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Dielectric relaxation studies of binary mixtures of N-methylacetamide and N-methylformamide in benzene solutions using microwave absorption data

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Using standard microwave X-band technique and by following Gopala Krishna's single frequency (9.90 GHz) concentration variational method, the dielectric relaxation times (τ) and the dipole moments (μ) of dilute solution of N-methylacetamide (NMA), N-methylformamide (NMF) and NMA + NMF binary mixtures in benzene solutions have been calculated at different temperatures. The energy parameters for the dielectric relaxation process for NMA + NMF binary mixture containing 30 mol% NMF 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 process can be treated as the rate process. From relaxation time behavior of NMA and NMF binary mixture in benzene solution, solute–solute types of the molecular association has been proposed.

Keywords: Dielectric relaxation; Solute–solute interaction; Relaxation times; Microwave absorption studies

1. Introduction

Dielectric relaxation studies of polar molecules in non-polar solvents using microwave absorption techniques have been frequently attempted by many research workers [1–7]. Amides form the basic building blocks in proteins; therefore, dielectric relaxation studies of binary mixtures of amides are expected to be of considerable interest. N-methylacetamide (NMA) is recognized as the non-aqueous dipolar, aprotic solvent having dielectric constant $\epsilon' = 178.9$ at 30°C and 165.5 at 40°C [8] and dipole moment $\mu = 3.50$ D [8]. N-methylformamide (NMF) is an important non-aqueous amide with a large value of dielectric constant [8] $\epsilon' = 182.4$ at 25°C and possessing a dipole-moment [8] $\mu = 4.00$ D approximately. From the solvent point of view, it is possible to have binary mixtures of NMA and NMF having dielectric constant and dipole moment value

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in between that of NMA and NMF. This has motivated the authors to undertake experimental work concerning dielectric relaxation process in the binary mixture of NMA and NMF, in order to throw light on the molecular association in the whole concentration range of NMF in the binary mixtures.

Dielectric relaxation studies of liquid mixtures in the microwave region have been recognized to characterize different types of molecular interactions such as solute–solute, solute–solvent and self-association in the solution [9–11]. In order to obtain some information about the behavior of NMA + NMF mixtures in the microwave region, dielectric relaxation measurements of the dilute solution of binary mixtures of these solvents in benzene have been performed at 9.90 GHz frequency of the microwave region.

2. Experimental details

N-methylacetamide (GC Grade) from Fluka, Germany was purified by repeated (three times) crystallization. N-methylformamide (GC Grade) from Fluka, Germany was dried with 4A° molecular sieves for 10 h with occasional shakings and then distilled through long vertical fractionating column. The middle fractions were collected for use. Benzene (Central Drug House Pvt Ltd, New Delhi) was dried by refluxing over freshly cut sodium metal for 6–8 h and distilled through a long vertical fractionating column and middle fraction of the distilled benzene was used. The X-band microwave bench was used to measure wavelength in the dielectric medium and voltage standing wave ratio (VSWR) using a short-circuiting plunger. The set up was tuned at microwave frequency 9.90 GHz. The experimental techniques of Arrawatia *et al.* used by Sharma and Sharma [12] for microwave measurements were used. All the measurements were carried out at 25, 30, 35 and 40°C by circulating water around the dielectric cell through a thermostat (Lauda Dr R. Wobser GmbH & Co. KG German manufactured). The whole of the equipment was standardized with the help of materials like methanol and pyridine.

The viscosity and density of the solution at various temperatures were measured with an Ubbelohde viscometer and a sealable type of pycnometer, respectively.

3. Results and discussion

Using standing wave microwave techniques and following the method of Heston *et al.* [13], the dielectric constant (ϵ') and the dielectric loss (ϵ'') of the dilute solutions of NMA, NMF and NMA + NMF binary mixtures containing 30, 50 and 70 mol% NMF in benzene solutions at 25°C have been calculated and are given in table 1.

The following equations have been used:

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

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

Mole-fraction of NMF in NMA + NMF in binary mixture	Weight fraction of solute in benzene	ϵ' ($\pm 0.5\%$)	ϵ'' ($\pm 1.67\%$)	$\tau/10^{-12}$ s	$\mu(D)$
0.0	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	0.00281	2.324	0.0205	5.08	
	0.00453	2.355	0.0296		
	0.00541	2.373	0.0361		
	0.00722	2.406	0.0462		
	0.00839	2.435	0.0591		
0.50	0.00346	2.324	0.0218	4.97	
	0.00475	2.352	0.0310		
	0.00554	2.373	0.0377		
	0.00675	2.406	0.0479		
	0.00773	2.435	0.0593		
0.70	0.00347	2.327	0.0213	4.74	
	0.00462	2.355	0.0292		
	0.00548	2.380	0.0371		
	0.00684	2.409	0.0481		
	0.00795	2.435	0.0548		
1.00	0.003	2.341	0.0196	4.47	3.99 (μ_{NMF})
	0.0042	2.373	0.0278		
	0.00573	2.417	0.0408		
	0.00645	2.447	0.0502		
	0.0080	2.481	0.0612		

and

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

Here λ_o , λ_c , λ_g and λ_d are the wavelengths 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 VSWR and $d\rho/dn$ is the slope of ρ versus n , where $n = (1, 2, 3, 4, \dots)$ such that $(n\lambda_d/2)$ represents the length of the dielectric filled waveguide. The ϵ' and ϵ'' values were estimated to be reproducible within ± 0.5 and $\pm 1.67\%$, respectively. Following Gopala Krishna's single frequency concentration variational method [14], the relaxation times (τ) and the dipole moments (μ) have been calculated.

Gopala Krishna's method makes use of Debye's theory of dielectric relaxation. Debye's equation for the complex dielectric constant for the dielectric medium as a function of frequency of the applied electric field [15] can be written as:

$$\frac{\epsilon^* - 1}{\epsilon^* + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \frac{4\pi N_1 \mu^2}{9kT} \frac{1}{1 + j\omega\tau}, \quad (3)$$

where N_1 is the number of polar molecules per unit volume and $\varepsilon^* = \varepsilon' - j\varepsilon''$ is the complex dielectric constant of the medium. ε_∞ is the optical permittivity, k is the Boltzmann constant, T is the absolute temperature and ω is the angular frequency.

Separating real and imaginary parts of both sides of equation (3),

$$\frac{\varepsilon'^2 + \varepsilon' + \varepsilon''^2 - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} + \frac{4\pi N_1 \mu^2}{9kT} \frac{1}{1 + \omega^2 \tau^2},$$

$$\frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} = \frac{4\pi N_1 \mu^2}{9kT} \frac{\omega \tau}{1 + \omega^2 \tau^2}.$$

Putting

$$X = \frac{\varepsilon'^2 + \varepsilon' + \varepsilon''^2 - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} \quad (4)$$

$$Y = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \quad (5)$$

and

$$P = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2},$$

in the above equations, one gets

$$X = P + \frac{Y}{\omega \tau}. \quad (6)$$

The value of P in equation (6) slightly varies over the range of concentration of dilute solutions. But as the variation of ε' and ε'' is far higher than the variation in the value of P due to the change in concentration of dilute solutions at microwave frequencies, it could be treated as constant over the range of concentration variation. From the slope of the curve Y versus X the value of relaxation time τ of polar molecules in non-polar solvents could be determined and it can be written as,

$$\tau = \frac{\lambda_o}{2\pi c} \left(\frac{dY}{dX} \right). \quad (7)$$

For the determination of dipole moment μ equation (6) can be written as

$$X = P + KWd_{12}, \quad (8)$$

with

$$K = \frac{4\pi N \mu^2}{9kTM(1 + \omega^2 \tau^2)},$$

and

$$N_1 = \frac{Nd_{12}W}{M},$$

where N is the Avogadro number, M is the molecular weight of polar substance, W is the weight fraction and d_{12} is the density of solution. At low concentration range,

variation of density of the solution with weight fraction W may be taken as linear given by the relation,

$$d_{12} = d_0(1 + \alpha W),$$

where d_0 is the density of the solvents. In the limited experimental range of concentration variation, the graph between X and W can be taken as a straight line with its slope (dX/dW) as Kd_0 . From this the value of dipole moment may be calculated, using the following relation:

$$\mu^2 = \frac{9kTM}{4\pi Nd_0} \left[1 + \left(\frac{dY}{dX} \right)^2 \right] \frac{dX}{dW}. \quad (9)$$

The values of ε' and ε'' , τ and ε'' thus determined are shown in tables 1 and 2. It is found that ε' and ε'' vary linearly with weight fraction of solute in benzene for all binary mixtures. This shows that there is no change in the nature of the rotating molecular entities in the benzene solution. This ensures the applicability of Gopala Krishna's method in the studied concentration range of the binary mixtures in the benzene solutions. It is found that dipole moments for pure NMA and NMF in benzene solution is very close to the literature values of the dipole moment. This shows that pure NMA and pure NMF exist in the monomer form in the benzene solution.

The energy parameters $(\Delta H_\varepsilon, \Delta F_\varepsilon, \Delta S_\varepsilon)$ for the dielectric relaxation process for NMA + NMF binary mixture containing 30 mol% NMF in benzene at 25, 30, 35 and 40°C and the corresponding energy parameters $(\Delta H_\eta, \Delta F_\eta, \Delta S_\eta)$ for the viscous flow

Table 2. Dielectric relaxation time (τ) and dipole moment (μ) for different mole-fractions of (NMA + NMF) mixtures in benzene solution at different temperatures.

Temperature (°C)	Mole fraction of NMF in binary mixtures	$\tau/10^{-12}$ s	μ (Debye)
25	0.00	4.13	3.74 (μ_{NMA})
	0.30	5.08	
	0.50	4.97	
	0.70	4.74	
	1.00	4.47	
30	0.00	4.02	3.62 (μ_{NMA})
	0.30	4.94	
	0.50	4.84	
	0.70	4.65	
	1.00	4.27	
35	0.00	3.91	3.55 (μ_{NMA})
	0.30	4.80	
	0.50	4.73	
	0.70	4.56	
	1.00	4.13	
40	0.00	3.80	3.52 (μ_{NMA})
	0.30	4.67	
	0.50	4.61	
	0.70	4.48	
	1.00	3.96	

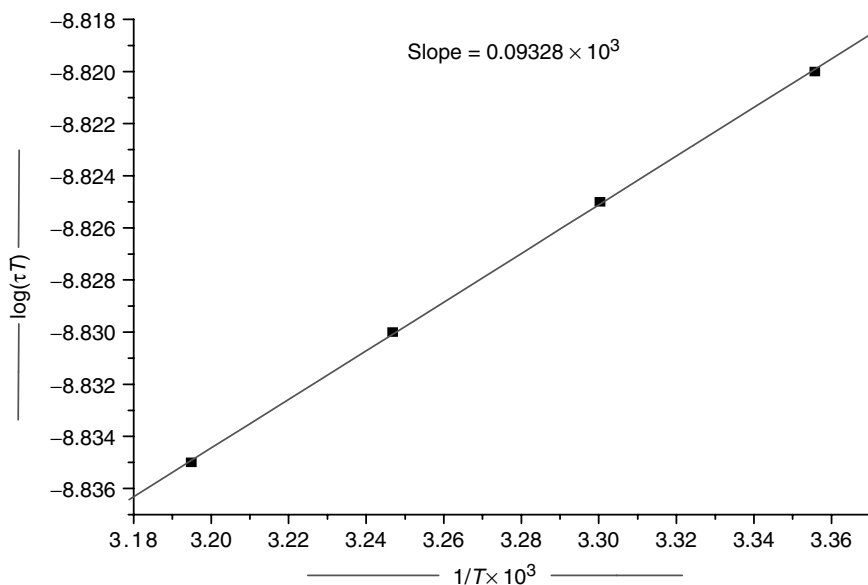


Figure 1. Plot between $\log(\tau T)$ vs. $10^3/T$ at 0.30 mol% of NMF in (NMA + NMF) binary mixture.

have been calculated by using Eyring *et al.* [16] relations for the rate process. In particular, the following relations were used:

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta F_\varepsilon}{RT}\right) \quad (10)$$

$$\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon \quad (11)$$

$$\eta = \frac{hN}{V} \exp\left(\frac{\Delta F_\eta}{RT}\right) \quad (12)$$

and

$$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta \quad (13)$$

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 dielectric relaxation process, and ΔH_η , ΔF_η and ΔS_η are corresponding parameters for the viscous flow.

The plot of $\log(\tau T)$ versus $10^3/T$ (figure 1) and $\log(\eta)$ versus $10^3/T$ according to equations (10) and (12) were found to be linear, which shows that both 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 $10^3/T$ and $\log(\eta)$ versus $10^3/T$, respectively using the relation: slope = $\Delta H/2.303R$. Both sets of energy parameters along with the dielectric relaxation times (τ) for NMA + NMF binary mixtures containing 30 mol% NMF in benzene solution at 25, 30, 35 and 40°C have been summarized in table 3.

Table 3. Relaxation time (τ), free energies of activation (ΔF_e , ΔF_η in kJ mol^{-1}), enthalpies of activation (ΔH_e , H_η in kJ mol^{-1}) and entropies of activation (ΔS_e , ΔS_η in $\text{J mol}^{-1} \text{ } ^\circ\text{K}^{-1}$) for (NMA + NMF) mixture containing 30 mol% of NMF in benzene solutions.

Temp ($^\circ\text{C}$)	$\tau/10^{-12}$ s	ΔF_e	ΔH_e	ΔS_e	ΔF_η	ΔH_η	ΔS_η
25	5.08	8.548	1.785	-22.695	12.180	10.969	-4.064
30	4.94	8.663	1.785	-22.700	12.209	10.969	-4.092
35	4.80	8.774	1.785	-22.692	12.236	10.969	-4.114
40	4.67	8.887	1.785	-22.690	12.299	10.969	-4.249

Table 2 shows the dielectric relaxation times (τ) and dipole moments (μ) for different mole-fractions of NMA + NMF binary mixtures at different temperatures in the benzene solution. The values of the relaxation times (τ) vary non-linearly with the increase in the mole-fraction of NMF in the binary mixtures NMA + NMF at all temperatures (25, 30, 35 and 40°C). The relaxation time depends upon 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, non-linear variation of the relaxation time with the mole-fraction is interpreted as due to the possible solute-solute molecular association in the binary mixtures.

In the binary mixtures of NMA + NMF system, the variation of relaxation time with increase in the mole fraction of NMF in benzene solution at 25, 30, 35 and 40°C presents an interesting behavior (figure 2). The relaxation time of NMA + NMF mixture increase as mole fraction of NMF in NMA + NMF is increased from 0 to 0.3. After this mole fraction relaxation time starts decreasing and falls towards the value of pure NMF in the benzene solution. This behavior indicates solute-solute type of molecular association between NMA and NMF with the result that the molecular entity becomes much more voluminous than the individual molecule. In its whole concentration range, the relaxation time of NMA + NMF mixtures remains longer than that pure NMF. Therefore, the solute-solute type of molecular association between NMA and NMF is indicated in its entire concentration range. In view of above results, it is proposed that in the binary mixtures of NMA and NMF, NMA exists in the dimer structure resulting because of H-bonding and dimer structure of NMA interests with the NMF molecule so as to give the maximum value of relaxation time at 30 mol% NMF binary mixture. The following type of molecular association (figure 3) arising from the interaction of the fractional negative charge on the oxygen atom of the NMA molecule and the fractional positive charge on the carbon atom of NMF molecule can be proposed. Solute-solvent association can be interpreted because of the molecular association arising from the fractional positive charge at the sight of C-atom of NMA molecules and π -delocalized electron cloud in the benzene ring of benzene molecule is shown in figure 4.

It is found that the free energy of activation (ΔF_e) for the dielectric relaxation process is less than the free energy of activation (ΔF_η) for the viscous flow process. It may be explained on the basis that the dielectric relaxation process involves the rotation of molecular entities whereas in the viscous flow process, the rotational as well as the

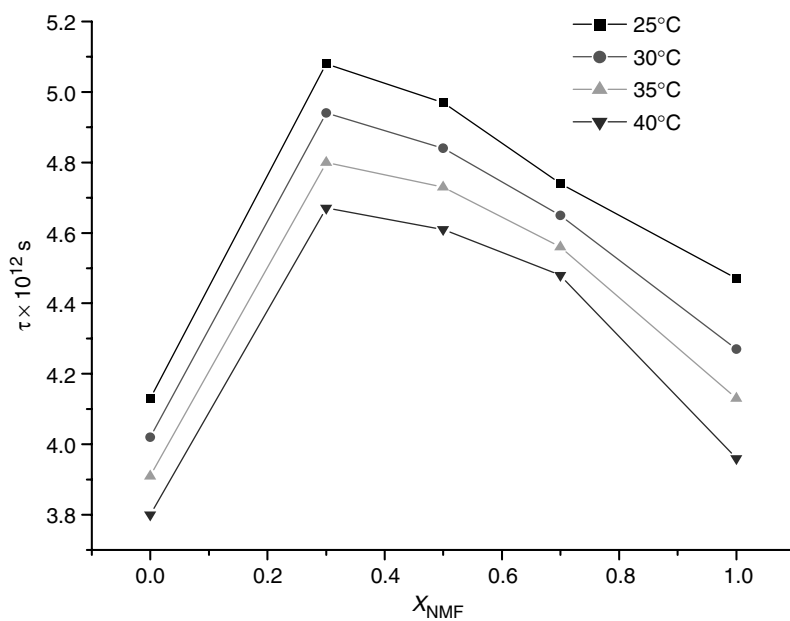


Figure 2. Plot of relaxation time (τ) vs. mole fraction of NMF (X_{NMF}) in (NMA + NMF) mixtures in benzene solution at different temperatures.

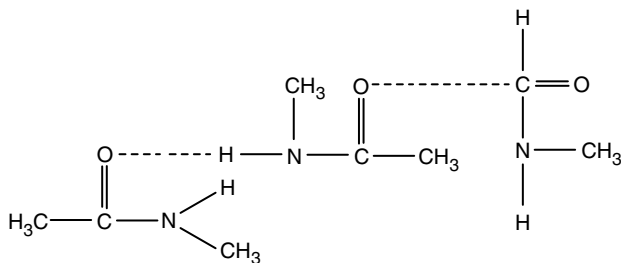


Figure 3. Solute-solute associations between NMA and NMF.

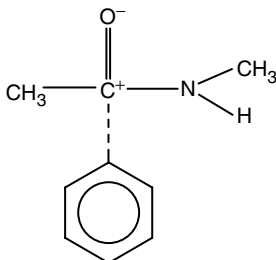


Figure 4. Solute-solvent association of NMA molecule in benzene.

translational motion of the molecules is involved. It is found that the enthalpy of activation for the dielectric relaxation process (ΔH_e) is less 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 for the enthalpy of activation indicate that the dielectric relaxation process and viscous flow process involve the breaking of bonds with the neighboring molecules in a different way and to a different extent. Entropy of a system is a measure of the orderly nature of the system. If the environment of the system is co-operative for the activated process, then the change in entropy (S) becomes $-ve$. Whereas the $+ve$ value of the change in the entropy (ΔS_e) for 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 co-operative like that of the activated viscous flow state.

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