

Dielectric relaxation of binary polar liquid mixture measured in benzene at 10 GHz frequency

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Abstract. The dielectric relaxation times τ_{jk} 's and dipole moments μ_{jk} 's of the binary (jk) polar liquid mixture of N,N-dimethyl acetamide (DMA) and acetone (Ac) dissolved in benzene (i) are estimated from the measured real σ'_{ijk} and imaginary σ''_{ijk} parts of complex high frequency conductivity σ^*_{ijk} of the solution for different weight fractions w_{jk} 's of 0.0, 0.3, 0.5, 0.7 and 1.0 mole fractions x_j of Ac and temperatures (25, 30, 35 and 40°C) respectively under 9.88 GHz electric field. τ_{jk} 's are obtained from the ratio of slopes of $\sigma''_{ijk}-w_{jk}$ and $\sigma'_{ijk}-w_{jk}$ curves at $w_{jk} \rightarrow 0$ as well as linear slope of $\sigma''_{ijk}-\sigma'_{ijk}$ curves of the existing method (Murthy *et al.*, 1989) in order to eliminate polar-polar interaction in the latter case. The calculated τ 's are in excellent agreement with the reported τ 's due to Gopalakrishna's method. μ_{jk} 's are also estimated from slopes β 's of total conductivity $\sigma_{ijk}-w_{jk}$ curves at $w_{jk} \rightarrow 0$ and the values agree well with the reported μ 's from G.K. method. The variation of τ_{jk} 's and μ_{jk} 's with x_j of Ac reveals that solute-solute molecular association occurs within 0.0–0.3 x_j of Ac beyond which solute-solvent molecular association is predicted. The theoretical dipole moments μ_{theo} 's are calculated from bond angles and bond moments to have exact μ 's only to show the presence of inductive, mesomeric and electromeric effects in the substituent polar groups. The thermodynamic energy parameters are estimated from $\ln(\tau_{jk}T)$ against $1/T$ linear curve from Eyring's rate theory to know the molecular dynamics of the system and to establish the fact that the mixture obeys the Debye-Smyth relaxation mechanism.

Keywords. Relaxation time; hf conductivity; dipole moment; solute-solute interaction.

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1. Introduction

Dielectric relaxation phenomena of binary polar mixture of amides dissolved in nonpolar solvent under 10 GHz (X-band) electric field are of special interest to research workers [1–3] since long. The various molecular associations as well as structure, shape and size of the polar molecules can be ascertained through the relaxation phenomenon which is one of the most unresolved problems of physics today [4]. Schallamach [5] proposed that two polar liquid mixtures involving separate

absorption centre exhibit sufficiently different resolutions. They may show molecular relaxation of sufficiently larger composition having indistinguishable, overall and average single absorption centre. According to Frost and Smyth [6] the polar mixture may show single absorption peak on superposition when the difference of electric field frequency is at least five times. Chatterjee *et al* [7], however, studied the relaxation mechanism of binary polar mixtures of amides like N,N-dimethyl formamide (DMF) + N,N-tetramethyl urea (TMU) and N,N-dimethyl acetamide (DMA) + N,N-dimethyl formamide (DMF) dissolved in C_6H_6 for different mole fractions of DMF at various temperatures under 9.88 GHz electric field using conductivity measurement technique. They proposed various types of molecular associations in the mixture as well as structure of the polar molecules.

Recently, Rangra and Sharma [8] measured the dielectric relaxation parameters like real ϵ'_{ijk} and imaginary ϵ''_{ijk} parts of complex relative permittivity ϵ^*_{ijk} of binary (jk) or single j or k polar molecule of (DMA+Ac) dissolved in nonpolar solvent (i) benzene for different weight fractions w_{jk} 's, w_j 's or w_k 's at 25, 30, 35 and 40°C temperatures respectively for 0.0, 0.3, 0.5, 0.7 and 1.0 mole fractions x_j 's of Ac under 9.88 GHz electric field. They intended to predict the solute–solute (dimer) or solute–solvent (monomer) types of molecular associations in the ternary mixture of the solutions.

We, therefore, thought to make an extensive study further with the available data on the binary (jk) polar mixture of (DMA+Ac) dissolved in C_6H_6 in terms of measured real σ'_{ijk} and imaginary σ''_{ijk} parts of high frequency complex conductivity σ^*_{ijk} for different weight fractions w_{jk} 's of polar solutes at 9.88 GHz electric field under identical state of molecular environment [8] in SI unit. Both the constituent binary polar mixtures are nonaqueous aprotic solvents [9] having wide applications. DMA [10] is a good solvent of polymers and copolymers used in the spinning of artificial fibers. It also acts as building blocks of proteins and enzymes. Acetone is found in normal urine in traces. The amount is found to increase in starvation and diabetes. The binary mixture of solvent DMA and Ac possesses the dipole moments μ_{jk} 's and relative permittivity ϵ_{jk} 's in between the two constituents to have the required characteristics [11]. Moreover, the conductivity measurement technique is concerned with bound molecular charge of the polar molecules unlike ϵ_{ijk} 's which are related to all types of polarization. The purpose of the present paper is also to see the applicability of Debye–Smyth model in the case of the binary polar mixture of (DMA+Ac) in C_6H_6 using well-known extrapolation type least squares fitting procedure on the measured σ_{ijk} 's of solution like earlier [12]. The polar–nonpolar mixture of DMA in C_6H_6 exhibits double relaxation times τ_2 and τ_1 due to rotation of the whole and the flexible parts of the molecule in their effective dispersion region [13] of 9.987 GHz electric field. Thus, it is worthwhile to study the temperature variation data of (DMA+Ac) in C_6H_6 under 9.88 GHz electric field to know the molecular dynamics of the systems in terms of thermodynamic energy parameters too.

2. Experimental procedures

The pure polar liquids Ac (Siso Research Laboratory, Mumbai) and DMA (Central Drug House, Mumbai) as well as solvent C_6H_6 (E. Merk, Mumbai) were dried

Dielectric relaxation of binary polar liquid mixture

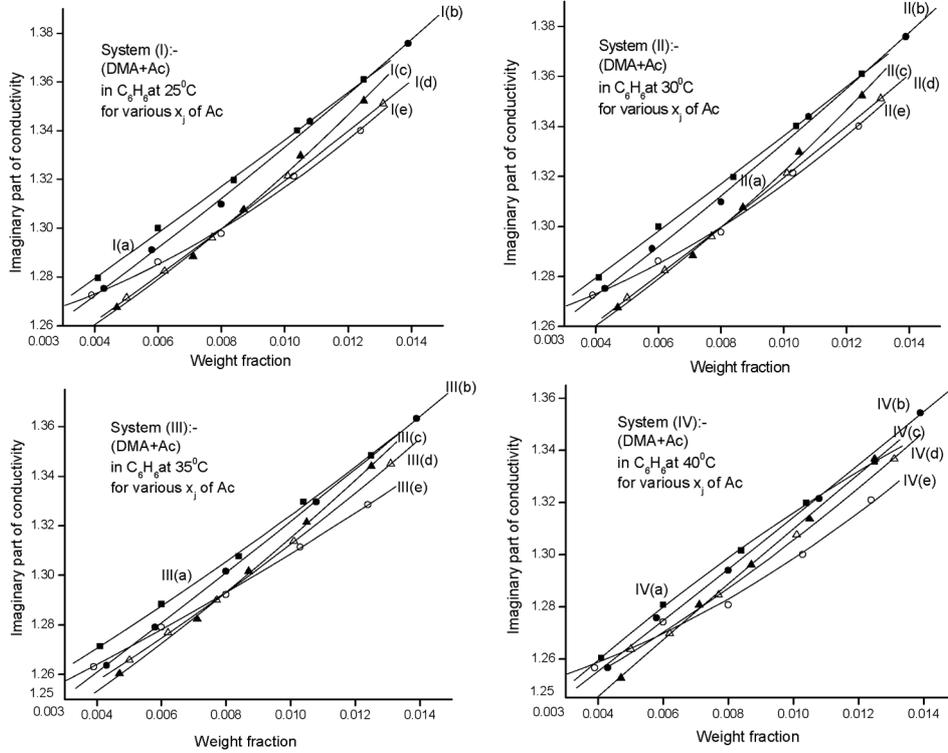


Figure 1. The variation of imaginary parts of conductivity σ''_{ijk} ($\Omega^{-1} \text{ m}^{-1}$) against weight fractions w_{jk} 's of binary polar mixture (DMA+Ac) dissolved in C_6H_6 for different x_j of acetone and temperatures under 9.88 GHz electric field. (a) \blacksquare , (b) \bullet , (c) \blacktriangle , (d) \triangle , (e) \circ , for 0.0, 0.3, 0.5, 0.7 and $1.0x_j$ of acetone respectively.

with 4 Å sieves for a long time with occasional shaking. The liquids were then distilled through a long vertical fractionating column and the middle fractions were collected for the preparation of binary polar mixture dissolved in solvent C_6H_6 . The real ε'_{ijk} ($\pm 1\%$) and imaginary ε''_{ijk} ($\pm 3\%$) parts of complex relative permittivity ε^*_{ijk} of binary solutes w_{jk} 's in C_6H_6 (i) were measured [8] from inexpensive X-band microwave facility at different temperatures (25, 30, 35 and 40°C) and mole fractions x_j 's of Ac (0.0, 0.30, 0.50, 0.70 and 1.0) respectively. The temperature of the dielectric cell containing the solution was controlled by a thermostat.

3. Results and discussions

The measured data can at best be qualitatively correlated with semi-empirical Debye [14] formula and equation of the form

$$\sigma''_{ijk} = \sigma_{\infty ijk} + (1/\omega\tau_{jk})\sigma'_{ijk}, \quad (1)$$

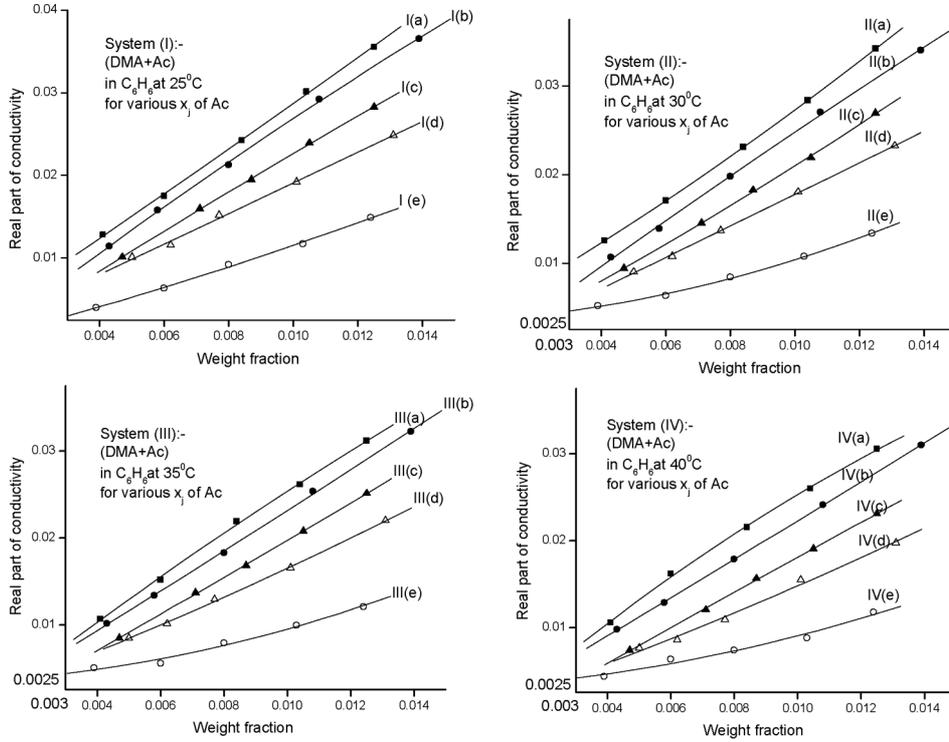


Figure 2. The variation of real parts of conductivity σ'_{ijk} ($\Omega^{-1} \text{ m}^{-1}$) against weight fractions w_{jk} 's of binary polar mixture (DMA+Ac) dissolved in C₆H₆ for different x_j of acetone and temperatures under 9.88 GHz electric field. (a) \blacksquare , (b) \bullet , (c) \blacktriangle , (d) \triangle , (e) \circ , for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of acetone respectively.

where $\sigma'_{ijk} = \omega \epsilon_0 \epsilon''_{ijk}$ and $\sigma''_{ijk} = \omega \epsilon_0 \epsilon'_{ijk}$ are the measured real and imaginary parts of complex high frequency conductivity σ^*_{ijk} in $\Omega^{-1} \text{ m}^{-1}$. The other symbols are of usual significance [12]. Both σ''_{ijk} and σ'_{ijk} are functions of w_{jk} 's. Equation (1) now becomes

$$\tau_{jk} = 1/\omega(\beta_2/\beta_1). \tag{2}$$

β_1 and β_2 are the slopes of $\sigma''_{ijk}-w_{jk}$ and $\sigma'_{ijk}-w_{jk}$ curves at $w_{jk} \rightarrow 0$ as shown in figures 1 and 2 to get τ_{jk} 's where polar-polar interactions are almost avoided.

On differentiation of eq. (1) with respect to σ'_{ijk} one gets τ_{jk} from

$$\tau_{jk} = 1/\omega\beta', \tag{3}$$

where $\beta' =$ linear slope of $\sigma''_{ijk}-\sigma'_{ijk}$ curve for different w_{jk} 's and experimental temperatures at a fixed x_j 's of Ac as shown in figure 3. The accuracy of measurement [8] in σ'_{ijk} and σ''_{ijk} and purity of the liquids are such that one cannot trust the data to better than 1% accuracy level. Figure 1 represents the nonlinear variation of σ''_{ijk}

Dielectric relaxation of binary polar liquid mixture

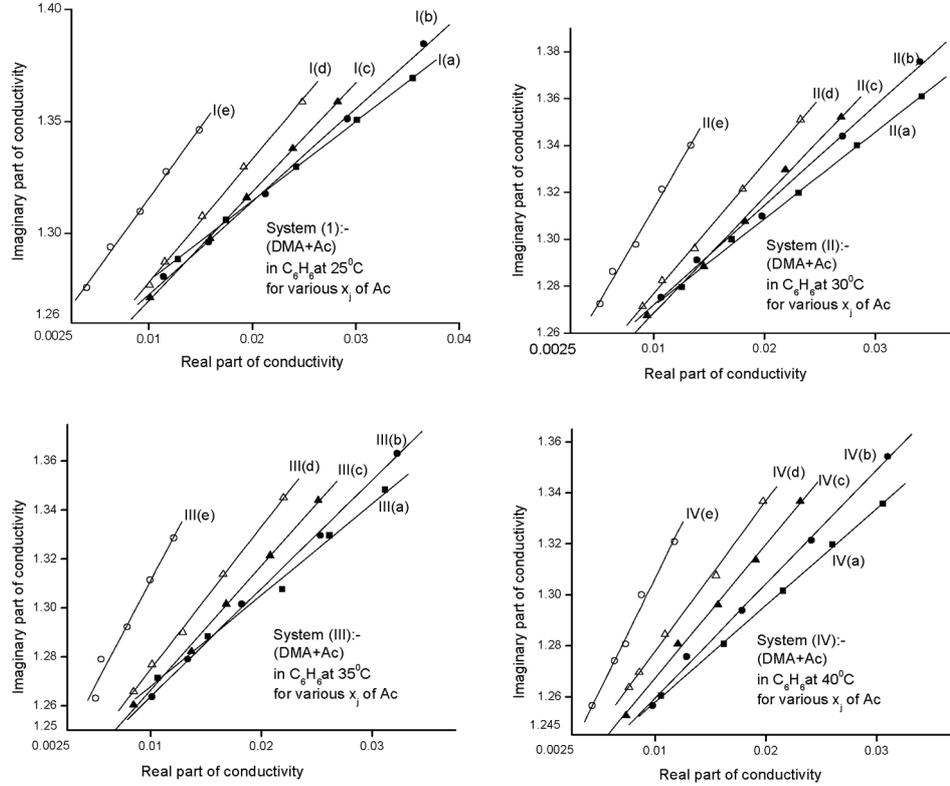


Figure 3. The linear plot of σ''_{ijk} against σ'_{ijk} of (DMA+Ac) polar mixture in benzene for different x_j of acetone and temperatures under 9.88 GHz electric field. (a) \blacksquare —, (b) \bullet —, (c) \blacktriangle —, (d) \triangle —, (e) \circ —, for 0.0, 0.3, 0.5, 0.7 and $1.0x_j$ of acetone respectively.

in $\Omega^{-1} \text{ m}^{-1}$ against w_{jk} 's at different temperatures and mole fractions of Ac for (DMA+Ac) in C_6H_6 solution. Similar observation is noted for $\sigma'_{ijk}-w_{jk}$ curves of figure 2. The correlation coefficients r 's for the fitted curves are very close to unity ($-1 \leq r \leq 1$) indicating the almost perfect correlation between the variables σ''_{ijk} or σ'_{ijk} with w_{jk} . τ 's are also estimated from the linear plot of $\sigma''_{ijk}-\sigma'_{ijk}$ curves of figure 3 following Murthy *et al* [15]. The graphs are not perfectly linear for the systems II(b) (\bullet —); III(a) (\blacksquare —) at 25 and 30°C temperatures for 0.3 and 0.0 x_j 's of Ac respectively with the measured experimental data. This significantly demands the applicability of ratio of slopes method using least squares fitting technique. In this case the polar-polar interactions are almost eliminated. It is evident from figure 1 that the magnitude of σ''_{ijk} in $\Omega^{-1} \text{ m}^{-1}$ is higher for pure DMA in C_6H_6 (at 0.0 x_j of Ac in the binary mixture) and then decreases with the increase of x_j of Ac exhibiting low value for pure Ac in C_6H_6 (for 1.0 x_j of Ac). Figure 2 representing the variations of σ'_{ijk} in $\Omega^{-1} \text{ m}^{-1}$ with w_{jk} for different mole fractions of Ac and

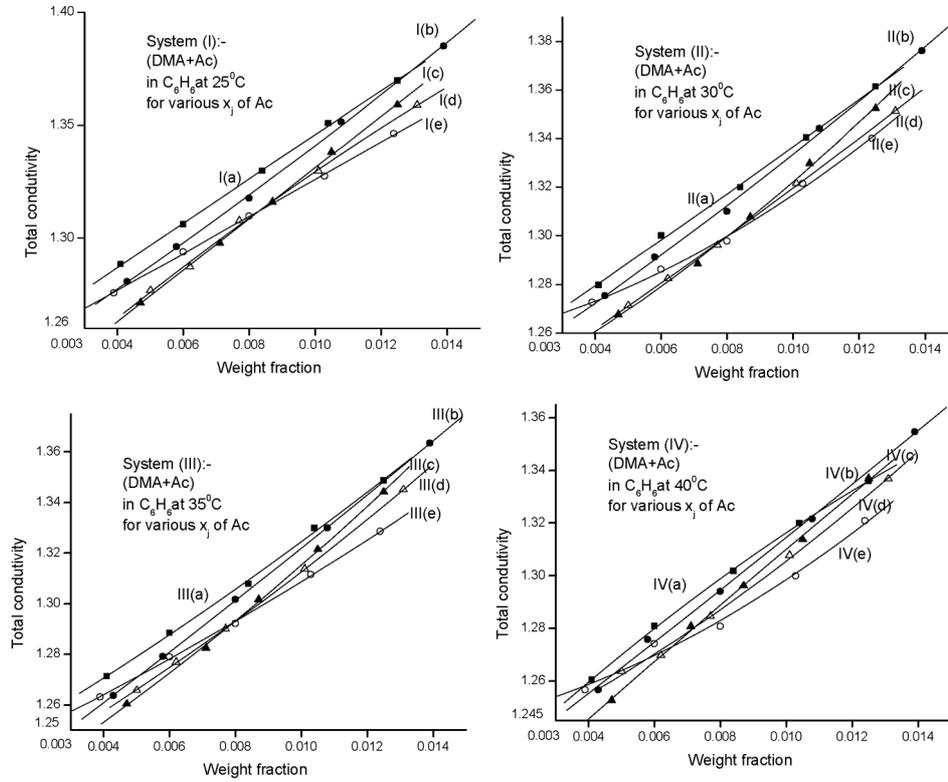


Figure 4. The variation of total hf conductivity σ_{ijk} ($\Omega^{-1} \text{ m}^{-1}$) against weight fractions w_{jk} 's of binary polar mixture (DMA+Ac) dissolved in C_6H_6 for different x_j of acetone and temperatures under 9.88 GHz electric field. (a) \blacksquare , (b) \bullet , (c) \blacktriangle , (d) \triangle , (e) \circ , for 0.0, 0.3, 0.5, 0.7 and $1.0x_j$ of acetone respectively.

temperatures are plotted to get the well-separated graphs of σ'_{ijk} having maximum and minimum value for pure DMA in C_6H_6 ($0.0x_j$ of Ac) and Ac in C_6H_6 ($1.0x_j$ of Ac) respectively. This type of behavior may be due to the maximum absorption of hf electric energy for DMA in C_6H_6 and minimum for Ac in C_6H_6 mixture. The estimated τ 's from both the methods of ratio of slopes (eq. (2)) and linear slope of eq. (3) are compared with the reported [8] τ 's due to Gopalakrishna's method. The average relaxation times τ_{jk} 's of the binary mixture are calculated taking the weighted sum of the individual components; $\tau_{jk} = \tau_j x_j + \tau_k x_k$; τ and x being the relaxation time and mole fraction of either j (Ac) or k (DMA) solute respectively. The agreement is found to be better with the measured values [8]. The dipole moments μ_{jk} 's of the j, k and jk 's polar mixtures were also measured from

$$\mu_{jk} = \frac{[27M_{jk}K_B T \beta]^{1/2}}{[N\rho_i(\varepsilon_i + 2)^2 \omega b]^{1/2}}, \quad (4)$$

where β is the slope of total conductivity $\sigma_{ijk} - w_{jk}$ curves at $w_{jk} \rightarrow 0$ as seen in

Dielectric relaxation of binary polar liquid mixture

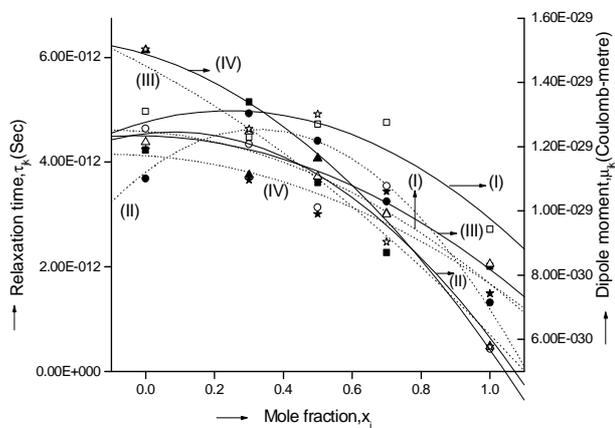


Figure 5. The variation of τ_{jk} 's and μ_{jk} 's of binary polar mixture (DMA+Ac) in C_6H_6 with mole fraction x_j of acetone at different temperatures under 9.88 GHz electric field. (I) $\cdots\blacksquare\cdots, -\square-$ at $25^\circ C$, (II) $\cdots\bullet\cdots, -\circ-$ at $30^\circ C$, (III) $\cdots\blacktriangle\cdots, -\triangle-$ at $35^\circ C$, (IV) $\cdots\star\cdots, -\star-$ at $40^\circ C$, for DMA+Ac in C_6H_6 respectively.

figure 4. Other symbols in eq. (4) carry usual meanings [12] in SI unit. The total conductivity σ_{ijk} 's in $\Omega^{-1} m^{-1}$ against w_{jk} 's are plotted for various mole fractions and temperatures to get parabolic curves as displayed in figure 4. Like $\sigma''_{ijk}-w_{jk}$ curves of figure 1, σ_{ijk} 's of binary polar mixture in benzene show higher value for 0.0 mole fraction of Ac (i.e. pure DMA in C_6H_6) whereas lower value for 1.0 mole fraction of Ac (i.e. pure Ac in C_6H_6) respectively at all temperatures. Nevertheless, the graphs are found to overlap with each other indicating a little variation in total conductivity with the change in mole fraction of Ac in the binary mixture. This type of behavior may be due to same polarity of the individual polar entity in the benzene solution [7]. The almost similar nature of the curves $\sigma''_{ijk}-w_{jk}$ and $\sigma_{ijk}-w_{jk}$ of figures 1 and 4 at once indicates the validity of the approximation $\sigma''_{ijk} \cong \sigma_{ijk}$. The nonlinear variation of τ and μ with x_j of Ac within the range 0.0–0.3 in figure 5 reveals solute–solute molecular association beyond which they decrease rapidly up to $1.0x_j$ of Ac. This type of behavior may be attributed to the fact that the formation of solute–solute molecular association occurs up to $0.3x_j$ of Ac and thereafter rupture of solute–solute association or solute–solvent association takes place. The agreement between τ 's from eqs (2) and (3) as well as μ 's in eq. (4) from both the methods are better indicating the validity of the same. The μ 's are higher at 0.0 mole fraction of Ac of figure 5 and then decreases slowly to yield low value of μ 's at 1.0 mole fraction of Ac respectively. The higher value μ_k 's for DMA in C_6H_6 (for $0.0x_j$ of Ac) may be ascribed to the fact that solute–solute molecular association occurs at lower mole fraction of Ac and rupture of solute–solute association or solute–solvent association takes place at higher x_j of Ac. The theoretical dipole moments μ_{theo} 's of the polar molecules DMA and Ac are calculated from the available bond angles and bond moments of substituent polar groups [13]. The bond moments are reduced by a factor μ_{cal}/μ_{theo} to have the exact average μ 's in terms of weighted sum of τ 's of individual polar entity. Each of

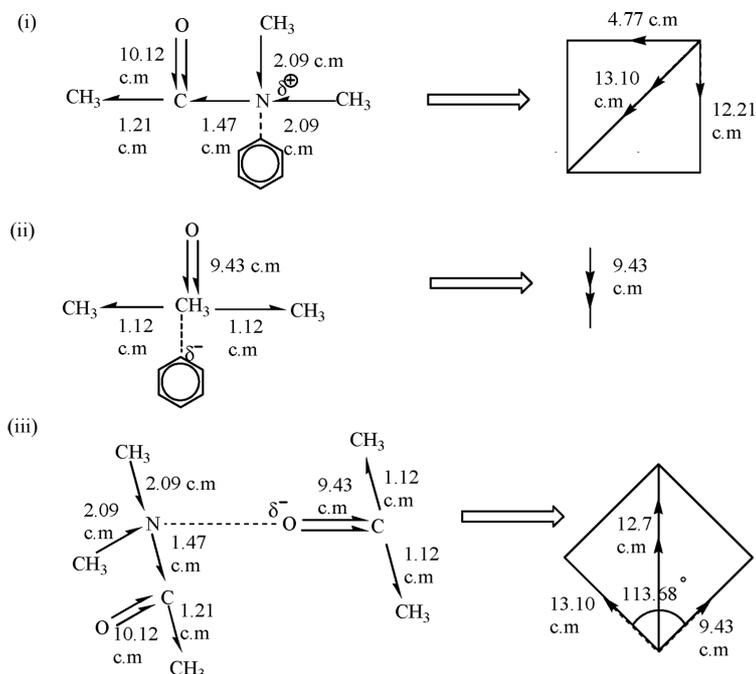


Figure 6. Theoretical dipole moments μ_{theo} 's from available bond angles and bond moments (multiples of 10^{-30} C·m) along with solute–solvent and solute–solute molecular associations. (i) DMA–C₆H₆, (ii) Ac–C₆H₆, (iii) DMA+Ac.

the polar molecule may exist either in monomer (solute–solvent) association with C₆H₆ or dimer (solute–solute) form with the participating molecular entities as shown in figure 6. The solute–solvent molecular association or monomer formation may occur due to the interaction of the fractional positive charge δ^+ at the side of N or C atom in DMA and Ac with the π -delocalized electron clouds in the benzene molecule as shown in figures 6(i) and 6(ii) respectively. The solute–solute molecular association may arise due to interaction of two adjacent highly polar groups $\text{N} \leftarrow \text{CH}_3$ and $\text{C} \leftarrow \text{O}$ present in DMA and Ac as shown in figure 6(iii). The polar nature of the substituent groups exists due to the inductive, mesomeric and electromeric effects among the two adjacent atoms due to their difference in electron affinity. The parabolic variations of measured μ_{jk} 's with temperature in K when mole fractions of the mixture is kept constant are represented in figure 7. All the curves are concave except for $x_j = 0.3$ which is almost constant with the rise of temperature. Similar nature of variations is observed for $\mu_{jk}-T$ curve (...) from eqs (3) and (4). This type of variation may be due to the elongation of bond moments and bond angles of the polar groups with the rise of temperature [12] under high frequency electric field. The thermodynamic energy parameters like enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and free energy of activation ΔF_τ are estimated from Eyring's rate theory [14] considering the dielectric relaxation as a rate process.

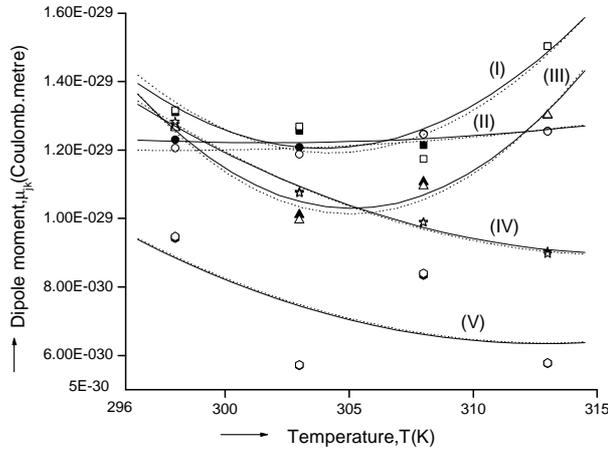


Figure 7. The variation of dipole moment μ_{jk} in Coulomb-metre (C·m) with temperature T in K for different x_j of acetone of DMA+Ac binary mixture under 9.88 GHz electric field. (I) \blacksquare —, $\cdots\blacksquare\cdots$, (II) \bullet —, $\cdots\bullet\cdots$, (III) \blacktriangle —, $\cdots\blacktriangle\cdots$, (IV) \star —, $\cdots\star\cdots$, (V) \blacklozenge —, $\cdots\blacklozenge\cdots$ for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of acetone from ratio of slopes (—) and Murthy *et al* (\cdots) respectively.

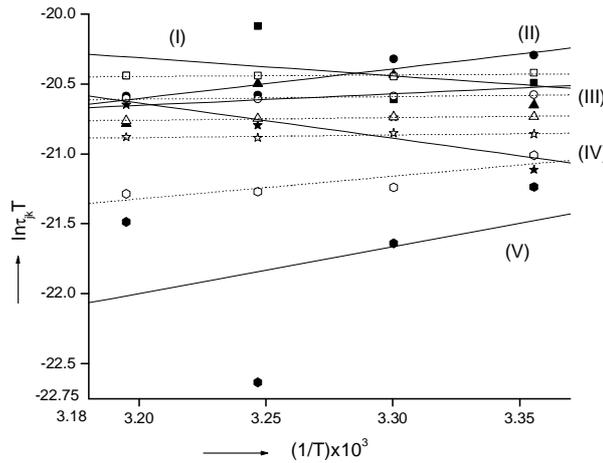


Figure 8. Linear plot of $\ln(\tau_{jk}T)$ against $1/T$ curve of DMA+Ac binary polar mixture in C_6H_6 under 9.88 GHz electric field. (I) \blacksquare —, $\cdots\blacksquare\cdots$, (II) \bullet —, $\cdots\bullet\cdots$, (III) \blacktriangle —, $\cdots\blacktriangle\cdots$, (IV) \star —, $\cdots\star\cdots$, (V) \blacklozenge —, $\cdots\blacklozenge\cdots$ for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of acetone from ratio of slopes (—) and Murthy *et al* (\cdots) respectively.

$$\ln(\tau_{jk}T) = \ln(Ae^{-\Delta S_\tau/R}) + \Delta H_\tau/RT. \quad (5)$$

Since $\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau$, eq. (5) is a linear equation of $\ln(\tau_{jk}T)$ against $1/T$ curve as shown in figure 8. ΔH_τ 's are -10.65 , 17.59 , 6.90 , -20.85 and 27.85 kJ/mole respectively for the systems (DMA + Ac) in C_6H_6 . Enthalpy of activations ΔH_η for

the viscous flow of the solvent are, however, positive for all the systems. Different values of ΔH_τ 's and ΔH_η 's indicate rupture of molecular bonds to a different order and nature. ΔS_τ 's for the system are negative except 0.3 and 1.0 mole fraction x_j of Ac. The entropy of a system indicates its orderliness. If the environment is cooperative for the activated process, the ΔS_τ 's become negative. Otherwise the systems are noncooperative for the positive ΔS_τ 's. The solvent environment of the solute molecule is determined by γ ($=\Delta H_\tau/\Delta H_\eta$) from:

$$\tau_{jk} = A\eta^\gamma/T, \quad (6)$$

where γ is the slope of linear equation $\ln(\tau_{jk}T)$ against $\ln \eta$, η being the viscosity of the solvent C_6H_6 . $\gamma = 1.93, 0.72$ and $3.23(>0.55)$ for the systems (DMA+Ac) in C_6H_6 at 0.3, 0.5 and 1.0 mole fractions x_j of Ac indicate that the binary polar mixture do not behave as solid phase rotator while $\gamma = -1.24, -2.25 (<0.45$ or even negative) for the system 0.0 and $0.7x_j$ of Ac indicate that the binary polar mixture behaves as solid phase rotator. The Debye factor $\tau_{jk}T/\eta$ and Kalman factor $\tau_{jk}T/\eta^\gamma$ are calculated for the binary polar mixture at different x_j of Ac and different temperatures. It is found that $\tau_{jk}T/\eta$ is of the same order of magnitude at different x_j of Ac and temperatures unlike Kalman factor indicating Debye–Smyth relaxation mechanism holds good for the systems under investigation.

References

- [1] A K Sharma and D R Sharma, *J. Phys. Soc. (Japan)* **53**, 4771 (1984)
- [2] V S Rangra and D R Sharma, *Indian J. Phys.* **B78(I)**, 111 (2004)
- [3] N Nandi, K Bhattacharyya and B Bagchi, *Chem. Rev.* **100**, 2013 (2000)
- [4] A K Jonscher, *Physics of dielectric solids*, invited paper edited by CHL Goodman, 1980
- [5] A Schallamach, *Trans. Faraday Soc.* **A42**, 180 (1946)
- [6] E Frost and C P Smyth, *J. Phys. Chem. Ithaca* **69**, 1294 (1965)
- [7] A K Chatterjee, U Saha, N Nandi, R C Basak and S Acharyya, *Indian J. Phys.* **B66**, 291 (1992)
- [8] V S Rangra and D R Sharma, *Indian J. Pure Appl. Phys.* **41**, 630 (2003)
- [9] J J Lagowski, *The chemistry of non-aqueous solvents* (Academic Press, New York and London, 1966)
- [10] G R Ueader and J F Gormley, *J. Am. Chem. Soc.* **73**, 5731 (1951)
- [11] A K Sharma and D R Sharma, *J. Phys. Soc. (Japan)* **61**, 1049 (1992)
- [12] S Sahoo, K Dutta, S Acharyya and S K Sit, *Indian J. Pure Appl. Phys.* **45**, 529 (2007)
- [13] S K Sit, K Dutta, S Acharyya, T Pal Majumder and S Roy, *J. Mole. Liquids* **89**, 111 (2000)
- [14] N E Hill, W E Vaughan, A H Price and M Davies, *Dielectric properties and molecular behaviour* (Van Nostrand Reinhold, London, 1969)
- [15] M B R Murthy, R L Patil and D K Deshpande, *Indian J. Phys.* **B63**, 491 (1989)