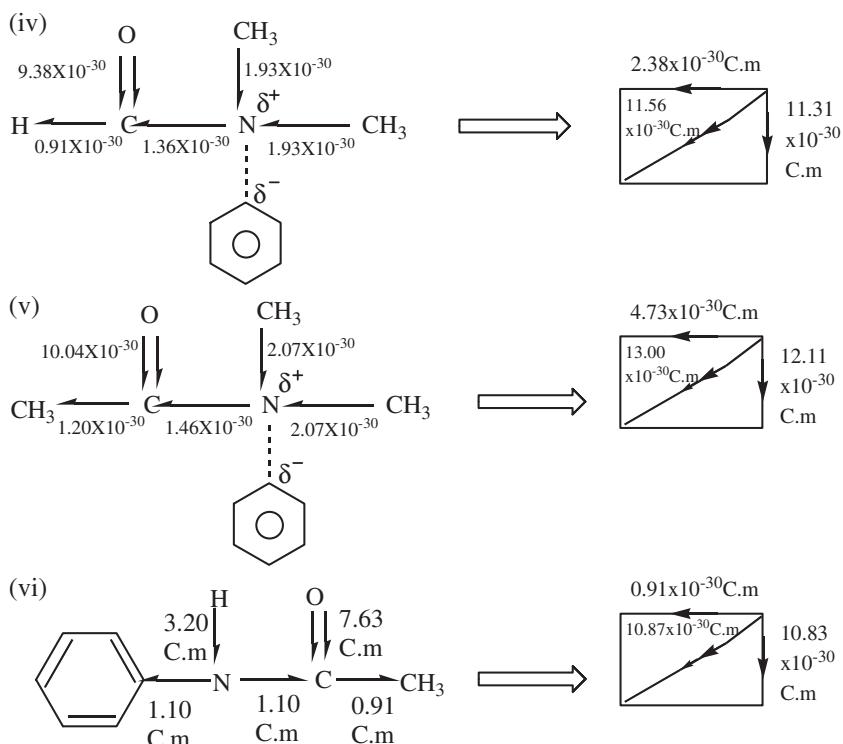


Figure 2. *Continued.*

The measured ϵ_{0ij} , $\epsilon_{\infty ij}$ and x_{ij} s are given in table 1 against w_j s of the solute. The static experimental parameters X_{ij} s are plotted against w_j s to get the parabolic curve of figure 1. The slopes a_1 of $X_{ij}-w_j$ curves are shown in table 2 along with the reported μ_j s and measured μ_s s using Debye model [8] of polar-nonpolar liquid mixture. The theoretical dipole moments μ_{theo} s are given in figure 2 to get exact μ_{cal} as shown in table 2.

2. Theoretical formulation

The dipole moment μ_s of a polar solute (j) in a nonpolar solvent (i) under static or low-frequency electric field at T K according to Debye [10] is

$$\frac{\epsilon_{0ij} - 1}{\epsilon_{0ij} + 2} - \frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} = \frac{\epsilon_{0i} - 1}{\epsilon_{0i} + 2} - \frac{\epsilon_{\infty i} - 1}{\epsilon_{\infty i} + 2} + \frac{N\mu_s^2 c_j}{9\epsilon_0 K_B T}, \quad (2)$$

where electronic polarization is assumed to be almost equal to 10% of the atomic polarization so that $\epsilon_{\infty ij} \approx n_{Dij}^2$. ϵ_0 = absolute permittivity of the free space = $8.854 \times 10^{-12} \text{ Fm}^{-1}$ and all other symbols carry usual significance in SI unit [11].

The molar concentration c_j in eq. (2) can be written in terms of w_j s of the polar solute as

$$c_j = \frac{\rho_{ij} w_j}{M_j} \quad (3)$$

If a polar solute of weight W_j and volume v_j is mixed with a nonpolar solvent of weight W_i and volume v_i to yield a solution density ρ_{ij} as

$$\rho_{ij} = \frac{W_i + W_j}{v_i + v_j} = \frac{W_i + W_j}{(W_i/\rho_i) + (W_j/\rho_j)} = \frac{\rho_i \rho_j}{\rho_i W_j + \rho_j W_i}$$

$$\rho_{ij} = \rho_i (1 - \gamma w_j)^{-1}, \quad (4)$$

the weight fractions w_i and w_j of the solvent and solute are

$$w_i = \frac{W_i}{W_i + W_j}, \quad w_j = \frac{W_j}{W_i + W_j},$$

where $w_i + w_j = 1$ and $\gamma = (1 - \rho_i/\rho_j)$, ρ_i and ρ_j being the densities of the pure solvent and solute respectively.

Now eq. (2) reduces to

$$\frac{\varepsilon_{0ij} - \varepsilon_{\infty ij}}{(\varepsilon_{0ij} + 2)(\varepsilon_{\infty ij} + 2)} = \frac{\varepsilon_{0i} - \varepsilon_{\infty i}}{(\varepsilon_{0i} + 2)(\varepsilon_{\infty i} + 2)} + \frac{N\rho_i\mu_s^2}{27\varepsilon_0M_jK_B T} w_j(1 - \gamma w_j)^{-1}$$

or

$$X_{ij} = X_i + \frac{N\rho_i\mu_s^2}{27\varepsilon_0M_jK_B T} w_j + \frac{N\rho_i\mu_s^2}{27\varepsilon_0M_jK_B T} \gamma w_j^2 + \dots \quad (5)$$

Equation (5) is a polynomial equation of X_{ij} against w_j as

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 + \dots \quad (6)$$

On comparing eqs (5) and (6) and equating the first power of w_j one gets static dipole moment μ_s as

$$\mu_s = \left(\frac{27\varepsilon_0M_jK_B T}{N\rho_i} a_1 \right)^{1/2}, \quad (7)$$

where a_1 is the slope of $X_{ij}-w_j$ curve at $w_j \rightarrow 0$ of figure 1 as shown in table 2.

3. Results and discussions

The measured ε_{0ij} and $\varepsilon_{\infty ij}$ for different w_j s of the solute along with static experimental parameters X_{ij} s are given in table 1. The concentrations of the polar solute for each dilute solution of polar–nonpolar liquid mixture are made extremely low. In that case one polar unit is sufficiently apart from the other so that a polar unit may be considered as quasi-isolated validating the applicability of Debye theory for polar molecule. The static experimental parameters $X_{ij} [= (\varepsilon_{0ij} - \varepsilon_{\infty ij})/(\varepsilon_{0ij} + 2)(\varepsilon_{\infty ij} + 2)]$ are plotted against w_j s of the solute to get the parabolic curve as shown in figure 1. Both the formamide and NMA of the systems I (–■–) and III (–▲–) may undergo self-association or solute–solute (dimer) molecular association through hydrogen bonding in 1,4-dioxan and C_6H_6 solvents with the increase in concentration of the solutes, thereby yielding higher μ_s s. μ_s s of the two polar molecules are directly proportional to the square root of slopes a_1 s of $X_{ij}-w_j$ curves of eq. (7) to show larger magnitude of slopes as evident from table 2 and figure 1. The almost

similar magnitude of slopes for other curves reveals their similar polarity [7]. The estimated μ_{sS} of these systems are, however, small when compared to the reported μ_{jS} from high-frequency conductivity measurement technique [6] which is solely concerned with the bound molecular charge of the polar molecules and the orientational polarization involved is due to the rotation of a part of the molecule under nearly 10 GHz electric field [7]. The substituent polar groups of these molecules induce subsidiary dipoles with the interaction of the nonpolar solvent yielding smaller μ_{sS} due to the formation of monomer or solute-solvent molecular association as given in figure 2. The theoretical dipole moments μ_{theoS} are predicted from the vector addition of available bond angles and bond moments of $C \leftarrow O$, $C \leftarrow NH_2$ (making an angle 100° with bond axis), $N \leftarrow CH_3$, $CH_3 \leftarrow C$, $H \leftarrow C$, $C \rightarrow N$, of 10.33×10^{-30} Coulomb-metre (C·m), 2.67×10^{-30} C·m, 2.13×10^{-30} C·m, 1.23×10^{-30} C·m, 1×10^{-30} C·m and 1.5×10^{-30} C·m respectively assuming that the molecules are planar. The bond moment is the characteristic of a particular bond and it is determined by chemical evidence. The magnitudes of bond moments are determined using infrared spectroscopy measurement technique. It is evident that the frequency of the electric field is the reason for the slight discrepancies of μ_{theoS} , μ_{sS} and μ_{jS} . The associational behaviours of the polar molecules are given in figure 2. The primary and secondary amides show the self-association or solute-solute (dimer) molecular association through the hydrogen bond in 1,4-dioxan or C_6H_6 [3,12]. One such typical solute-solute (dimer) association for NMA in C_6H_6 is given in figure 2(iii(b)). The solute-solvent (monomer) molecular association in secondary (NMA) and tertiary (DMF and DMA) amides may arise by the interaction of the π delocalized electron cloud of the benzene ring with the fractional +ve charge at the site of the nitrogen atom in the amide group. They are seen in figures 2(iii(a)), 2(iv), 2(v) and 2(vi). A dipole adjacent to a polar group within the same polar molecule or formation of π bonds in the molecules containing conjugated bonds induces an intramolecular charge distribution due to inductive, mesomeric or electromeric effects. Each substituent bond moment of a polar molecule is thus reduced by a factor

$$\mu_R = \frac{\mu_s}{\mu_{theo}} \times \text{theoretical bond moment.} \quad (8)$$

The exact dipole moment μ_{cal} of the polar molecule can be calculated using vectorial addition formula of the reduced bond moments as

$$\mu_{cal} = \sqrt{\mu_{R_1}^2 + \mu_{R_2}^2 + 2\mu_{R_1}\mu_{R_2}\cos\theta}, \quad (9)$$

where θ is the angle between two polar units μ_{R_1} and μ_{R_2} . A good agreement is observed between μ_{sS} and the calculated μ_{calS} which certainly take into account the contribution of inductive, mesomeric and electromeric effects from the individual bond moments.

4. Conclusion

The simple Debye theory gives an adequate representation of the relation between polarization and molecular dipole moment of a dilute solution of polar-nonpolar mixture usually accepted as a correct μ_s for an isolated polar molecule. The existence of solute-solute (dimer) and solute-solvent (monomer) molecular associations are almost eliminated by extrapolation of $X_{ij}-w_j$ curve at infinite dilutions, i.e. $w_j \rightarrow 0$, to get slope a_1 and hence

μ_s to arrive at the structural and associational behaviour of amides and formamides dissolved in the nonpolar solvents 1,4-dioxan and benzene under low-frequency electric field. Solute–solute (dimer) molecular associations are predicted for formamide and acetamide in 1,4-dioxan and N-methyl acetamide (NMA) in C_6H_6 . The other formamides and amides exhibit solute–solvent (monomer) molecular association. Inductive, electromeric and mesomeric effects come into play to change the bond angles and bond moments by a factor μ_s/μ_{theo} . So dielectric behaviours of amides and formamides are easily ascertained by the straightforward and simple approach of Debye model of polar–nonpolar liquid mixture.

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