Double relaxation times $\tau_2$ and $\tau_1$ 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$_6$H$_6$ have been estimated analytically from complex high frequency orientational susceptibility $\chi_{ijk}^{*}$ 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 $\tau_2$ and $\tau_1$ at different molecular environment. $\tau_2$'s of eleven systems whereas $\tau_1$ of nine systems agree well with the reported & measured $\tau'$s indicating a part of the molecule is rotating under high frequency electric field. The plot of $\tau_{jk}$ and $\mu_{jk}$ 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. $\mu_2$ and $\mu_1$ as well as static $\mu_0$'s are compared reported value to see the applicability of Debye-Pellat theory in the measurement of $\varepsilon_{0ijk}$ and $\varepsilon_{\infty ij}$ 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 $\tau_{jk}T/\eta^2$ 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. Nothing can relax from perfection. It thus gained attention of a large number of workers to shed light on the structure, shape and sizes of polar liquid molecules as well as their associational behaviour through various established methods. 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 $\tau$ and dipole moment $\mu$ 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 measured $\tau$ and $\mu$ of the binary polar mixtures of N, methyl acetamide and acetone (NMA+Ac) dissolved in C$_6$H$_6$ for 0.0, 0.3,0.5,0.7 and 1.0 mole fractions $x_j$’s of acetone(CH$_3$COCH$_3$) 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, however, measured $\tau$ and $\mu$ of the binary polar liquid mixture under identical molecular environment using high frequency conductivity technique to infer structural and associational behaviour as well as molecular dynamics from measured thermodynamic energy parameters. The conductivity $\sigma_n$’s
measurement technique, is related to bound molecular charge\(^3\) of the polar molecules unlike relative permittivity \(\varepsilon_{ij}\) which is concerned with all types of polarizations. The susceptibility \(\chi_{ij}\)'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\(^2,3,4\). However, no such study on the existence of double relaxation mechanism for the binary polar mixture of (NMA+Ac) dissolved in \(\text{C}_6\text{H}_6\) 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 \(\text{C}_6\text{H}_6\) under same molecular environment\(^6\) in terms of measured real \(\chi_{ijk}'\)\((=\varepsilon_{ijk}' - \varepsilon_{wijk})\) and imaginary \(\chi_{ijk}''\) \((=\varepsilon_{ijk}''\)\) parts of high frequency orientational susceptibility \(\chi_{ijk}'\) \((=\varepsilon_{ijk}' - \varepsilon_{wijk})\) and \(\chi_{ijk}''\) \((=\varepsilon_{ijk}'' - \varepsilon_{wijk})\) which is real from single frequency susceptibility measurement technique\(^9\). The double relaxation times \(\tau_2\) and \(\tau_1\) due to end over end rotation of the whole molecule and their flexible parts under high frequency electric field as well as \(\mu_2\) and \(\mu_1\) enable one to get information on intra and inter-molecular interactions and their structures. \(\tau_2\) and \(\tau_1\) are very much sensitive and required to be measured accurately the high frequency relative permittivity \(\varepsilon_{wijk}\) and static relative permittivity \(\varepsilon_{0ijk}\)\(^10\). In absence of reliable available measured data of \(\varepsilon_{wijk}\) and \(\varepsilon_{0ijk}\) 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. \(\varepsilon_{wijk}\) and \(\varepsilon_{0ijk}\) thus estimated are used to get static dipole moment \(\mu_{0ij}\) 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 \(\text{N, methyl acetamide (NMA)}\) 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 \(\text{C}_6\text{H}_6\) in terms of measured \(\tau\) and \(\mu\) 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 \(\sim\) 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 \(\mu_{0ij}\) and double relaxation times \(\tau_2\) and \(\tau_1\) as well as \(\mu_2\) and \(\mu_1\) 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 \(\mu_{0ij}\)'s and \(\mu_{jk}\)'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 \(\Delta H\)\(^1\), entropy of activation \(\Delta S\)\(^1\), and free energy of activation \(\Delta G\)\(^1\) considering the rotation of the binary polar mixture under high frequency electric field as a rate process\(^15\).

**EXPERIMENTAL**

The solvent \(\text{C}_6\text{H}_6\), NMA and Ac were distilled through a long vertical fractionating column 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 \(\varepsilon_{ijk}^r\) \((\pm0.5\%)\) and imaginary \(\varepsilon_{ijk}^\prime\) \((\pm1.7\%)\) parts of complex relative permittivity \(\varepsilon_{ijk}^\ast\) were measured\(^6\) using X-band microwave bench tuned at 9.88 GHz frequency for different weight fractions \(w_{jk}\)'s \((\pm 4.37\times10^{-4} \%)\) of binary polar mixture at 25,30,35
and 40°C experimental temperatures. $\varepsilon_{\text{ijk}}$ and $\varepsilon_{0\text{ijk}}$ at different $w_{jk}$’s of polar liquid are estimated using standard form of Debye-Pellat equation from measured relaxation time $\tau$. The accuracies of the measured data $\varepsilon_{\text{ijk}}$ and $\varepsilon_{0\text{ijk}}$ are within ±1%. $\varepsilon_{\text{ijk}}$ and $\varepsilon_{0\text{ijk}}$ 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 $\mu_{0s}$**

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

$$\varepsilon_{0\text{ijk}} - \varepsilon_{\text{ijk}} = (\varepsilon_{0i} + 2)(\varepsilon_{\text{ijk}} + 2) + \frac{N\rho_i\mu_{js}^2}{27\varepsilon_{0i}M_{jk}K_bT} w_{jk} (1 - \psi w_{jk})^{-1}$$

where $\varepsilon_0$ is the absolute permittivity of free space $= 8.854 \times 10^{-12}$ Fm$^{-1}$. All other symbols carry usual meanings $13$.

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

$$\frac{\varepsilon_{0\text{ijk}} - \varepsilon_{\text{ijk}}}{\varepsilon_{0\text{ijk}} + 2} = \frac{\varepsilon_{0i} - \varepsilon_{\text{ijk}}}{\varepsilon_{0i} + 2} + \frac{N\rho_i\mu_{js}^2}{27\varepsilon_{0i}M_{jk}K_bT} w_{jk} (1 - \psi w_{jk})^{-1}$$

$$X_{\text{ijk}} = X_i + \frac{N\rho_i\mu_{js}^2}{27\varepsilon_{0i}M_{jk}K_bT} w_{jk} + \frac{N\rho_i\mu_{js}^2}{27\varepsilon_{0i}M_{jk}K_bT} \psi w_{jk}^2$$

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

$$\mu_{0s} = \left[ \frac{27\varepsilon_{0i}M_{jk}K_bT a_i}{N\rho_i} \right]^{\frac{1}{2}}$$

where $a_i$ is the slope of $X_{\text{ijk}}$ - $w_{jk}$ curve at $w_{jk} \to 0$. The curves of $X_{\text{ijk}}$ - $w_{jk}$ for 0.5 $x_j$ of Ac is shown in Figure 1. $M_i$ 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 $\mu_{0s}$’s with reported $\mu$’s signify the validity of method adopted in measuring $\varepsilon_{\text{ijk}}$ and $\varepsilon_{0\text{ijk}}$ at different $w_{jk}$’s by Debye-Pellat theory.

**(ii) Double relaxation times $\tau_1$ and $\tau_2$ and relative contributions $c_1$ and $c_2$**

Bergmann et al $18$ suggested a graphical method to get $\tau_1$ and $\tau_2$ of a binary (jk) polar liquid mixture dissolved in benzene (i) in terms of measured $\chi_{\text{ijk}}$, $\chi_{0\text{ijk}}$ and $\chi_{\text{ijk}}$ under different frequency of GHZ electric field and temperature T K as:

$$\frac{\chi_{\text{ijk}}}{\chi_{0\text{ijk}}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2}$$

$$\frac{\chi_{\text{ijk}}}{\chi_{0\text{ijk}}} = \frac{c_1 \omega \tau_1}{1 + \omega^2 \tau_1^2} + \frac{c_2 \omega \tau_2}{1 + \omega^2 \tau_2^2}$$

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

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

$$\frac{X_{ijk} - X_{0ijk}}{X_{0ijk}} = \omega (\tau_2 + \tau_1) \frac{\dot{X}_{ijk}}{X_{0ijk}} - \omega^2 \tau_1 \tau_2$$

(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 $\frac{X_{0ijk} - X_{ijk}}{X_{ijk}}$ plotted against $\frac{\dot{X}_{ijk}}{X_{ijk}}$ for different $w_{jk}$’s under a given angular frequency $\omega (=2\pi f)$. The intercepts and slopes yield $\tau_2$ and $\tau_1$.

$\tau$’s were also calculated from the linear slope of $\dot{X}_{ijk}$ against $X_{ijk}$ for different $w_{jk}$’s under a given angular frequency $\omega$ as suggested by Murthy et al.

$$\frac{d\dot{X}_{ijk}}{dw_{jk}} \bigg|_{w_{jk} \to 0} = \omega \tau$$

(7)

Both $X_{ijk}$ and $\dot{X}_{ijk}$ are the functions of $w_{jk}$’s. To avoid polar-polar interactions one could use the ratio of slopes of $\dot{X}_{ijk} - w_{jk}$ and $\dot{X}_{ijk} - w_{jk}$ curves at $w_{jk} \to 0$ to measure $\tau$.

$$\left( \frac{d\dot{X}_{ijk}}{dw_{jk}} \right)_{w_{jk} \to 0} = \omega \tau$$

(8)

$\tau$’s from equations (7) and (8) agree excellently with reported $\tau$ due to Gopalakrishna’s method. Symmetrical $\tau$, and characteristics $\tau_c$, are also compared with most probable $\tau_0$ of nine systems.

A continuous distribution of $\tau$’s between two extreme values of $\tau_2$ and $\tau_1$ for nine systems inspires one to calculate $c_1$ and $c_2$ from equations (4) and (5) as follows:

$$c_1 = \frac{\left( \frac{X_{ijk} - X_{0ijk}}{X_{0ijk}} \right) \left( \frac{X_{0ijk} - X_{ijk}}{X_{ijk}} \right)}{\alpha_2 - \alpha_1} \left( 1 + \alpha_1^2 \right)$$

(9)

$$c_2 = \frac{\left( \frac{X_{ijk} - X_{0ijk}}{X_{0ijk}} \right) \left( \frac{X_{0ijk} - X_{ijk}}{X_{ijk}} \right)}{\alpha_2 - \alpha_1} \left( 1 + \alpha_2^2 \right)$$

(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 $\dot{X}_{ijk} / X_{0ijk}$ and $\dot{X}_{ijk} / X_{0ijk}$ 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 $\dot{X}_{ijk} / X_{0ijk}$ and $\dot{X}_{ijk} / X_{0ijk}$ following Frolich’s equations.

(iii) Symmetric and asymmetric distribution parameter $\gamma$ and $\delta$

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:
where $\gamma$ = symmetric and $\delta$ = asymmetric distribution parameters related to symmetric $\tau_s$ and characteristic relaxation times $\tau_c$, respectively.

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

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

(13)

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

(14)

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

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

$$
\frac{1}{\phi} \log(\cos(\phi)) = \left( \frac{\chi'_{ijk}}{\chi''_{ijk}} \right) \left( \frac{\cos(\phi\delta)}{\cos(\delta)} \right) \left( \frac{\chi''_{ijk}}{\chi_{0ijk}} \right)
$$

(15)

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

(16)

where $\tan(\phi) = \omega \tau_c$.

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

(iv) Dipole moments $\mu_{jk}$ 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$^9$:

$$
\chi'_{ijk} = \frac{N \rho_{ijk} \mu_{jk}^2}{27 \epsilon_0 M_{jk} K_B T} \left( \frac{\omega \tau_{jk}}{1 + \omega^2 \tau_{jk}^2} \right) (\epsilon_i + 2) w_{jk}
$$

(17)

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

$$
\left. \frac{d \chi_{ijk}}{d w_{jk}} \right|_{w_{jk} \to 0} = \frac{N \rho_{ijk} \mu_{jk}^2}{27 \epsilon_0 M_{jk} K_B T} \left( \frac{\omega \tau_{jk}}{1 + \omega^2 \tau_{jk}^2} \right) (\epsilon_i + 2) w_{jk}
$$

(18)
where $\mu_{jk}$ is the dipole moment of binary polar mixture of molecular weight $M_{jk} = M_jx_j + M_kx_k$; $x_j$ 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:

$$\frac{dX_{ijk}}{dw_{jk}} \bigg|_{w_{jk} \to 0} = \frac{N\rho_j\mu^2_{jk}}{27\varepsilon_0 M_{jk}K_BT} \left( \frac{1}{1 + \omega^2 \tau^2_{jk}} \right) (\varepsilon_i + 2)^2$$ \hspace{1cm} (19)

Equation (19) yields dipole moment $\mu_{jk}$ as:

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

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

### RESULTS AND DISCUSSION

The measured data of static $\varepsilon_{ijk}$ and high frequency relative permittivity $\varepsilon_{\omega_{ijk}}$ 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 $\tau$ 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 $\varepsilon_{ijk}$ (±1%) and $\varepsilon_{\omega_{ijk}}$ (±1%) at different $w_{jk}$’s (± 4.37x10\(^{-4}\)% ) and $x_j$’s of $Ac$ are utilized to estimate static dipole moment $\mu_{ijk}$ from the slope $a_i$ of experimental parameter $X_{ijk}$ against $w_{jk}$ parabolic curve. $\mu_{ijk}$’s (±5%) are in excellent agreement with the measured $\mu_{ijk}$ due to Gopalakrishna’s method in the high frequency electric field validating the measurements of $\varepsilon_{ijk}$ and $\varepsilon_{\omega_{ijk}}$ 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 40°C 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 $\tau_2$ and $\tau_1$ accurate up to ± 10% \(^{13}\) at different experimental temperatures and mole fractions $x_j$’s of $Ac$ under 9.88 GHz electric field. $\tau$’s were also calculated from ratio of slopes of $\chi_{ijk}' - w_{jk}$ and $\chi_{ijk}' - w_{jk}$ curves of equation (8) and linear slope $\chi_{ijk}' - w_{jk}$ curve of equation (7). The estimated $\tau$’s from both the methods are in excellent agreement with the reported $\tau$’s due to Gopalakrishna’s method. $\tau_1$’s or $\tau_2$’s for the systems showing either double or single relaxation mechanism are also in excellent agreement with the reported $\tau$’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 $\tau_c$ and characteristics $\tau_{cs}$ respectively. The estimated $\tau_0$ agree well with the $\tau_c$ in comparison to larger $\tau_{cs}$ 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 $\gamma$ are also very low in comparison to asymmetric distribution parameters $\delta$ 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.

The estimated $\tau$'s are found to decrease with the rise of temperature obeying the Debye relaxation mechanism as observed. The relative contributions $c_1$ and $c_2$ due to $\tau_1$ and $\tau_2$ were calculated from the graphical plots of $X_{ijk}/X_{oijk}$ and $X_{ijk}/X_{oijk}$ against $w_{jk}$ at infinite dilution i.e. $w_{jk} \rightarrow 0$ as shown in Figures 2 and 3.
Theoretical values of $c_1$ and $c_2$ were also calculated using Fröhlich’s equations. The calculated experimental $c_1 + 1$ and $c_2$ is zero or –ve having very low value. Nevertheless, the experimental $c_1 + c_2 = 1$. This is probably due to the fact that a part of the molecule is responsible for rotation in the hf electric field thereby yielding almost full contribution to $c_1$.

The agreement of $τ_1$ with the most probable or average $τ_0 (\tau_1 \tau_2)$ 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 $c_1 + c_2 = 1$ 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 $X^{ijk}_{jk}$ and $X^{ijk}_{0ijk}$ against $w_{jk}$ of Figures-2 and 3 are all parabolic and fail to exhibit the usual concave and convex shape. This fact invariably demands the accurate measurements of $ε_{0ijk}$ and $ε_{wijk}$ at different $w_{jk}$. Dipole moments $μ_2$ and $μ_1$ due to dimensionless parameter b’s and slope B’s of $X^{ijk}_{jk}$ against $w_{jk}$ 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. The $X^{ijk}_{jk}$ curves of nine systems showing double relaxation phenomena are sketched in Figure (4). The variation of $τ_0$’s or $τ_2$’s as well as $μ_{ij}$’s or $μ_0$’s at different experimental temperatures of 25, 30, 35 and 40°C 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 the variation of $τ$’s for the system I exhibit convex shape up to $x_j = 0.3$ of Ac and then decreases, $μ$’s, on the other hand, show convex nature for I 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, $\mu_{\text{theo}}$'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 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 $\mu_{0jk}$ against $t$ in $^\circ$C 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 $\mu_{0jk} - t$ 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, the thermodynamic energy parameters like enthalpy of activation $\Delta H_\tau$, entropy of activation $\Delta S_\tau$ and free energy of activation $\Delta F_\tau$ were calculated from the slopes and intercepts (Figure-7) of $\ln (\tau_0T)$ against $1/T$ curves at different $x_j$'s of Ac of following form:

$$\ln(\tau_0T)=\ln(Ae^{-\Delta S_\tau/R})+\Delta H_\tau/RT$$

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

The enthalpy of activation $\Delta H_\tau$ of the binary polar mixture due to viscous flow of the solvent was, however, related to $\tau_{jk}$ at different temperatures by:

$$\tau_{jk} = \frac{A\eta_T}{T}$$

where $\eta$ is the coefficient of viscosity of the solvent $C_6H_6$ and $\gamma$ is the slope of $\ln (\tau_0T)$ against $\ln \eta$ 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.

The greater magnitude of $\Delta H_\tau$ may reveal the different types of bonding and breaking of bonds to different extent in the dielectric relaxation process. $\Delta S_\tau$'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 $\tau_{jk}$ or $\mu_{jk}$ of binary polar mixture(NMA + Ac)in C$_6$H$_6$ 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 $\mu_{jk}$ against temperature $t$ in °C of binary polar mixture(NMA +Ac)in C$_6$H$_6$ 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 $\gamma (=\Delta H_r/\Delta H_0)$ for the systems are ascertained from the slope of ln ($\tau_r/T$) against ln $\eta$ curve to shed light on the solvent environment of the binary polar mixture. $\gamma >0.55$(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 $\gamma<0.45$ (Class II) exhibiting solid Phase rotator behaviour. $\gamma(=\Delta H_r/\Delta H_\eta)$ 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 $\tau$ of polar solute and transport property $\eta$ of the non polar solvent in ordinary fluids as $\tau \propto \eta/T$ 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 $\tau/\eta$ 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 $\gamma$ exponent and Kalman factor. The magnitude of estimated Kalman factor $\tau_{jk}/\eta$ vary system to system whereas Debye factor $\tau_{jk}/\eta$ 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 $\ln(\tau_{jk}/T)$ 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 $\tau_2$ and $\tau_1$ 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 $\chi_{ijk}$’s for different $w_{ijk}$’s of solutes using single frequency susceptibility measurement technique at 9.88 GHz electric field. Reported and measured $\tau$’s from linear slope and ratio of slopes methods are found to agree excellently with the $\tau_1$’s of nine systems exhibiting double relaxation mechanism and $\tau_2$’s of the rest eleven systems showing monorelaxation behaviour. The most probable $\tau$’s and $\mu$’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 thereafter upto $x_j=1.0$ of Ac. The static dipole moment $\mu_0$’s are measured from $\chi_{ijk}$ and $\chi_{\infty ij}$ at different $w_{ijk}$’s using Debye-Pellat theory and compared with high frequency $\mu$’s validating the applicability of the method. The solvent environment around the solute molecule is established from $\gamma$ exponent using Eyring’s rate theory equation. The Debye- Stokes- Einstein (DSE) model based on hydrodynamic basis relates $\tau$ of polar solutes with viscosity $\eta$ of the solvent in ordinary fluids whereas breakdown occurs for viscous fluids.
REFERENCES

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