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RELAXATION PHENOMENA OF BINARY APROTIC POLAR LIQUID MIXTURE DISSOLVED IN NONPOLAR SOLVENTS UNDER STATIC AND HIGH FREQUENCY ELECTRIC FIELD

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ABSTRACT

Double relaxation times τ_2 and τ_1 due to whole molecular rotation and the flexible parts of the binary(jk) polar liquid mixture N, methyl acetamide (NMA) and Acetone(Ac) dissolved in C_6H_6 have been estimated analytically from complex high frequency orientational susceptibility χ_{ijk}^* measurement for different weight fractions w_{jk}'s and mole fractions x_j's of Ac under 9.88 GHz at various experimental temperatures. Nine systems among twenty exhibit τ_2 and τ_1 at different molecular environment. τ_2's of eleven systems whereas τ_1 of nine systems agree well with the reported & measured τ's indicating a part of the molecule is rotating under high frequency electric field. The plot of τ_{jk} and μ_{jk} against x_j's of Ac reveals solute-solute (dimer) molecular associations up to x_j=0.3 and solute-solvent(monomer) association thereafter to explain convex curves. μ_2 and μ_1 as well as static μ_{0s} are compared reported value to see the applicability of Debye-Pellat theory in the measurement of ε_{0ijk} and $\varepsilon_{\infty ijk}$ for different w_{jk}'s. The molecular dynamics of the polar mixture is ascertained from Eyring rate theory. The Debye factor $\tau_{jk}T/\eta$ and Kalman factor $\tau_{jk}T/\eta^{\gamma}$ are calculated to show that Debye relaxation mechanism holds good. This study signifies that Debye-Stokes- Einstein model for ordinary fluids holds good whereas breakdown occurs for viscous fluid.

Keywords: Double relaxation times, dipole moment, monomer, dimer.

INTRODUCTION

Relaxation phenomenon is one of the most unresolved problems of physics today[1]. Nothing can relax from perfection. It thus gained attention of a large number of workers[2,3] to shed light on the structure, shape and sizes of polar liquid molecules as well as their associational behaviour through various established methods [4,5]. Nowadays, TDR and network analyser are available to study the dielectric dispersion and absorption phenomenon of complex molecular systems. Nevertheless, single frequency measurement technique at microwave frequency has the capability to detect weak molecular associations. The method is usually involved with measurement of relaxation time τ and dipole moment μ of a polar molecule(j)or a binary polar mixture(jk) dissolved in a nonpolar solvent (i) and estimation of energy parameters to know the molecular environment. Rangra and Sharma[6] measured τ and μ of the binary polar mixtures of N, methyl acetamide and acetone (NMA+Ac) dissolved in C_6H_6 for 0.0, 0.3,0.5,0.7 and 1.0 mole fractions xj's of acetone(CH_3COCH_3) at different temperatures (25,30, 35 and 40°C) using standard standing waves microwaves techniques and Gopalakrishna's single frequency(9.88 GHz) concentration variation method to propose solute-solute and solute-solvent types of molecular association for NMA. They also suggested dielectric relaxation process as a rate process like viscous flow process. Sahoo et al [7] ,however, measured τ and μ of the binary polar liquid mixture under identical molecular environment [6] using high frequency conductivity technique to infer structural and associational behaviour as well as molecular dynamics from measured thermodynamic energy parameters. The conductivity σ_{ij}'s

measurement technique, is related to bound molecular charge[3] of the polar molecules unlike relative permittivity ε_{ij}'s which is concerned with all types of polarizations. The susceptibility χ_{ij}'s, on the other hand, is involved with orientational polarization alone. Several attempts have already been made to study the relaxation phenomena of binary polar liquid mixtures dissolved in non polar solvent from high frequency conductivity measurement technique [7,8].However, no such study on the existence of double relaxation mechanism for the binary polar mixture of (NMA+Ac) dissolved in C_6H_6 has been done so far using susceptibility measurements technique.

Under such context, we thought to study further the existence of double relaxation phenomena on the aforesaid binary polar mixture of (NMA+Ac) in C_6H_6 under same molecular environment[6] in terms of measured real χ'_{ijk} $(=\varepsilon'_{ijk} - \varepsilon_{\infty ijk})$and imaginary χ''_{ijk} $(=\varepsilon''_{ijk})$ parts of high frequency orientational susceptibility χ^*_{ijk} $(=\varepsilon^*_{ijk} - \varepsilon_{\infty ijk})$and χ_{0ijk} $(=\varepsilon_{0ijk} - \varepsilon_{\infty ijk})$which is real from single frequency susceptibility measurement technique [9]. The double relaxation times τ_2 and τ_1 due to end over end rotation of the whole molecule and their flexible parts under high frequency electric field as well as μ_2 and μ_1 enable one to get information on intra and inter-molecular interactions and their structures. τ_2 and τ_1 are very much sensitive and required to be measured accurately the high frequency relative permittivity $\varepsilon_{\infty ijk}$ and static relative permittivity ε_{0ijk} [10]. In absence of reliable available measured data of $\varepsilon_{\infty ijk}$ and ε_{0ijk} one can safely use standard form of Debye-Pellat [11] equation to get those parameters at different weight fractions w_{jk}'s of binary polar mixture. $\varepsilon_{\infty ijk}$ and ε_{0ijk} thus estimated are used to get static dipole moment μ_{0s} in terms of the static experimental parameter X_{ijk} at different w_{jk} within the framework of Debye model of binary polar liquid mixture. In the present investigation, one of the polar constituents N, methyl acetamide (NMA) is a nonaqueous aprotic solvent. It is the building blocks of proteins and enzymes. Saha and Acharyya[12] suggested the presence of strong solute-solvent association for NMA in C_6H_6 in terms of measured τ and μ from conductivity measurement technique at 9.987 GHz electric field. The other polar molecule acetone (Ac) is a good aprotic solvent for the manufacturer of smokeless powder and used as raw materials for the production of iodoform and chloroform. Aprotic polar solute(j) dissolved in benzene (i) usually showed[13] double and single relaxation mechanism under ~ 10 GHz electric field.

Disubstituted benzenes alone when dissolved in benzene show always double relaxation phenomena under the effective dispersive region of 9.945 GHz electric field[14].The purpose of the present paper is to see the occurrence of double relaxation phenomena of (NMA+Ac) binary polar mixture dissolved in benzene at different experimental temperatures and mole fractions x_j's of acetone using susceptibility measurement technique and applicability of Debye -Pellat equation [11] to observe the real advancement of the paper with respect to literature. The static dipole moment μ_{0s} and double relaxation times τ_2 and τ_1 as well as μ_2 and μ_1 are estimated simultaneously and compared with the measured values to see how far they agree with each other. Moreover, it is the aim of the study to observe whether a part of the molecule is rotating for binary polar mixture under hf electric field like earlier [9-13] and how far μ_{0s}'s and μ_{jk}'s vary with frequency of the electric field employing rotational dynamic of polar molecules in apolar solvents. The molecular environment surrounding the binary polar mixture is also studied from the estimated energy parameters like enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and free energy of activation ΔF_τ considering the rotation of the binary polar mixture under high frequency electric field as a rate process [15].

EXPERIMENTAL

The solvent C_6H_6 ,NMA and Ac were distilled through a long vertical fractionating coloumn for purification. The binary polar mixture of fixed mole fraction x_j of acetone is prepared by mixing them in appropriate proportions of weights with solvent benzene. The real ε'_{ijk} (±0.5%)and imaginary ε''_{ijk} (±1.7%) parts of complex relative permittivity ε^*_{ijk} were measured[6] using X-band microwave bench tuned at 9.88 GHz frequency for different weight fractions w_{jk}'s(± 4.37×10^{-4} %) of binary polar mixture at 25,30,35

and 40°C experimental temperatures. $\varepsilon_{\infty ijk}$ and ε_{0ijk} at different w_{jk}'s of polar liquid are estimated using standard form of Debye- Pellat equation from measured relaxation time τ . The accuracies of the measured data $\varepsilon_{\infty ijk}$ and ε_{0ijk} are within ±1%. $\varepsilon_{\infty ijk}$ and ε_{0ijk} thus obtained are then plotted against w_{jk}'s in the low concentration region to see that Heston et al[16] equation is satisfied. Temperature of the dielectric sample is controlled by a thermostat.

Theoretical formulations

(i) Static dipole moment μ_{0s}

The static dipole moment μ_{0s} of a binary polar mixture (jk) dissolved in benzene (i) under static or low frequency electric field at temperature T K within the frame work of Debye model[11] is given by :

$$\frac{\varepsilon_{0ijk}-1}{\varepsilon_{0ijk}+2}-\frac{\varepsilon_{\infty ijk}-1}{\varepsilon_{\infty ijk}+2}=\frac{\varepsilon_{0i}-1}{\varepsilon_{0i}+2}-\frac{\varepsilon_{\infty i}-1}{\varepsilon_{\infty i}+2}+\frac{N\mu_{0s}^2 c_{jk}}{9\varepsilon_0 K_B T} \qquad (1)$$

where ε_0 is the absolute permittivity of free space = $8.854\text{x}10^{-12}$ Fm^{-1}.All other symbols carry usual meanings [13].

Introducing w_{jk} in place of c_{jk} , equation (1) can now be written as :

$$\frac{\varepsilon_{0ijk}-\varepsilon_{\infty ijk}}{(\varepsilon_{0ijk}+2)(\varepsilon_{\infty ijk}+2)}=\frac{\varepsilon_{0i}-\varepsilon_{\infty i}}{(\varepsilon_{0i}+2)(\varepsilon_{\infty i}+2)}+\frac{N\rho_i\mu_s^2}{27\varepsilon_0 M_{jk} K_B T} w_{jk}(1-\gamma w_{jk})^{-1}$$

$$X_{ijk}=X_i+\frac{N\rho_i\mu_s^2}{27\varepsilon_0 M_{jk} K_B T} w_{jk}+\frac{N\rho_i\mu_s^2}{27\varepsilon_0 M_{jk} K_B T}\gamma w_{jk}^2 \qquad (2)$$

Equation (2) is a polynomial equation of X_{ijk} against w_{jk}. On differentiation of equation (2) with respect to w_{jk} and at $w_{jk}\to 0$ one gets :

$$\mu_{0s}=\left[\frac{27\varepsilon_0 M_{jk} K_B T a_1}{N\rho_i}\right]^{\frac{1}{2}} \qquad (3)$$

where a_1 is the slope of X_{ijk} - w_{jk} curve at $w_{jk}\to 0$. The curves of X_{ijk} - w_{jk} for 0.5 x_j of Ac is shown in Figure 1. M_{jk} being the average molecular weight of binary polar mixture (jk) such that $M_{jk}=M_j x_j+ M_k x_k$; x_j and x_k are the mole fractions of polar molecules j and k i.e. $x_j+x_k=1$. . All other symbols are expressed in SI units [17]. The excellent agreement of μ_{0s}'s with reported μ's signify the validity of method adopted in measuring $\varepsilon_{\infty ijk}$ and ε_{0ijk} at different w_{jk}'s by Debye-Pellat theory.

(ii) Double relaxation times τ_2 and τ_1 and relative contributions c_1 and c_2

Bergmann et al[18] suggested a graphical method to get τ_1 and τ_2 of a binary (jk) polar liquid mixture dissolved in benzene (i) in terms of measured χ'_{ijk} , χ''_{ijk} and χ_{0ijk} under different frequency of GH_Z electric field and temperature T K as :

$$\frac{\chi'_{ijk}}{\chi_{0ijk}}=\frac{c_1}{1+\omega^2\tau_1^2}+\frac{c_2}{1+\omega^2\tau_2^2} \qquad (4)$$

$$\frac{\chi''_{ijk}}{\chi_{0ijk}}=c_1\frac{\omega\tau_1}{1+\omega^2\tau_1^2}+c_2\frac{\omega\tau_2}{1+\omega^2\tau_2^2} \qquad (5)$$

where c_1 , c_2 are the relative contributions due to two broad Debye type dispersions such that $c_1 + c_2 = 1$.

Equations (4) and (5) are solved for c_1 and c_2 to get a straight line equation as :

$$\frac{\chi_{0ijk} - \chi'_{ijk}}{\chi'_{ijk}} = \omega(\tau_2 + \tau_1)\frac{\chi''_{ijk}}{\chi'_{ijk}} - \omega^2\tau_1\tau_2 \quad (6)$$

where $\omega(\tau_2 + \tau_1)$ and $-\omega^2\tau_1\tau_2$ are the slopes and intercepts of equation (6) obtained by least squares fitting procedures of variables $\frac{\chi_{0ijk} - \chi'_{ijk}}{\chi'_{ijk}}$ plotted against $\frac{\chi''_{ijk}}{\chi'_{ijk}}$ for different w_{jk}'s under a given angular frequency $\omega(=2\pi f)$. The intercepts and slopes yield τ_2 and τ_1.

τ's were also calculated from the linear slope of χ''_{ijk} against χ'_{ijk} as suggested by Murthy et al [19]

$$\frac{d\chi''_{ijk}}{d\chi'_{ijk}} = \omega\tau \quad (7)$$

Both χ''_{ijk} and χ'_{ijk} are the functions of w_{jk}'s. To avoid polar- polar interactions one could use the ratio of slopes of χ''_{ijk} - w_{jk} and χ'_{ijk} - w_{jk} curves at $w_{jk} \to 0$ to measure τ.

$$\left(\frac{d\chi''_{ijk}}{dw_{jk}}\right)_{w_{jk}\to 0} \Big/ \left(\frac{d\chi'_{ijk}}{dw_{jk}}\right)_{w_{jk}\to 0} = \omega\tau \quad (8)$$

τ's from equations (7) and (8) agree excellently with reported τ due to Gopalakrishna's method. Symmetrical τ_s and characteristics τ_{cs} are also compared with most probable τ_0 of nine systems.

A continuous distribution of τ's between two extreme values of τ_2 and τ_1 for nine systems inspires one to calculate c_1 and c_2 from equations (4) and (5) as follows :

$$c_1 = \frac{\left(\frac{\chi'_{ijk}}{\chi_{0ijk}}\alpha_2 - \frac{\chi''_{ijk}}{\chi_{0ijk}}\right)(1+\alpha_1^2)}{\alpha_2 - \alpha_1} \quad (9)$$

$$c_2 = \frac{\left(\frac{\chi''_{ijk}}{\chi_{0ijk}} - \frac{\chi'_{ijk}}{\chi_{0ijk}}\alpha_1\right)(1+\alpha_2^2)}{\alpha_2 - \alpha_1} \quad (10)$$

where $\alpha_1 = \omega\tau_1$ and $\alpha_2 = \omega\tau_2$ such that $\alpha_2 > \alpha_1$.

The experimental c_1 and c_2 were calculated from the parabolic fitted curve of χ'_{ijk}/χ_{0ijk} and χ''_{ijk}/χ_{0ijk} against w_{jk} at $w_{jk} \to 0$ as shown in Figures 2 and 3 respectively. The theoretical c_1 and c_2 were also calculated in terms of χ'_{ijk}/χ_{0ijk} and χ''_{ijk}/χ_{0ijk} following Frolich's equations[9].

(iii) Symmetric and asymmetric distribution parameter γ and δ

The nine systems of (NMA + Ac) in C_6H_6 for different mole fractions x_j's of Ac exhibiting molecular non- rigidity are expected to show symmetric or asymmetric distribution of relaxation parameters as :

$$\frac{\chi^{*}_{ijk}}{\chi_{0ijk}} = \frac{1}{1+\left(j\omega\tau_{s}\right)^{1-\gamma}} \tag{11}$$

$$\frac{\chi^{*}_{ijk}}{\chi_{0ijk}} = \frac{1}{\left(1+j\omega\tau_{cs}\right)^{\delta}} \tag{12}$$

where γ = symmetric and δ = asymmetric distribution parameters related to symmetric τ_s and characteristic relaxation times τ_{cs} respectively .

Equation (11), on simplification of real and imaginary parts yields :

$$\gamma = \frac{2}{\pi}\tan^{-1}\left[\left(1-\frac{\chi^{'}_{ijk}}{\chi_{0ijk}}\right)\frac{\chi^{'}_{ijk}}{\chi^{''}_{ijk}} - \frac{\chi^{''}_{ijk}}{\chi_{0ijk}}\right] \tag{13}$$

$$\tau_s = \frac{1}{\omega}\left[1\Big/\left\{\left(\frac{\chi^{'}_{ijk}}{\chi^{''}_{ijk}}\right)\cos\left(\frac{\gamma\pi}{2}\right)-\sin\left(\frac{\gamma\pi}{2}\right)\right\}\right]^{\frac{1}{1-\gamma}} \tag{14}$$

where $\frac{\chi^{'}_{ijk}}{\chi_{0ijk}}$ and $\frac{\chi^{''}_{ijk}}{\chi_{0ijk}}$ are obtained from Figures 2 and 3 at $w_{jk} \to 0$.

On simplification of equation (12) further, one gets:

$$\frac{1}{\phi}\log(\cos\phi) = \frac{\log\left[\left(\chi^{'}_{ijk}/\chi_{0ijk}\right)/\cos(\phi\delta)\right]}{(\phi\delta)} \tag{15}$$

$$\tan(\phi\delta) = \frac{\left(\chi^{''}_{ijk}/\chi_{0ijk}\right)}{\left(\chi^{'}_{ijk}/\chi_{0ijk}\right)} \tag{16}$$

where tan $\phi = \omega\tau_{cs}$.

Measured parameter of $\left[\log\left\{\left(\chi^{'}_{ijk}/\chi_{0ijk}\right)/\cos(\phi\delta)\right\}\right]/\phi\delta$ of equations (15) and (16) are estimated and the value of ϕ is ascertained from the theoretical curve of $1/\phi \log(\cos\phi)$ against ϕ [13]. δ can also be found out from the known ϕ of equation [16].

(iv) Dipole moments μ_{jk} from susceptibility measurement technique

The imaginary part of dielectric orientational susceptibility $\chi^{''}_{ijk}$ as a function of w_{jk} of a binary polar mixture can be written as[9] :

$$\chi^{''}_{ijk} = \frac{N\rho_{ijk}\mu^{2}_{jk}}{27\varepsilon_0 M_{jk} K_B T}\left(\frac{\omega\tau_{jk}}{1+\omega^{2}\tau^{2}_{jk}}\right)\left(\varepsilon_{ijk}+2\right)^{2} w_{jk} \tag{17}$$

On differentiation of above equation w.r. to w_{jk} and at infinite dilution i.e $w_{jk} \to 0$ yields:

$$\left(\frac{d\chi^{''}_{ijk}}{dw_{jk}}\right)_{w_{jk}\to 0} = \frac{N\rho_{i}\mu^{2}_{jk}}{27\varepsilon_0 M_{jk} K_B T}\left(\frac{\omega\tau_{jk}}{1+\omega^{2}\tau^{2}_{jk}}\right)\left(\varepsilon_{i}+2\right)^{2} \tag{18}$$

where μ_{jk} is the dipole moment of binary polar mixture of molecular weight $M_{jk} = M_j x_j + M_k x_k$; x_j being the mole fraction of Ac (j) in the binary polar mixture of j and k such that $x_j + x_k = 1$.

At infinite dilution i.e $w_{jk} \to 0$, the density of solution $\rho_{ijk} \to \rho_i$ and $(\varepsilon_{ijk} + 2)^2 \to (\varepsilon_i + 2)^2$. The other symbols carry usual meaning in SI unit as mentioned elsewhere[9].

On comparison of equations (8) and (18) one gets :

$$\left(\frac{d\chi'_{ijk}}{dw_{jk}}\right)_{w_{jk}\to 0} = \frac{N\rho_i \mu_{jk}^2}{27\varepsilon_0 M_{jk} K_B T}\left(\frac{1}{1+\omega^2\tau_{jk}^2}\right)(\varepsilon_i + 2)^2 \qquad (19)$$

Equation (19) yields dipole moment μ_{jk} as:

$$\mu_{jk} = \left[\frac{27\varepsilon_0 M_{jk} K_B T \beta}{N\rho_i (\varepsilon_i + 2)^2 b}\right]^{\frac{1}{2}} \qquad (20)$$

where β is the slope of χ'_{ijk} - w_{jk} curve at $w_{jk} \to 0$ and b is a dimensionless parameter.

RESULTS AND DISCUSSION

The measured data of static ε_{0ijk} and high frequency relative permittivity $\varepsilon_{\infty ijk}$ at different w_{jk}'s and mole fraction x_j's of Ac of the binary polar mixture were extracted from the Debye- pellat theory [11] using measured τ due to Gopalakrishna's method. The data are again plotted against w_{jk}'s in the low concentration region and found to obey the linear relation of Heston et al[16]. The measured ε_{0ijk} (±1%) and $\varepsilon_{\infty ijk}$ (±1%) at different w_{jk}'s(± 4.37x10^{-4} %) and x_j's of Ac are utilized to estimate static dipole moment μ_{0s} from the slope a_1 of experimental parameter X_{ijk} against w_{jk} parabolic curve. μ_{0s}'s(± 5 %) are in excellent agreement with the measured μ_{jk} due to Gopalakrishna's method in the high frequency electric field validating the measurements of ε_{0ijk} and $\varepsilon_{\infty ijk}$ at different x_j's of Ac employing Debye-Pellat theory. All the curves of X_{ijk} against w_{jk} at different x_j's of Ac are parabolic and well separated for 25,30,35 and 40ºC temperatures respectively. A typical example of such curves for 0.50 x_j's of Ac is shown in Figure (1). As evident from Figure-1 that the polarization is maximum at lower temperature and increases gradually with the rise of weight fractions w_{jk}'s of binary polar mixture. Nine systems as seen in Figures 2 and 3 out of twenty exhibit double relaxation times τ_2 and τ_1 accurate upto ± 10% [13] at different experimental temperatures and mole fractions x_j's of Ac under 9.88 GHz electric field. τ's were also calculated from ratio of slopes of χ''_{ijk} - w_{jk} and χ'_{ijk} - w_{jk} curves of equation (8) and linear slope χ''_{ijk} - χ'_{ijk} curve of equation (7). The estimated τ's from both the methods are in excellent agreement with the reported τ's due to Gopalakrishna's method. τ_1's or τ_2's for the systems showing either double or single relaxation mechanism are also in excellent agreement with the reported τ's. This fact signifies that double relaxation phenomena offer better understanding of relaxation behaviour of binary polar mixture by yielding microscopic as well as macroscopic relaxation as observed [13], in case of a polar molecule dissolved in nonpolar solvent. The most probable relaxation time $\tau_0 = \sqrt{\tau_1 \tau_2}$ are also estimated along with symmetric τ_s and characteristics τ_{cs} respectively. The estimated τ_0 agree well with the τ_s in comparison to larger τ_{cs} signifying the fact that the nine non-rigid binary polar mixture obey the symmetric relaxation mechanism rather than asymmetric distribution of relaxation behavior. The values of symmetric distribution parameters γ are also very low in comparison to asymmetric distribution parameters δ establishing the above fact.

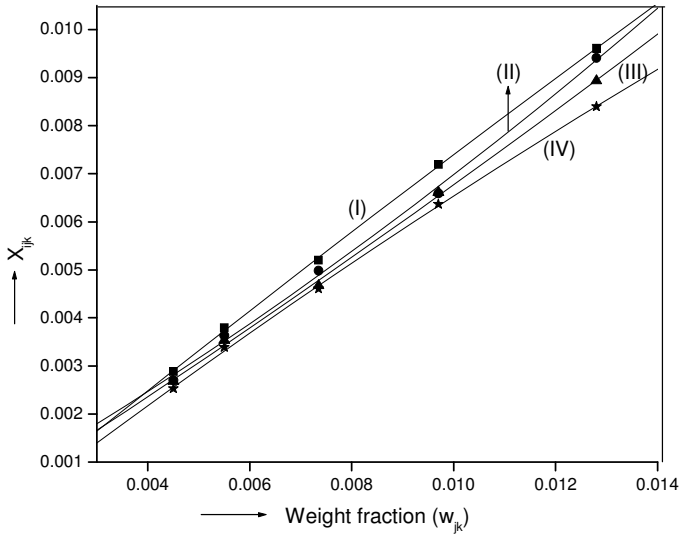

Fig.-1: Variations of static experimental parameter X_{ijk} against weight fractions w_{jk}'s for 0.50 mole fraction x_j of acetone at different temperatures.(I) __■__ (II) __●__ (III) __▲__ (IV) __★__ for 25, 30,35 and 40 ° C respectively.

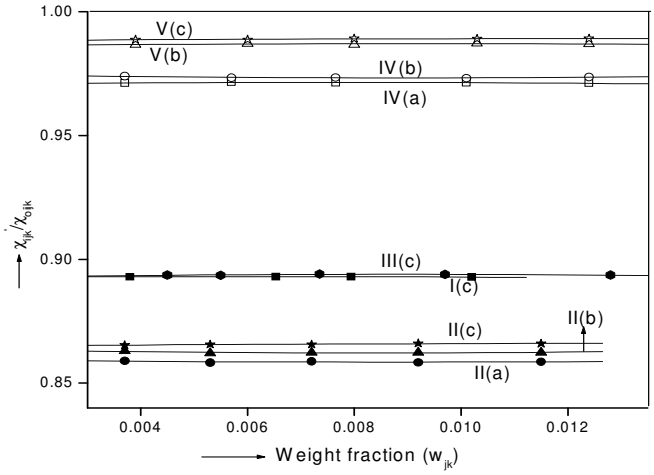

Fig.-2: Variations of $\frac{\chi'_{ijk}}{\chi_{0ijk}}$ against w_{jk}'s of binary polar mixture(NMA + Ac)in C_6H_6 under 9.88 GHz electric field.
I(c) __■__ for x_j=0.00 at 35 ° C; II(a) __●__ for x_j=0.30 at 25 ° C; II(b) __▲__ for x_j=0.30 at 30 ° C; II(c) __★__ for x_j=0.30 at 35 ° C; III(c) __⬢__ for x_j=0.50 at 35 ° C; IV(a) __□__ for x_j=0.70 at 25 ° C; IV(b) __○__ for x_j=0.70 at 30 ° C; V(b) __△__ for x_j=1.0 at 30 ° C; V(c) __☆__ for x_j=1.0 at 35 ° C respectively.

The estimated τ's are found to decrease with the rise of temperature obeying the Debye relaxation mechanism as observed [7].

The relative contributions c_1 and c_2 due to τ_1 and τ_2 were calculated from the graphical plots of χ'_{ijk}/χ_{0ijk} and χ''_{ijk}/χ_{0ijk} against w_{jk} at infinite dilution i.e. $w_{jk}\rightarrow 0$ as shown in Figures 2 and 3.The

theoretical values of c_1 and c_2 were also calculated using Fröhlich's equations[11].The calculated experimental $c_1 \cong 1$ and c_2 is zero or –ve having very low value. Nevertheless, the experimental $c_1 + c_2 \cong 1$. This is probably due to the fact that a part of the molecule is responsible for rotation in the hf electric field[13] thereby yielding almost full contribution to c_1.

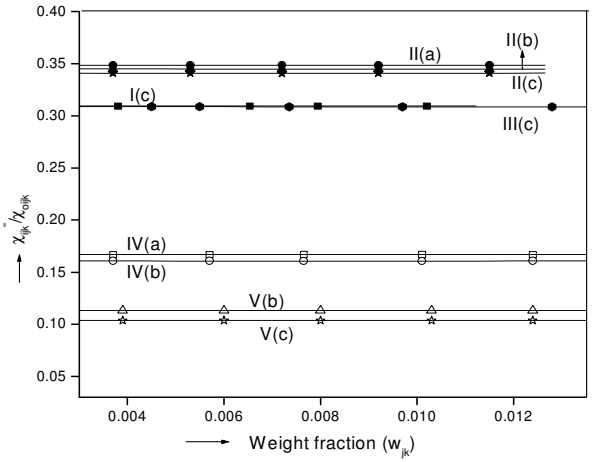

Fig.-3: Variations of $\frac{\chi''_{ijk}}{\chi_{0ijk}}$ against w_{jk}'s of binary polar mixture(NMA + Ac)in C_6H_6 under 9.88 GHz electric field. I(c) __■__ for x_j=0.00 at 35° C; II(a) __●__ for x_j=0.30 at 25° C; II(b) __▲__ for x_j=0.30 at 30° C; II(c) __★__ for x_j=0.30 at 35° C; III(c) __⬢__ for x_j=0.50 at 35° C; IV(a) __□__ for x_j=0.70 at 25° C; IV(b) __○__ for x_j=0.70 at 30° C; V(b) __△__ for x_j=1.0 at 30° C; V(c) __☆__ for x_j=1.0 at 35° C respectively.

The agreement of τ_1 with the most probable or average $\tau_0 (= \sqrt{\tau_1 \tau_2})$ calculated from measured τ_1 and τ_2 is in accord with above facts. The theoretical c_1's and c_2's are of reasonable values but $c_1 + c_2 \geq 1$ in almost all cases rule out the possible existence of distribution of τ's between two discrete τ_1 and τ_2. The graphs of $\chi'_{ijk} / \chi_{0ijk}$ and $\chi''_{ijk} / \chi_{0ijk}$ against w_{jk} of Figures-2 and 3 are all parabolic and fail to exhibit the usual concave and convex shape [9].This fact invariably demands the accurate measurements of ε_{0ijk} and $\varepsilon_{\infty ijk}$ [10] at different w_{jk}. Dipole moments μ_2 and μ_1 due to dimensionless parameter b's and slope β's of χ'_{ijk} - w_{jk} curves were estimated along with μ's due to τ's from ratio of slopes (equation-8) and linear slope (equation-7) respectively. They are compared with those of μ_2 and μ_1. The reported μ's are in excellent agreement with μ_2 or μ_1 for eleven and nine systems respectively. Estimated μ's are slightly lower than the reported μ's of pure Ac in benzene. This is probably due to the fact that the molecule Ac exists in solute-solvent association i.e. monomer form as observed earlier [6].The χ'_{ijk} - w_{jk} curves of nine systems showing double relaxation phenomena are sketched in Figure (4).The variation of τ_{jk}'s or τ_0's as well as μ_{jk}'s or μ_0's at different experimental temperatures of 25,30,35 and 40ºC are plotted against x_j's of Ac of all the four systems as shown in Figure (4). Unlike the systems III (-▲-) the variation of τ's for the system I (-■-), II (-●-) and IV (-*-) exhibit convex shape upto x_j =0.3 of Ac and then decreases.μ's, on the other hand, show convex nature for I (…□…),II (…○…) and concave nature for III (…△…) and IV (…☆…) respectively.

The convex nature of the curves may be due to the solute – solute (dimer) molecular associations occurring up to x_j = 0.3 of Ac and then rupture of dimer happens to facilitate solute-solvent (monomer) molecular association up to x_j = 1.0 of Ac. At suitably higher temperature solute – solvent molecular

association occurs initially instead of solute – solute molecular association resulting in concave nature of curve up to certain x_j's of Ac thereafter solute – solute (dimer) association results with the enrichment of Ac. Molecular associations can also be inferred from the theoretical dipole moment, μ_{theo}'s of the available bond angles and bond moments of the polar molecules. The possible existence of solute –solute (dimer) or solute-solvent (monomer) molecular association may arise [9] due to difference in electron affinity between the two adjacent atoms of a polar group causing inductive, mesomeric and electromeric effects in them. The variation of μ_{0jk} against t in ºC for all the systems are, however, convex except x_j = 0.50 or 1.00 of Ac for systems III (-▲-) and V (-⬢-) .The variation of μ_{0jk} – t as shown in figure 6 is explained on the basis of elongation of bond angles and bond moments at higher temperature. Considering the rotation of binary polar mixture dissolved in non polar solvent under high frequency electric field as a rate process[15] ; the thermodynamic energy parameters like enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and free energy of activation ΔF_τ were calculated from the slopes and intercepts (Figure-7) of ln ($\tau_0 T$) against 1/T curves at different x_j's of Ac of following form :

$$\ln(\tau_0 T)=\ln(Ae^{-\Delta S\tau / R})+\Delta H_\tau / RT \qquad (21)$$

where $\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau$

The enthalpy of activation ΔH_η of the binary polar mixture due to viscous flow of the solvent was, however, related to τ_{jk} at different temperatures by :

$$\tau_{jk} = \frac{A\eta^{\gamma}}{T} \qquad (22)$$

where η is the coefficient of viscosity of the solvent C_6H_6 and γ is the slope of ln ($\tau_0 T$) against ln η curve. $\Delta H_\tau > \Delta H_\eta$ for all the systems except x_j = 0.0 and 0.5 of Ac. It may be due to the fact that enthalpy of activation depends upon the bonding nature of the molecules and excitations to activated states involves breaking of bonds.

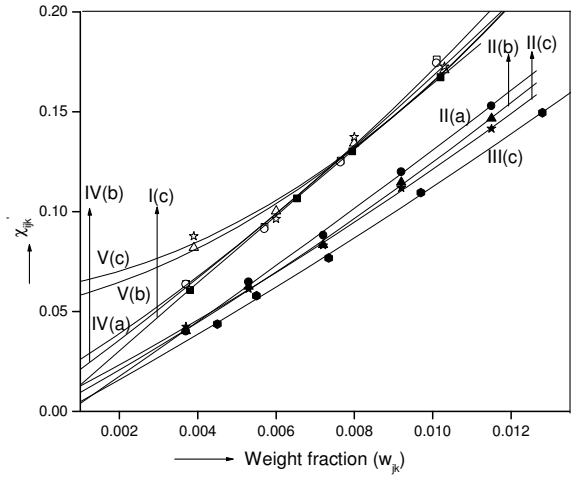

Fig.-4: Variation of χ'_{ijk} against weight fractions w_{jk}'s of nine systems exhibiting double relaxation phenomena for different x_j's of acetone and experimental temperatures under 9.88 GHz electric field. I(c) __■__ for x_j=0.00 at 35 ° C; II(a) __●__ for x_j=0.30 at 25 ° C; II(b) __▲__ for x_j=0.30 at 30 ° C; II(c) __★__ for x_j=0.30 at 35 ° C; III(c) __⬢__ for x_j=0.50 at 35 ° C; IV(a) __□__ for x_j=0.70 at 25 ° C; IV(b) __○__ for x_j=0.70 at 30 ° C; V(b) __△__ for x_j=1.0 at 30 ° C; V(c) __☆__ for x_j=1.0 at 35 ° C respectively.

The greater magnitude of ΔH_τ may reveal the different types of bonding and breaking of bonds to different extent in the dielectric relaxation process[6]. ΔS_τ's for the systems are -ve for x_j = 0.0 , 0.50 and 1.0 respectively. This indicates that the change of entropy of the systems in the activated process is

cooperative unlike rest of the systems showing non cooperative environment resulting activated states are unstable.

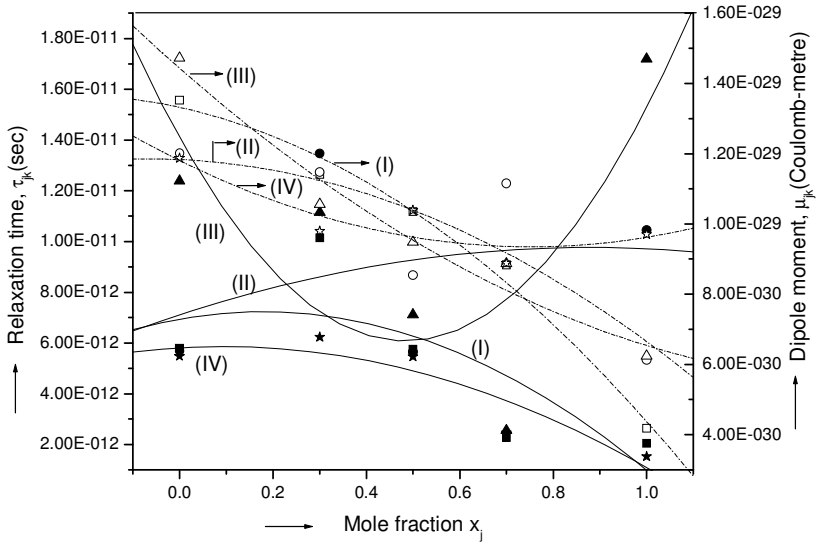

Fig.-5: Variation of τ_{jk} or μ_{jk} of binary polar mixture(NMA + Ac)in C_6H_6 under 9.88 GHz electric field. (I) __■__ and …□… at 25° C; (II) __●__ and …○…at 30° C; (III) __▲__ and …△…at 35° C; (IV) __★__ and …☆…at 40° C.

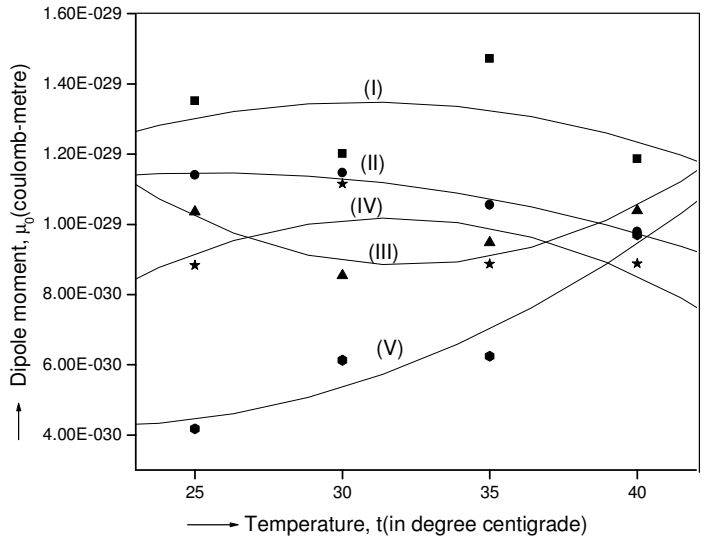

Fig.-6: Variation of dipole moment μ_{jk} against temperature t in° C of binary polar mixture(NMA +Ac)in C_6H_6 under 9.88 GHz electric field. (I)__■__ (II) __●__(III) __▲__(IV) __★__(V) __⬢__ for x_j=0.0,0.30,0.50,0.70 and 1.0 of Ac respectively.

The value of γ (= $\Delta H_\tau/\Delta H_\eta$)for the systems are ascertained from the slope of ln (τ_0T) against ln η curve to shed light on the solvent environment of the binary polar mixture. γ>0.55(Class I) for x_j = 0.3 and 0.7 of Ac reveal that the systems do not behave as solid phase rotator, the rest other systems for x_j = 0.0, 0.5 and

1.0 of Ac; it is observed that γ<0.45(Class II) exhibiting solid Phase rotator behaviour [20]. γ (= $\Delta H_\tau / \Delta H_\eta$) exponent found for Kalman factor suggests that successful insight into the molecular dynamics of polar liquids can be gained through Debye- Stokes- Einstein(DSE) model based on hydrodynamic basis. This model correlates a connection between relaxation time τ of polar solute and transport property η of the non polar solvent in ordinary fluids[21] as $\tau \alpha \eta/T$ in Debye factor. In viscous fluids, both the translational and rotational motion of the .molecules are involved indicating the breakdown of DSE model. It is evident that τ/η will vary markedly with temperature revealing a change of transport mechanism and an approximate and empirical relation can at best be formulated in terms of γ exponent and Kalman factor[21] The magnitude of estimated Kalman factor $\tau_{jk}T/\eta^{\gamma}$ vary system to system whereas Debye factor $\tau_{jk}T/\eta$ remains constant for all systems revealing the fact that Debye relaxation mechanism match well for the binary polar mixture of (NMA + Ac) in C_6H_6.

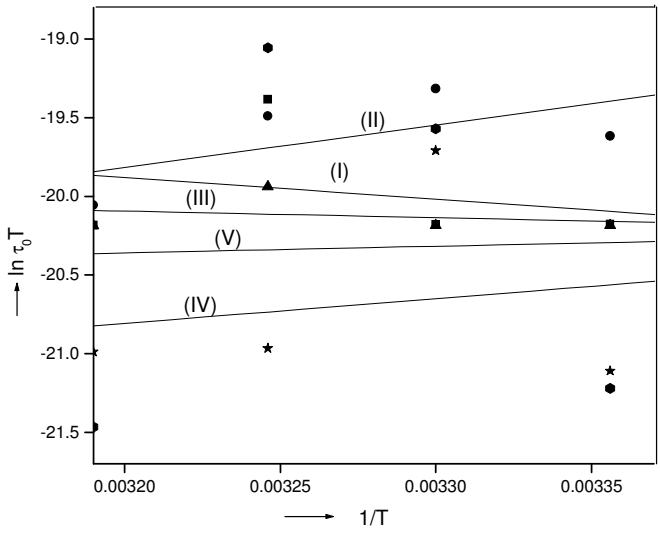

Fig.-7: Linear plot of ln(τ_0 T) against 1/T curve of binary polar mixture(NMA + Ac)in C_6H_6 under 9.88 GHz electric field. (I)__ ■ __ (II) __ ● __(III) __ ▲ __(IV) __ ★ __(V) __ ⬢ __ for x_j=0.0,0.30,0.50,0.70 and 1.0 of acetone respectively.

CONCLUSIONS

A simple and straight forward analytical method is proposed to study the double relaxation times τ_2 and τ_1 due to whole molecular rotation and flexible part of the binary polar mixture (NMA+Ac) in C_6H_6 at different temperatures and x_j's of Ac in terms of measured susceptibility χ_{ijk}'s for different w_{jk}'s of solutes using single frequency susceptibility measurement technique at 9.88 GHz electric field. Reported and measured τ's from linear slope and ratio of slopes methods are found to agree excellently with the τ_1's of nine systems exhibiting double relaxation mechanism and τ_2's of the rest eleven systems showing monorelaxation behaviour. The most probable τ's and μ's are plotted against x_j's of Ac at different temperatures to show solute-solute(dimer) molecular association upto x_j=0.3 and solute-solvent(monomer) association thetreafter upto x_j=1.0 of Ac. The static dipole moment μ_{0s}'s are measured from ε_{0ijk} and $\varepsilon_{\infty ijk}$ at different w_{jk}'s using Debye-Pellat theory and compared with high frequency μ's validating the applicability of the method. The solvent environment around the solute molecule is established from γ exponent using Eyring's rate theory equation. The Debye- Stokes-Einstein(DSE) model based on hydrodynamic basis relates τ of polar solutes with viscosity η of the solvent in ordinary fluids whereas breakdown occurs for viscous fluids.

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