Dielectric Relaxation Studies of Mixtures of *N*-Methylacetamide and Ethanol in Benzene Solutions Using Microwave Absorption Technique

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Using standard standing wave microwave X-band techniques, and by following Gopala Krishna's single frequency (9.90 GHz) concentration variational method, the dielectric relaxation times (τ) and dipole moments (μ) of binary mixtures of different molar concentrations of ethanol (EtOH) in binary mixtures of *N*-methylacetamide (NMA) and ethanol in benzene solutions at 25, 30, 35 and 40 °C have been calculated. The activation parameters (ΔH_ε, ΔF_ε, ΔS_ε) for the dielectric relaxation process of binary mixtures containing 30 mol% of EtOH have been calculated at 25, 30, 35 and 40 °C and compared with the corresponding viscosity parameters. A good agreement between the free energy of activation from these two sets of values shows that the dielectric relaxation process, like the viscous flow, can be treated as a rate process. From relaxation time behaviour of NMA and EtOH binary mixtures in benzene solution, solute-solute and solute-solvent types of the molecular association have been predicted.

Key words: Dielectric Relaxation; Solute-Solute Interaction; Relaxation Times; Microwave Absorption Studies.

1. Introduction

N-Methylacetamide (NMA) is a non-aqueous dipolar, aprotic solvent having the dielectric constant $\varepsilon' = 178.9$ at 30 °C and 165.5 at 40 °C [1], and the dipole moment $\mu = 3.50$ D [1]. Ethanol (EtOH) has the dipole moment $\mu = 1.69$ D and the dielectric constant $\varepsilon' = 24.55$ [2]. Its boiling and melting points are 78.3 and -114.5 °C [2]. EtOH is hygroscopic and miscible with water in all proportions. This molecular aspects of NMA and EtOH motivated us to study the dielectric relaxation behaviour of their mixtures. Dielectric relaxation studies of polar molecules in non-polar solvents, using microwave absorption techniques, have frequently been performed [3 – 9].

To measure the dielectric constant (ε') and dielectric loss (ε'') of dilute solutions of (NMA + EtOH) mixtures in benzene. Gopala Krishna's single frequency concentration variational method has been used [10]. The dielectric measurements have been made for binary mixtures with the mole fractions 0.0, 0.3, 0.5, 0.7, 1.0 of NMA and EtOH at 25, 30, 35 and 40 °C. The energy parameters have been calculated for the binary mixtures with the mole fraction 0.3 of EtOH.

2. Experimental

N-Methylacetmamide (GC grade) from Fluka, Germany, was purified by three-fold crystallization. Ethanol (Fabro Chemical Supplies, Beijing, China) was distilled using a long vertical fractionating column. The middle fraction was collected for use. Benzene (Central Drug House P Ltd, New Delhi) was dried by refluxing over freshly cut sodium metal for 6 – 8 h and distilled using a long vertical fractionating column. The middle fraction of the distilled benzene was used. All measurements were made using an X-band microwave bench. The set up was tuned at microwave frequency of 9.90 GHz. A set of dilute solutions of the binary mixtures in the benzene solution was made. Using the microwave techniques of Heston et al. [11], the dielectric constant (ε') and the dielectric loss (ε'') of the dilute solutions were calculated. The temperature of the solution was controlled by circulating thermostated water around the dielectric cell. The dielectric relaxation time (τ) and dipole moment (μ) of the molecular entities in the benzene solutions were calculated following the single frequency concentration variational method of Gopala Krishna [10].

Table 1. Dielectric constant (ε'), dielectric loss (ε''), relaxation time (τ) and dipole moment (μ) of ethanol in (NMA + EtOH) binary mixtures in benzene at 25 °C.

Mole fraction of EtOH in binary mixture	Weight fraction of solute in benzene	ε' ($\pm 0.5\%$)	ε'' ($\pm 1.67\%$)	τ (10^{-12} s)	μ (D)
0.00	0.0049	2.355	0.0418	4.13	3.74 μ_{NMA}
	0.0058	2.370	0.0468		
	0.00736	2.402	0.0558		
	0.00856	2.432	0.0632		
	0.0093	2.443	0.0672		
0.30	0.0026	2.310	0.0175	4.48	
	0.00403	2.334	0.0246		
	0.00504	2.352	0.0286		
	0.00635	2.380	0.0369		
	0.00785	2.417	0.0493		
0.50	0.00322	2.287	0.0167	3.81	
	0.00555	2.321	0.0251		
	0.00717	2.345	0.0309		
	0.00855	2.380	0.0402		
	0.00982	2.398	0.0448		
0.70	0.00308	2.297	0.0111	3.59	
	0.00477	2.324	0.0179		
	0.00658	2.348	0.0238		
	0.00829	2.373	0.0287		
	0.00989	2.398	0.0353		
1.00	0.0120	2.327	0.00927	2.95	1.74 μ_{EtOH}
	0.0176	2.373	0.0171		
	0.0206	2.395	0.0224		
	0.0247	2.420	0.0264		
	0.0301	2.466	0.0353		

The viscosities and densities of the solutions at various temperatures were measured by an Ubbelohde viscometer and a sealable type of pycnometer, respectively [9].

3. Results and Discussion

Using standard standing wave microwave techniques and following the method of Heston et al. [11], the dielectric constant (ε') and dielectric loss (ε'') of the dilute solutions of NMA, EtOH and (NMA + EtOH) binary mixtures at 25 °C were calculated and are given in Table 1.

We used the equations

$$\varepsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \tag{1}$$

and

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_0}{\lambda_d}\right)^2 \cdot \frac{\lambda_g}{\lambda_d}\left(+\frac{d\rho}{dn}\right), \tag{2}$$

where λ_0, λ_c, λ_g, and λ_d are the wavelength in free space, the cut-off wavelength, the waveguide wavelength, and the wavelength in the waveguide filled with solution, respectively. ρ is the inverse of voltage standing wave ratio (VSWR) and $d\rho/dn$ is the slope of the curve of ρ versus n, where n is the integer (1, 2, 3, 4, ...) such that $n\lambda_d/2$ represents the length of the dielectric filled waveguide. ε' and ε'' were reproducible within $\pm 0.5\%$ and $\pm 1.67\%$, respectively.

Following Gopala Krishna's single frequency concentration variational method [10], the dielectric relaxation time (τ) and the dipole moment (μ) have been calculated according to the procedure outlined in [9].

It is found that the dipole moment for pure NMA and EtOH in benzene solution is very close to the literature values. This shows that pure NMA and pure EtOH are monomers in the benzene solution. The energy parameters ΔH_ε, ΔF_ε, ΔS_ε of the dielectric relaxation process for the (NMA + EtOH) binary mixture containing 30 mol% EtOH in benzene at 25, 30, 35 and 40 °C and the corresponding energy parameters ΔH_η, ΔF_η, ΔS_η for the viscous flow have been calculated by using the relations of Eyring et al. [12] for this rate process. The following relations were used:

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta F_\varepsilon}{RT}\right), \tag{3}$$

$$\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon, \tag{4}$$

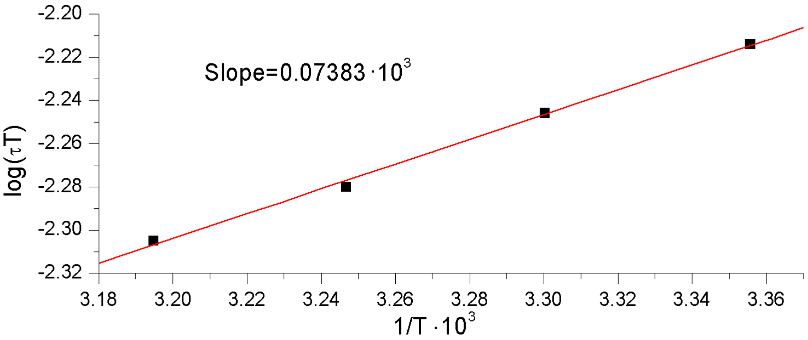

Fig. 1. $\log(\tau T)$ versus $10^3/T$ at 0.30 mol% EtOH in (NMA + EtOH) binary mixtures.

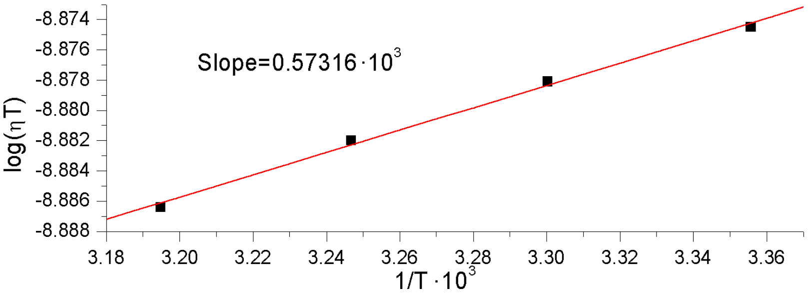

Fig. 2. $\log(\eta T)$ versus $10^3/T$.

Table 2. Relaxation time (τ), free energies of activation (ΔF_ε, ΔF_η in kJ mol^{-1}), enthalpies of activation (ΔH_ε, ΔH_η in kJ mol^{-1}) and entropies of activation (ΔS_ε, ΔS_η in J mol^{-1} deg^{-1} K^{-1}) for (NMA + EtOH) mixture containing 30 mol% of EtOH in benzene solutions.

Temp. (°C)	τ (10^{-12} s)	ΔF_ε	ΔH_ε	ΔS_ε	ΔF_η	ΔH_η	ΔS_η
25	4.48	8.236	1.413	−22.896	12.180	10.969	−4.064
30	4.37	8.354	1.413	−22.908	12.209	10.969	−4.092
35	4.26	8.468	1.413	−22.906	12.236	10.969	−4.114
40	4.15	8.580	1.413	−22.898	12.299	10.969	−4.249

$$\eta = \frac{hN}{V} \exp\left(\frac{\Delta F_\eta}{RT}\right), \tag{5}$$

and

$$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta, \tag{6}$$

where V is the molar volume of the solvent and all other symbols have their usual significance. ΔH_ε, ΔF_ε, and ΔS_ε are the enthalpy, free energy, and entropy of activation, respectively, for the dielectric relaxation process, and ΔH_η, ΔF_η, and ΔS_η are the corresponding parameters for the viscous flow. The plot of $\log(\tau T)$ versus $10^3/T$ and $\log(\eta)$ versus $10^3/T$ according to (3) and (5) were found to be linear, which shows that the relaxation and viscous processes can be considered as rate processes. The ΔH_ε and ΔH_η values were computed from the slope of the linear plot of $\log(\tau T)$ versus $10^3/T$ (Fig. 1) and $\log(\eta)$ versus $10^3/T$ (Fig. 2), respectively, using the relation slope = $\Delta H/2.303R$. Both sets of energy parameters, along with the dielectric relaxation time (τ) for (NMA + EtOH) binary mixtures containing 30 mol% EtOH in the benzene solution at 25, 30, 35, and 40 °C are summarized in Table 2.

Table 3. Dielectric relaxation time (τ) and dipole moment (μ) of (NMA + EtOH) mixtures in benzene solution at different temperatures.

Temperature (°C)	Mole fraction of EtOH in binary mixture	τ (10^{-12} s)	μ (D)
25	0.00	4.13	3.74 μ_{NMA}
	0.30	4.48	
	0.50	3.81	
	0.70	3.59	
	1.00	2.95	1.74 μ_{EtOH}
30	0.00	4.02	3.62 μ_{NMA}
	0.30	4.37	
	0.50	3.71	
	0.70	3.50	
	1.00	2.77	1.73 μ_{EtOH}
35	0.00	3.91	3.55 μ_{NMA}
	0.30	4.26	
	0.50	3.61	
	0.70	3.41	
	1.00	2.60	1.71 μ_{EtOH}
40	0.00	3.80	3.52 μ_{NMA}
	0.30	4.15	
	0.50	3.51	
	0.70	3.32	
	1.00	2.43	1.69 μ_{EtOH}

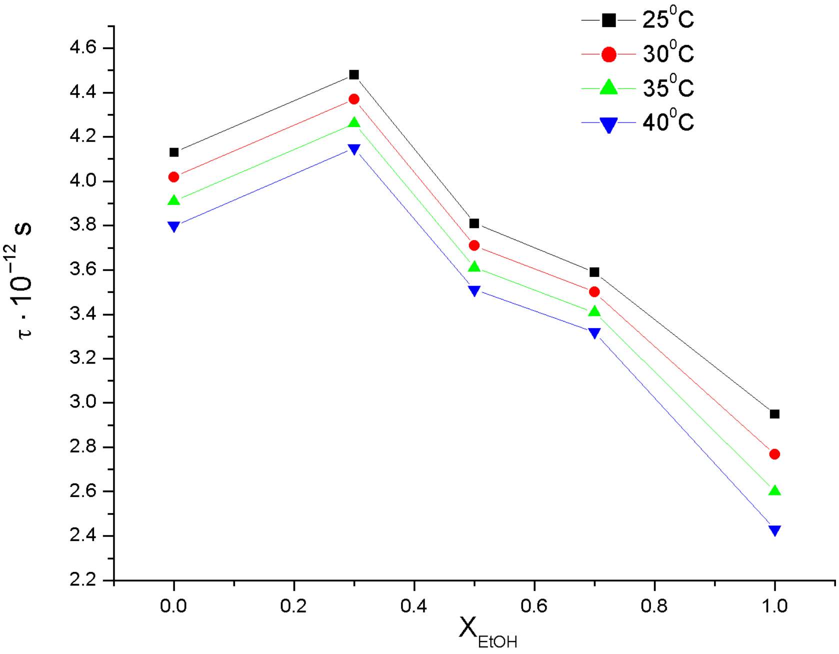

Fig. 3. Relaxation time (τ) versus mole fraction of EtOH (x_{EtOH}) in (NMA + EtOH) mixtures in benzene solution at different temperatures.

Table 3 represents the values of the dielectric relaxation time (τ) and dipole moment (μ) for (NMA + EtOH) binary mixtures in benzene at 25, 30, 35, and 40 °C for different mole fractions of EtOH in the binary mixtures. Non-linear variation of the relaxation time with the increase in the mole fraction of EtOH in the binary mixtures (NMA + EtOH) at all temperatures has been observed (Fig. 3). The relaxation time depends on the size and shape of the rotating molecular entities in the solution. This method determines the average value of the relaxation time for the participating molecular entities in the solution. The linear variation of the relaxation time from its value corresponding to one constituent to the value corresponding to the other constituent with the mole fraction variation in the whole concentration range may be taken as the absence of any solute-solute association in the mixtures. On the other hand, the non-linear variation of the relaxation time with the mole fraction is interpreted as a possible solute-solute molecular association in the binary mixtures.

The relaxation time τ first increases with increase of the mole fraction of EtOH in the (NMA + EtOH) binary mixture and attains a maximum at 30 mol% EtOH. Then, with further increase in the mole fraction of EtOH, there is seen a sharp decrease in the relaxation time, which falls towards the value of pure EtOH in benzene solution. This indicates a solute-solute type of molecular association between NMA and EtOH and shows that the molecular association is maximal at 30 mol% EtOH in the (NMA + EtOH) binary mixture. The solute-solute type of molecular association is predicted in the whole concentration range in the binary mixture. The molecular entity becomes much more voluminous than the individual molecule due to this association. The experiment was repeated a number of times to ensure the reproducibility of the above results. It was found that the above results are reproducible within the experimental accuracy. The binary mixture of NMA and EtOH was prepared by mixing NMA and EtOH in the required proportion. And then by mixing this binary solution in the benzene solvent, dilute solutions of binary mixtures in benzene were made. In view of the above results, it is proposed that

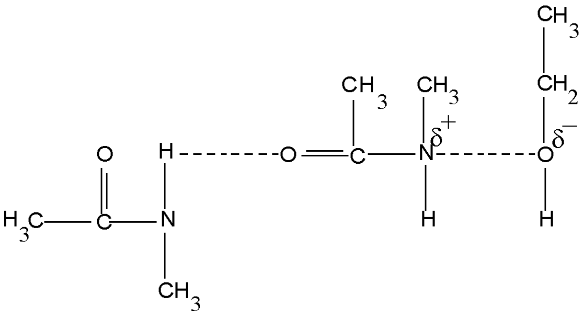

Fig. 4. Solute-solute associations between NMA and EtOH.

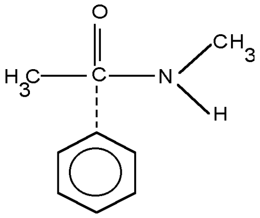

Fig. 5. Solute-solvent association of NMA molecule in benzene.

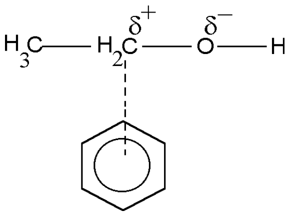

Fig. 6. Solute-solvent association of EtOH molecule in benzene.

in the binary mixtures of NMA and EtOH, NMA exists as dimer because of the H bonding, and this dimer structure of NMA interacts with the EtOH molecules so as to give the maximum value of relaxation time at the 30 mol% EtOH binary mixture. This type of molecular interaction is proposed in Figure 4.

The small variation in the dipole moment with rise in temperature may be attributed to a possible solute-solvent association. Solute-solvent association can be interpreted because of the molecular association arising from the interaction of a fractional positive charge at the site of a carbon atom in NMA molecules and a delocalized π-electron cloud in the benzene molecule (Fig. 5). The variation with temperature of the dipole moment of EtOH indicates the presence of a solute-solvent molecular association of EtOH in the benzene solution. The molecular association arises because of the interaction of a fractional positive charge at the site of the carbon the atom in an EtOH molecule and a delocalized π-electron cloud in the benzene molecule (Fig. 6).

This observation shows that the free energy of activation (ΔF_ε) of the dielectric relaxation process is smaller than the free energy of activation (ΔF_η) of the viscous flow process. This may be explained on the basis that the dielectric relaxation process involves only the rotation of molecular entities, whereas in the viscous flow process rotational as well as translational motions of the molecules are involved. It is found that the enthalpy of activation for the dielectric relaxation process (ΔH_ε) is smaller than the enthalpy of activation (ΔH_η) for the viscous flow process. The enthalpy of activation depends upon the local environment of the molecules. Different values of the enthalpy of activation indicate that the dielectric relaxation process and viscous flow process involve the breaking of bonds to the neighbouring molecules in a different way and to a different extent. The entropy of a system is a measure of the orderly nature of the system. If the environment of the system is cooperative for the activated process, then the change in entropy (ΔS_ε) becomes $-ve$. Whereas the $+ve$ value of the change in the entropy (ΔS_ε) for an activated process indicates the non-cooperative environment of the system, and the activated state is unstable. In the present case it is observed that the change in entropy of the dielectric relaxation process is $-ve$, indicating that the environment of the system is cooperative like that of the activated viscous flow state.

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