

An investigation on molecular dynamics of binary mixtures of N-methylformamide and Ethanol in microwave region

Vimal Sharma^{a*}, Nagesh Thakur^b and Rajesh Kumar^c

^aDept. of Physics, National Institute of Technology, Hamirpur, Himachal Pradesh, India,

^bDept. of Physics, H. P. University, Shimla, India.

^cDept. of Physics, Govt. Degree College, Sarkaghat, Mandi, (H. P.)

ABSTRACT

The dielectric constant (ϵ') and dielectric loss (ϵ'') of the binary mixtures of N-methylformamide and Ethanol have been calculated at 9.883GHz by using standard standing microwave techniques. Gopalakrishna's single frequency concentration variation method has been used to calculate dipole moment (μ) and dielectric relaxation time (τ) for different mole-fractions of NMF in the binary mixture at different temperatures of 25^oC, 30^oC, 35^oC and 40^oC. The variation of dielectric relaxation time with the mole-fraction of NMF in the whole concentration range of the binary mixtures was found to be non-monotonic. The solute-solute and solute-solvent type of molecular associations may be proposed based upon above observations. Using Eyring rate equations the energy parameters ($\Delta H, \Delta F, \Delta S$) for the dielectric relaxation process and the viscous flow process have been calculated. It is found from the comparison of energy parameters that just like the viscous flow process the dielectric relaxation process can also be treated as the rate process.

Keywords: Dielectric relaxation, Microwave absorption, Binary mixture, Molecular association, Energy parameters.

INTRODUCTION

The dielectric properties of binary liquid mixtures are important both in fundamental studies of solvent structure determination and its dynamics as well as in the practical application of microwave heating process [1, 2]. The dynamics of molecules and molecular interaction can be understood through dielectric relaxation spectroscopy and this method is one of the most important as it opens problems of molecular physics of the liquid state. N-methylformamide is an important non-aqueous amide having dielectric constant value $\epsilon' = 182.4$ and dipole moment value $\mu = 3.82D$. The structural investigation of NMF is an interesting subject for biochemists,

because the molecule contains a peptide linkage and a study of its hydrogen bonding yields insight into the nature of protein structures [3, 4]. NMF is also of considerable medical interest since it possesses anti-tumor activities [5]. Ethanol is a non-aqueous protic solvent with dielectric constant $\epsilon' = 24.3$ and dipole moment $\mu = 1.70\text{D}$ [6, 7]. Ethanol is used in herbal medicinal products as an extraction solvent in liquid extracts and tinctures. The use of ethanol is necessary for extraction of some constituents that are important for efficacy [8]

It is possible to prepare binary mixtures of NMF and Ethanol having dielectric constant and dipole moment values in between those of NMF and Ethanol. NMF and Ethanol molecules have quite different dipole moments and dielectric constant values. This motivated the authors to perform experimental study concerned with the dielectric relaxation process in binary mixtures of NMF and ethanol in order to understand the molecular association in the whole concentration range of NMF in the binary mixture. Amides form the basic building block in proteins; therefore, the dielectric studies of binary mixtures of amides are expected to be of great interest. Binary mixtures of amides have been studied and reported by number of research workers. Recently the dielectric relaxation mechanism of dilute solutions of amides was studied by Malathi [9] and solute-solute type of molecular associations was proposed. Dielectric relaxation behavior of binary mixtures of DMF + TMU and DMA + DMF was studied by Chatterjee et al [10] and the binary mixture of NMA + DMA in benzene solution by Kumar et al [11]. However no information is available about the dielectric relaxation mechanism of the binary mixture of NMF and EtOH.

In the present investigation the dielectric relaxation properties of the binary mixtures of NMF and EtOH in benzene solution at different temperatures (25°C , 30°C , 35°C & 40°C) using 9.88 GHz frequency have been studied. Measurements of dielectric constant (ϵ'), dielectric loss (ϵ''), dielectric relaxation time (τ) and dipole moment (μ) have been made for binary mixtures with different mole fractions of NMF (0.0, 0.3, 0.5, 0.7, and 1.0). The plots of dielectric relaxation time versus the mole fraction of NMF in the binary mixtures at different temperatures propose solute-solute associations. The energy parameters ($\Delta H, \Delta F, \Delta S$) have been calculated for the 0.5-mole fraction of NMF in the binary mixture. It was found that the dielectric relaxation process is a rate process like the viscous flow process.

MATERIALS AND METHODS

NMF (Fluka, Germany) was dried with 4Å molecular sieves for about 10 h and then distilled through a long vertical fractionating column under the reduced pressure. Ethanol (AR Grade) from Merck, Darmstadt (Germany) was distilled through a long vertical fractionating column. Benzene (GR grade) from E. Merck Ltd. (Mumbai India) was dried by refluxing over freshly cut sodium metal and then distilled through a long vertical fractionating column. The middle fraction of each solution was collected for use.

Microwaves produced by klystron are passed through an isolator, screw tuner, variable attenuator, frequency meter, slotted line section fitted with a tunable traveling probe and a 1N 23B crystal detector, E-plane bend and dielectric cell. The microwave bench was used to measure the voltage standing wave ratio (VSWR), the wavelength of microwaves in the waveguide (λ_g), in the dielectric (λ_d) in the free space (λ_0) and the cutoff wavelength (λ_c). Heston et al [12] method adopted for short circuited terminations was used to calculate the dielectric constant and dielectric loss. The accuracy in the measurement of ϵ' and ϵ'' is about $\pm 1\%$ and $\pm 3\%$ respectively.

All the measurements were made at different temperatures of 25, 30, 35 & 40^oC. Thermostat with a water bath was used to circulate water around the dielectric cell to maintain a constant temperature within accuracy limit of ± 0.05 ^oC. The viscosities and densities of the solutions were measured by an ubbelohde viscometer and a sealable type of pycnometer, respectively.

RESULTS AND DISCUSSION

The dielectric constant of the mixture is measured using Rodert and Von Hippel's method [13]. The shift of the first minima of standing wave pattern produced by a short circuit in the space in front of the sample depends upon the wavelength of the electromagnetic wave in the dielectric material and hence is related to the dielectric permittivity (ϵ') of the material.

The phase constant along the axis of a hollow waveguide of uniform cross-section and highly conducting walls, is given by

$$\gamma_d = \frac{2\pi g}{\lambda_o} \left[\epsilon^* - \left(\frac{\lambda_o}{\lambda_c} \right)^2 \right]^{\frac{1}{2}} \quad (1)$$

where $\epsilon^* = \epsilon' - j\epsilon''$, λ_o is the free space wavelength and λ_c cutoff wavelength. Separating the real and imaginary parts of ϵ^* we get

$$\epsilon' = \left(\frac{\lambda_o}{\lambda_c} \right)^2 + \left(\frac{\lambda_o}{\lambda_d} \right)^2 \quad (2)$$

$$\epsilon'' = \frac{2}{\pi} \left(\frac{\lambda_o}{\lambda_d} \right)^2 \frac{\lambda_g}{\lambda_d} \frac{d\rho}{dn} \quad (3)$$

here λ_g , λ_d , and ρ are the waveguide wavelength, the wavelength in the waveguide filled with the dielectric and the inverse of the voltage standing wave ratio respectively. $\frac{d\rho}{dn}$ is the slope of the curve of ρ versus n . Here n is an integer ($n = 1, 2, 3, \dots$), such that $\left(\frac{n\lambda_d}{2} \right)$ represents the length of the dielectric filled waveguide.

Single frequency and concentration variation method of Gopala Krishna [14] was used to calculate the relaxation time (τ) and dipole moment (μ) of the molecular entities.

$$X = \frac{\epsilon'^2 + \epsilon''^2 + \epsilon' - 2}{(\epsilon' + 2)^2 + \epsilon''^2} \quad (3)$$

$$Y = \frac{3\epsilon''}{(\epsilon' + 2)^2 + \epsilon''^2} \quad (4)$$

$$\tau = \frac{\lambda_o}{2\pi c} \left(\frac{dY}{dX} \right) \quad (5)$$

$$\mu^2 = \frac{9kTM}{4\pi Nd} \left[1 + \left(\frac{dY}{dX} \right)^2 \right] \frac{dX}{dW} \quad (6)$$

Here X and Y are intermediate parameters which depend upon ϵ' and ϵ'' .

Energy parameters ($\Delta H_\epsilon, \Delta F_\epsilon, \Delta S_\epsilon$) for dielectric relaxation process of binary mixtures in benzene have been calculated using Eyring rate equations [15] and compared with corresponding energy

parameters for viscous flow process ($\Delta H_\eta, \Delta F_\eta, \Delta S_\eta$). Following equations have been used to calculate the energy parameters.

$$\tau = \frac{h}{kT} \exp\left[\frac{\Delta F_\epsilon}{RT}\right] \quad (7)$$

$$\Delta F_\epsilon = \Delta H_\epsilon - T\Delta S_\epsilon \quad (8)$$

$$\eta = \left(\frac{hN}{V}\right) \exp\left[\frac{\Delta F_\eta}{RT}\right] \quad (9)$$

$$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta \quad (10)$$

The values of dielectric constant and dielectric loss for the binary mixture of different mole fractions of NMF have been tabulated (Table 1). Table 2 represents the values of the dipole moment (μ) and relaxation time (τ) and for the binary mixtures of different mole-fractions of NMF in the binary mixture at different temperatures. The values of ($\Delta H_\epsilon, \Delta F_\epsilon, \Delta S_\epsilon$) and ($\Delta H_\eta, \Delta F_\eta, \Delta S_\eta$) are tabulated in table 3.

Dielectric constant and Dielectric loss

The plots of ϵ' and ϵ'' versus W (Weight fraction) of the solute in benzene for all binary mixtures were found to be linear (Figs.1 & 2).

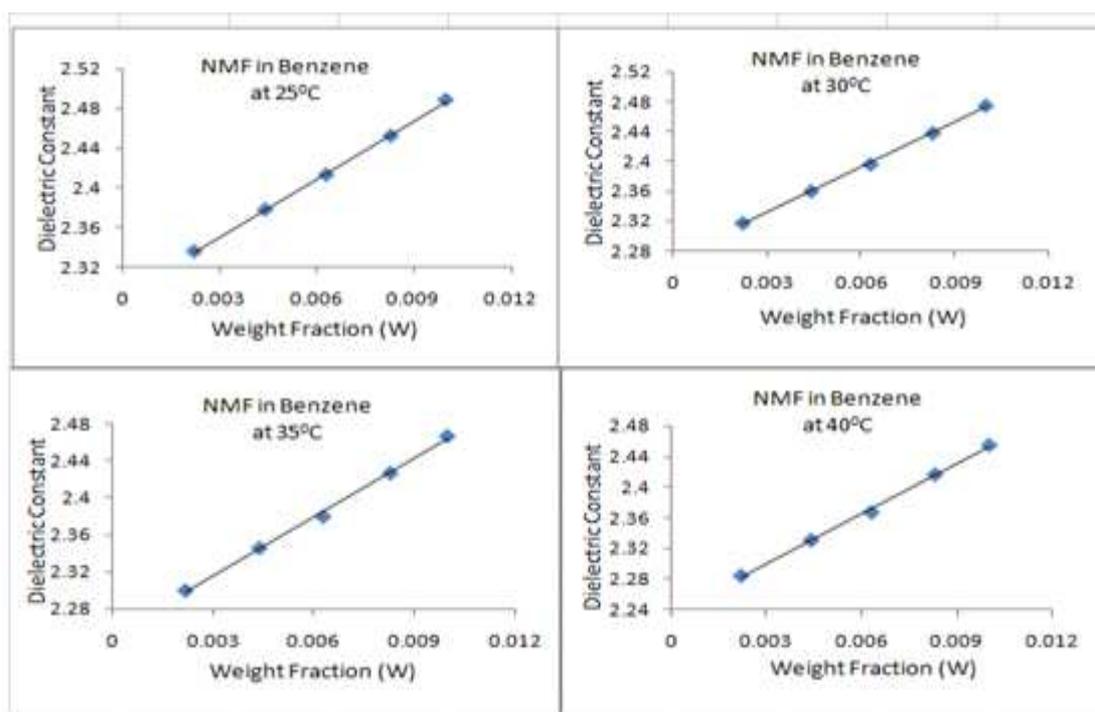


Fig. 1 Variation of dielectric constant (ϵ') with weight fraction (W) of NMF in benzene at different temperatures

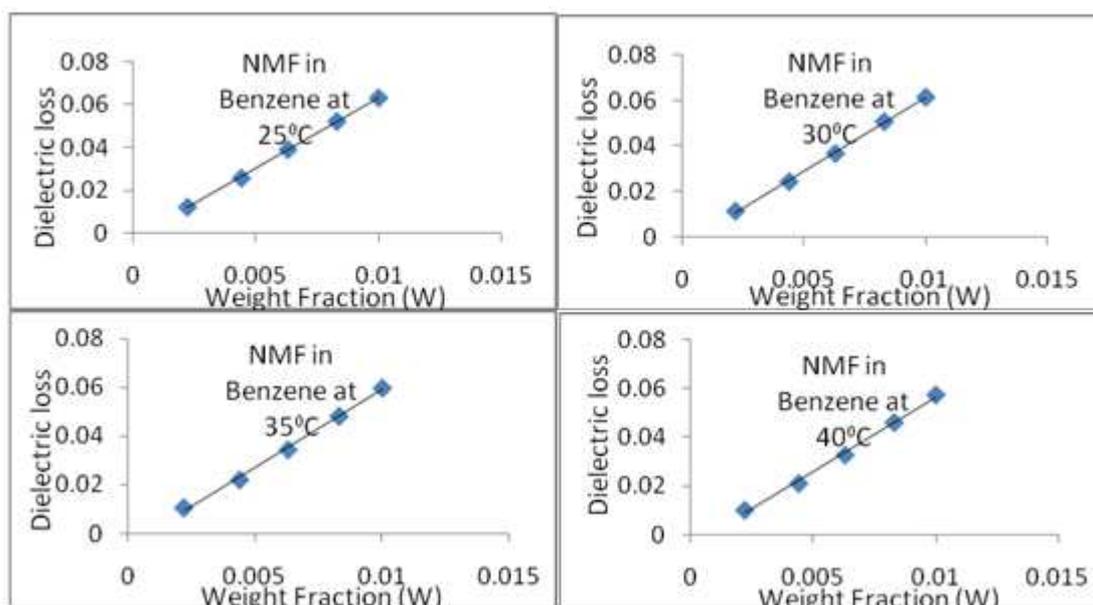


Fig. 2 Variation of dielectric loss (ϵ'') with weight fraction (W) of NMF in benzene at different temperatures

This shows that the molecular entities retain their configuration, shape and size in the studied concentration range of the binary mixtures in the benzene solutions and ensures the applicability of the Debye theory and hence Gopala Krishna's method.

Table 1: Dielectric constant (ϵ') and dielectric loss (ϵ'') for (NMF+EtOH) mixture for different mole fractions of NMF in the binary mixture at 25^oC

Mole fraction of NMF in binary mixture	Weight fraction of the binary mixture in benzene	ϵ'	ϵ''
0.00	0.0096	2.402	0.0107
	0.0124	2.424	0.0141
	0.0142	2.434	0.0151
	0.0188	2.465	0.0202
	0.0205	2.480	0.0225
0.30	0.0022	2.324	0.0108
	0.0042	2.369	0.0228
	0.0061	2.403	0.0363
	0.0084	2.446	0.0524
	0.0102	2.484	0.0630
0.50	0.0020	2.334	0.0105
	0.0040	2.360	0.0203
	0.0061	2.391	0.0325
	0.0079	2.418	0.0433
	0.0104	2.452	0.0561
0.70	0.0022	2.362	0.0121
	0.0043	2.407	0.0280
	0.0068	2.465	0.0476
	0.0076	2.488	0.0574
	0.0112	2.566	0.0845
1.00	0.0022	2.336	0.0121
	0.0044	2.378	0.0257
	0.0063	2.413	0.0391
	0.0083	2.452	0.0523
	0.0100	2.488	0.0634

Relaxation Time

The relaxation time for pure NMF is found to be more than that of pure EtOH at all temperatures. The relaxation time increases with the size of the molecule and may be discussed in terms of the molecular shape and solvent microscopic viscosity. This shows that the size of NMF molecule is more than EtOH molecule. The decrease in the relaxation time with rise in temperature can be explained on the basis of Debye theory [16]. Thermal energy of the system increases with rise in temperature and decreases the relaxation time of the molecular entities. At higher temperature, due to more number of collisions, rate of loss of energy increases hence reorientation of molecules becomes faster. The non-monotonic variation of the dielectric relaxation time with the mole fraction of NMF in the binary mixtures at all temperatures was observed [Fig.3].

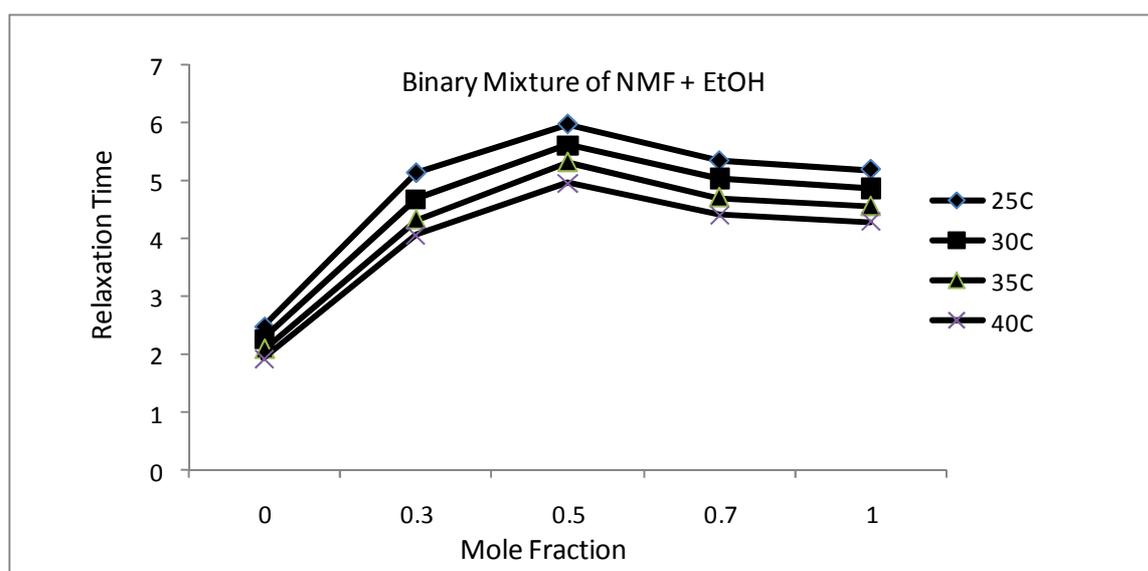


Fig. 3 Variation of relaxation time with mole fraction of NMF in binary mixture (NMF + EtOH) in benzene solution at different temperatures

The monotonic variation of the relaxation time, from its value corresponding to one single constituent to the value which corresponds to the pure other constituent, with varying mole fraction in the whole concentration range may be taken as the absence of any solute-solute association in the mixture [17]. On the other hand the non monotonic variation of the relaxation time with the mole fraction is interpreted as a possible solute-solute molecular association in the binary mixture [18]. In the present study, the non-monotonic variation of the relaxation time with the change in mole-fraction of NMF in the binary mixture was observed. The relaxation time increases sharply with the increase in mole-fraction from 0.0 to 0.3. The peak is formed at 0.5 mole-fraction of NMF in the binary solution and the relaxation time attains maximum value at this mole-fraction. With the further increase in the mole fraction of NMF in the mixture there is a decrease in the relaxation time and falls towards the value of pure NMF in the benzene solution. This predicts the solute-solute type of molecular association between NMF and EtOH. The solute-solute type of molecular association may arise because of dipole-dipole interaction between NMF and EtOH molecules. The presence of fractional negative charge at the site of oxygen atom of NMF and positive charge on the hydrogen atom of EtOH molecule results in solute-solute association.

Table 2: Dipole moment (μ) and dielectric relaxation time (τ) for (NMF+EtOH) mixture at different temperatures and mole fractions of NMF in the binary mixture

Temp. / $^{\circ}$ C	Mole fraction of NMF in the binary mixture	Dielectric relaxation time ($\tau/10^{-12}$ s)	Dipole moment (μ/D)
		4.7%	3.6%
25	0.00	2.48	$\mu_{EtOH} = 1.62$
	0.30	5.14	
	0.50	5.98	
	0.70	5.35	
	1.00	5.20	$\mu_{NMF} = 3.566$
30	0.00	2.27	$\mu_{EtOH} = 1.64$
	0.30	4.69	
	0.50	5.62	
	0.70	5.05	
	1.00	4.87	$\mu_{NMF} = 3.625$
35	0.00	2.09	$\mu_{EtOH} = 1.66$
	0.30	4.33	
	0.50	5.32	
	0.70	4.71	
	1.00	4.56	$\mu_{NMF} = 3.740$
40	0.00	1.92	$\mu_{EtOH} = 1.68$
	0.30	4.07	
	0.50	4.96	
	0.70	4.41	
	1.00	4.30	$\mu_{NMF} = 3.805$

Dipole Moment

The calculated dipole moments of NMF and EtOH were found to be very near to the literature values. This shows that pure NMF and pure EtOH exist in the monomer form in benzene solution. Dipole moment of the molecular entities depends on the size, structure and charge separation in the molecular entities. The variation of dipole moment with rise in temperature shows solute-solvent association while no change in dipole moment with temperature shows absence of solute-solvent association. The small change in dipole moment with temperature may be due to the stretching of bond moments and change in bond angles. This change may also be due to the breaking of solute-solvent associations with rise in temperature.

Energy Parameters

Plot of $\log(\tau T)$ versus $\frac{10^3}{T}$ for 0.5 mole fraction of NMF in the binary mixtures (Fig. 4) is found to be linear which indicates that the dielectric relaxation process can be treated as a rate process.

Energy parameters ($\Delta H_{\epsilon}, \Delta F_{\epsilon}, \Delta S_{\epsilon}$) for dielectric relaxation process and viscous flow process ($\Delta H_{\eta}, \Delta F_{\eta}, \Delta S_{\eta}$) have been calculated and compared. It is found that the free energy of activation of the dielectric relaxation process is less than the free energy of activation of the viscous flow process. This may be explained with the argument that the dielectric relaxation process involves the rotation of molecular entities, whereas in the flow process the rotational as well as the translational motions of the molecules are involved. The enthalpy of activation depends on the local environment of the molecules. The enthalpy of activation of the dielectric relaxation process was found to be different from the enthalpy of activation of a viscous flow process.

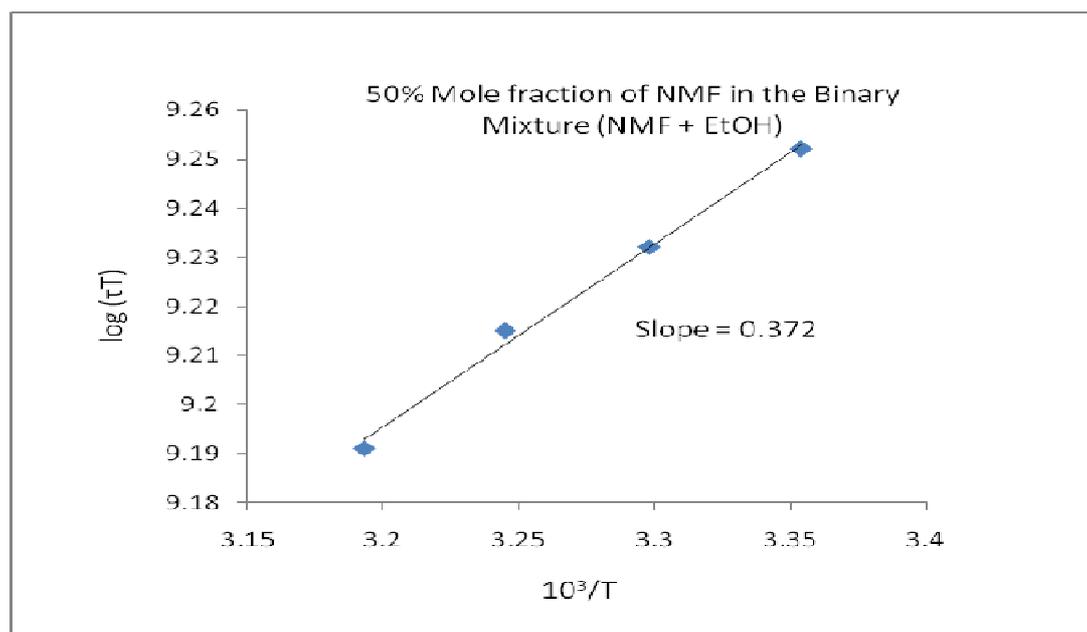


Fig. 4 Plot of $\log(\tau T)$ versus $10^3/T$ for 50% mole fraction of NMF in binary mixture of NMF and EtOH in benzene solution

Table 3: Free energies of activation (ΔF_e , ΔF_η in kcal mole⁻¹), enthalpies of activation (ΔH_e , ΔH_η in kcal mole⁻¹) and entropies of activation (ΔS_e , ΔS_η in cal mole⁻¹ K⁻¹) for (NMF + EtOH) mixture containing 50 mol% of NMF in benzene solution at different temperatures

Temp. (°C)	ΔF_e ±0.14	ΔH_e ±0.17	ΔS_e ±0.31	ΔF_η	ΔH_η	ΔS_η
25	2.145	1.705	-1.475	2.9167	2.623	-0.9855
30	2.153	1.705	-1.478	2.9235	2.623	-0.9917
35	2.165	1.705	-1.493	2.9301	2.623	-0.9970
40	2.167	1.705	-1.475	2.9451	2.623	-1.0290

This difference shows that the dielectric relaxation process comprises different types of bonding and breaking of the bonding to different extents. According to Branin and Smyth [19], a negative value of the entropy of activation indicates that a comparatively smaller number of configurations is possible in an activated state, which is more ordered in comparison to the normal state. This again indicated the presence of a cooperative orientation of the molecules by the steric forces or by strong dipole-dipole interaction with the dipole being better aligned in an activated state. However, the positive value of the activation entropy indicates that the activated state is more disordered. In the present case it is observed that the change in entropy of the dielectric relaxation process is negative indicating that the environment of the system is cooperative like that of the activated viscous flow state

CONCLUSION

The dielectric relaxation parameters have been reported for the binary mixtures of NMF and EtOH in benzene solution for various concentrations at different temperatures. The variation of dipole moment of NMF and EtOH in benzene with temperature indicates solute-solvent type of molecular association. The relaxation time of NMF is found to be more than that for EtOH. This is due to bigger size of NMF than EtOH. Solute-solute molecular association between polar

constituents of the binary mixture (NMF + EtOH) is evident from non monotonic variation of the relaxation time of the binary mixture with concentration of NMF in the mixture. Linearity of $\log(\tau T)$ versus $10^3/T$ graph shows that dielectric relaxation process is a rate process.

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