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An investigation on molecular dynamics of binary mixtures of N-methylacetamide and tetramethylurea in microwave region

Raman Kumar Chaudhary[a]*, Raman Kumar[b] & V S Rangra[c]
[a]Physics Department, Government College Dhaliara, Kangra 177 103, India
Government College Rakkar, Kangra 177 043, India
[c]Physics Department, Himachal Pradesh University, Shimla 171 005, India

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The dielectric relaxation times (τ) and the dipole moments (μ) of the binary mixtures of different molar concentrations of tetramethylurea (TMU) in the binary mixtures of N-methylacetamide (NMA) and tetramethylurea (TMU) in benzene solutions have been calculated by using standard standing wave microwave techniques and Gopala Krishna's single frequency (9.90 GHz) concentration variational method at different temperatures (25 °C, 30 °C, 35 °C and 40 °C). The energy parameters (ΔH_ε, ΔF_ε, ΔS_ε) for the dielectric relaxation process of binary mixtures containing 30% mole-fraction of TMU have been calculated at the respective given temperatures and the comparison has been made with the corresponding energy parameters (ΔH_η, ΔF_η, ΔS_η) for the viscous flow. On the basis of the observations, it is found that the dielectric relaxation process can be treated as the rate process like the viscous flow process. The solute-solute and solute-solvent types of the molecular associations have been predicted.

Keywords: Dielectric relaxation, Binary mixtures, Microwave absorption studies

1 Introduction

The dielectric relaxation studies of the binary mixtures of polar molecules in non-polar solvents using microwave absorption methods have been attempted by many researchers[1-7]. Amides form the basic building blocks in proteins; therefore, dielectric relaxation studies of binary mixtures of amides are expected to be of great interest. N-Methylacetamide (NMA) is recognized as the non-aqueous dipolar, aprotic solvent having dielectric constant[8] $\varepsilon' = 178.9$ at 30 °C and 165.5 at 40 °C. It has dipole moment[8] $\mu = 3.50$ D. Tetramethylurea (TMU) has a low dielectric constant $\varepsilon' = 23.45$ and dipole moment[9] $\mu = 3.47$ D. Its liquid range is -1.2 to 176 °C. It has a slight not unpleasant smell and is non-toxic. It is possible to prepare binary mixtures of given dielectric constant value lying between that of NMA and TMU by mixing respective solvents in proper proportions. This motivated the authors to undertake the experimental work concerned with the dielectric relaxation process in the binary mixture of NMA and TMU in order to understand the molecular association in the whole concentration range of TMU in the binary mixtures.

The dielectric relaxation studies in the microwave region provide meaningful information about self-association, solute-solute and solute-solvent type of the molecular associations among the polar molecules[10-12]. The present study is concerned with the molecular association in the binary mixture of NMA+TMU at different temperatures (25 °C, 30 °C, 35 °C and 40 °C). Standard standing wave microwave techniques and single frequency concentration variational method of Gopala Krishna have been used. This method makes use of benzene as the suspension medium for the study of the suspended rotating molecular entities. This method consists in measuring dielectric constant (ε') and the dielectric loss (ε'') of series of dilute solutions of polar molecules (of binary solutions) in non-polar solvents (benzene).

2 Experimental Details

N-methylacetmamide (GC Grade) from FLUKA, Germany was purified by repeated (three times) crystallization. Tetramethylurea (FLUKA) was dried over anhydrous BaO powder for 48 h and then distilled through long vertical fractionating column. The middle fractions were collected for use. Benzene GR (E Merck (India), Ltd. Mumbai) was dried by refluxing over freshly cut sodium metal for 6-8 h and then distilled

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*Corresponding author (E-mail: raman.phy.hpu@gmail.com)

through a long vertical fractionating column. The middle fraction of the distilled benzene was collected for use. 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 & Sharma[13] for microwave measurements were used. Set of dilute solutions of the binary mixtures in the benzene solutions were prepared and all the measurements were carried out at 25 °C, 30 °C, 35 °C and 40 °C by circulating water around the dielectric cell through a thermostat (LAUDA DR R WOBSER GMBH & CO. KG German made). Measuring the dipole moments of purified acetone, methanol and pyridine tested the precision and working of the equipment. The viscosity and densities of the solutions at various temperatures were measured by Ubbelohde viscometer and sealable type of pycnometer, respectively.

3 Results and Discussion

Using standard standing wave microwave techniques and following the method of Heston *et al.*[14], the dielectric constant (ε') and the dielectric loss (ε'') at 25 °C for the dilute solutions of NMA, TMU and NMA+TMU mixtures containing 30, 50 and 70 mol% TMU in benzene have been calculated and given in Table 1.

Following equations have been used:

$$\varepsilon' = \left(\frac{\lambda_o}{\lambda_c}\right)^2 + \left(\frac{\lambda_o}{\lambda_d}\right)^2 \qquad \ldots (1)$$

and

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_o}{\lambda_d}\right)^2 \cdot \frac{\lambda_g}{\lambda_d}\left(\frac{d\rho}{dn}\right) \qquad \ldots (2)$$

where 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 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. The ε'

Table1 – Values of dielectric constant (ε′), dielectric loss (ε″), relaxation time (τ) and dipole moment (μ) of (NMA+TMU) mixtures in benzene solution at 25 °C.

Mole-fraction of TMU in binary mixture	Weight fraction of solute in benzene	ε′ (±0.5%)	ε″ (±1.67%)	$\frac{\tau}{10^{-12}}$ (s)	μ (D)
0.00	.0049	2.355	0.0418	4.13	3.74 μ_{NMA}
	.0058	2.370	0.0468		
	.00736	2.402	0.0558		
	.00856	2.432	0.0632		
	.0093	2.443	0.0672		
0.30	.00357	2.287	0.0198	4.86	
	.00435	2.300	0.0239		
	.00641	2.327	0.0333		
	.00729	2.341	0.0377		
	.00849	2.362	0.0434		
0.50	.00331	2.267	0.0196	3.48	
	.00453	2.287	0.0231		
	.00601	2.317	0.0299		
	.00844	2.359	0.0401		
	.00993	2.395	0.0487		
0.70	.00318	2.277	0.0173	3.34	
	.00427	2.304	0.0224		
	.00573	2.327	0.0274		
	.00766	2.362	0.0354		
	.00944	2.398	0.0434		
1.00	.00311	2.264	0.0162	5.32	3.43 μ_{TMU}
	.00446	2.273	0.0196		
	.00607	2.293	0.0262		
	.00772	2.307	0.0297		
	.00983	2.331	0.0395		

and ε'' values were reproducible within $\pm 0.5\,\%$ and $\pm 1.67\,\%$, respectively.

Following the Gopala Krishna's single frequency concentration variational method[15], the dielectric relaxation time (τ) and the dipole moment (μ) have been calculated.

$$X = \frac{\varepsilon'^2 + \varepsilon' + \varepsilon''^2 - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad \ldots (3)$$

$$Y = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad \ldots (4)$$

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

and

$$\mu^2 = \frac{9kTM}{4\pi N d_0}\left[1 + \left(\frac{dY}{dX}\right)^2\right]\frac{dX}{dW} \qquad \ldots (6)$$

The values of ε', ε'', τ and μ, thus determined are given in Table 1 and Table 2. It is found that ε' and ε'' vary linearly with weight fraction of solute in benzene solution for all binary mixtures. This ensures that the rotating molecular entities retain their configuration in the concentration range studied. The essential condition for the application of the Gopala Krishna method for the study of dielectric relaxation time and dipole moment using single frequency concentration variational method is the proper choice of the concentration range. This concentration range of dilute solutions of polar molecules in non-polar solvents should be such that the Debye theory is applicable and the participating molecular entities do not change their configuration in that concentration variation range. Thus the linear variation of ε' and ε'' with the weight fraction of the solute ensures the applicability of Gopala Krishna's method for the determination of dielectric relaxation time and dipole moment of polar molecules in non-polar solvents. It is found that dipole moments for pure NMA and TMU in benzene solution are very close to the literature values of the dipole moment. This shows that pure NMA and pure TMU exist in the monomer form in the benzene solution.

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

Temperature (°C)	Mole fraction of TMU in binary mixtures	$\frac{\tau}{10^{-12}}$ (s)	μ (D)
25	0.00	4.13	3.74μ_{NMA}
	0.30	4.86	
	0.50	3.48	
	0.70	3.34	
	1.00	5.32	3.43 μ_{TMU}
30	0.00	4.02	3.62 μ_{NMA}
	0.30	4.67	
	0.50	3.23	
	0.70	3.09	
	1.00	5.15	3.44 μ_{TMU}
35	0.00	3.91	3.55 μ_{NMA}
	0.30	4.50	
	0.50	3.03	
	0.70	2.83	
	1.00	4.96	3.66 μ_{TMU}
40	0.00	3.80	3.52 μ_{NMA}
	0.30	4.36	
	0.50	2.82	
	0.70	2.57	
	1.00	4.80	3.69 μ_{TMU}

The energy parameters for the dielectric relaxation process (ΔH_ε, ΔF_ε, ΔS_ε) and the corresponding energy parameters (ΔH_η, ΔF_η, ΔS_η) for the viscous flow for NMA+TMU mixtures for instance, containing 30 mol% of TMU in benzene have been calculated by using Eyring *et al.*[16], relations for the rate process. Following relations were used:

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta F_\varepsilon}{RT}\right) \qquad \ldots (7)$$

$$\Delta F_\varepsilon = \Delta \mathrm{H}_\varepsilon - T\Delta S_\varepsilon \qquad \ldots (8)$$

$$\eta = \frac{hN}{V}\exp\left(\frac{\Delta F_\eta}{RT}\right) \qquad \ldots (9)$$

And

$$\Delta F_\eta = \Delta \mathrm{H}_\eta - T\Delta S_\eta \qquad \ldots (10)$$

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 plots of $\log(\tau T)$ versus $10^3/T$ (Fig. 1) and $\log(\eta)$ versus $10^3/T$ according to Eqs (7) and (9) 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= $\Delta H/2.303R$, where R is the gas constant. Both sets of energy parameters along with the dielectric relaxation time (τ) for NMA+TMU binary mixtures containing 30 mol% TMU in benzene solution at 25 °C, 30 °C, 35 °C and 40 °C have been summarized in Table 3.

Table 2 shows the dielectric relaxation times (τ) and dipole moment (μ) for different mole-fractions of NMA+TMU binary mixtures at different temperatures in the benzene solution. The values of the relaxation time (τ) vary non-linearly with the increase in the mole-fraction of TMU in the binary mixtures NMA+TMU at all temperatures (25 °C, 30 °C, 35 °C, 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 the possible solute-solute molecular association in the binary mixtures.

Relaxation time of TMU is found to be longer than that of NMA (Table 1 and 2). This may be attributed to the larger size and shape of TMU molecules as compared with the NMA molecules. Figure 2 shows the variation of relaxation time (τ) with the increase of mole fraction of TMU in the mixtures. We observed an interesting behaviour in the relaxation time, it first increases and then decreases and then again increases with the mole fraction of TMU. Similar type of behaviour is found in the whole studied temperature range. So, if the relaxation time of NMA+TMU binary mixture linearly with the mole fraction of TMU (X_{TMU}), no molecular association can be inferred. However, if the relaxation time of NMA+TMU mixture varies non-linearly, a solute-

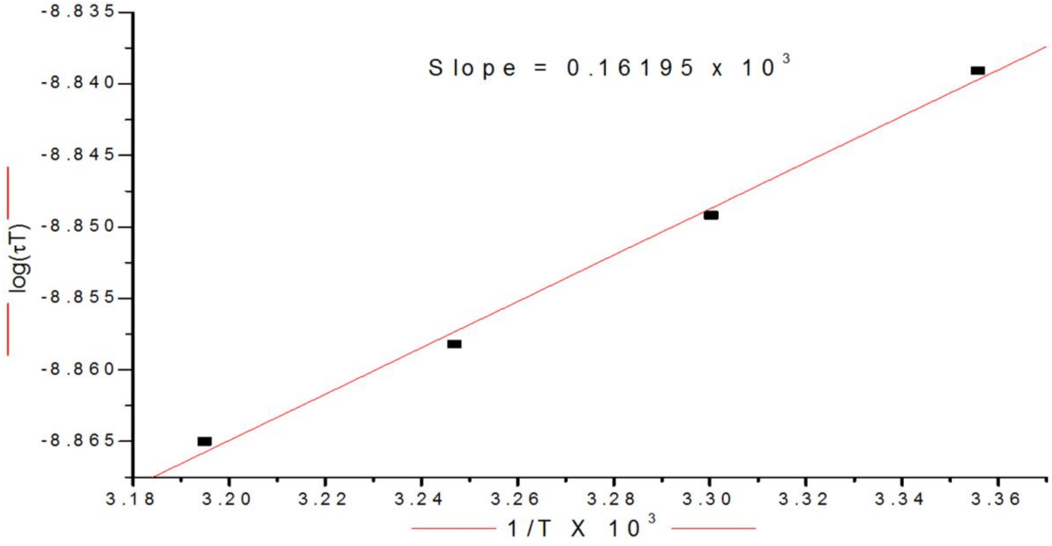

Fig. 1 – Plot between log (τT) versus $10^3/T$ at 0.30 mol% of TMU in (NMA+TMU) binary mixture.

Table 3 – Relaxation time (τ), Free energies of activation (ΔF_ε, ΔF_η in kJmole^{-1}), enthalpies of activation (ΔH_ε, ΔH_η in kJmole^{-1}) and entropies of activation (ΔS_ε, ΔS_η in Jmole^{-1}deg^{-1}K^{-1}) for (NMA+TMU) mixture containing 30 mol% of TMU in benzene solutions.

Temperature (°C)	$\frac{\tau}{10^{-12}}$ (s)	ΔF_ε	ΔH_ε	ΔS_ε	ΔF_η	ΔF_η	ΔS_η
25	4.86	8.438	3.099	-17.916	12.180	10.969	-4.064
30	4.67	8.521	3.099	-17.894	12.209	10.969	-4.092
35	4.50	8.609	3.099	-17.890	12.236	10.969	-4.114
40	4.36	8.708	3.099	-17.920	12.299	10.969	-4.249

solute type of molecular association NMA and TMU may be inferred. The value of relaxation time is found to be maximum at 30 mol% TMU in the binary mixture. This shows that molecular association is maximum at 30 mol% TMU in NMA+TMU binary mixture. Solute-solute type of molecular association is predicated 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 molecular association between TMU and NMA has a maximum at a 30:70 mol% ratio and than decreases and than again increases at mole fraction of TMU equal to 1.00. The experiment was repeated number of times so as to ensure the reproducibility of the above results. It is found that the above results are reproducible within the experimental accuracy range. The binary mixture of NMA and TMU was prepared by mixing NMA and TMU in required proportions. And then by mixing this binary solution in the benzene solvent, dilute solutions of binary mixtures in benzene were made. It is observed that maximum value of the relaxation time is found in the NMA rich region. This type of behaviour shows the presence of solute-solute type of association arising because of the interaction of TMU molecules with a number of NMA molecules. Molecular association arising because of the interaction between the fractional positive charge at site of nitrogen atom of NMA molecule and the negative charge at the site of oxygen atom of TMU molecule. In view of above results, it is proposed that in the binary mixtures of NMA and TMU, NMA exists in the dimer structure resulting because of H-bonding and dimer structure of NMA interacts with the TMU molecules so as to give the maximum value of relaxation time at 30 mol% TMU binary mixture. This type of molecular interaction has been proposed in Fig. 3. In the TMU rich region, the increases of relaxation time with the decrease of NMA indicates the presence of solute-solvent association.

The dipole moment of NMA varies slightly with rise in temperature and approaches towards the literature value. Small variation of dipole moment with rise of temperature may be associated with the breaking nature of the solute-solvent type of molecular association. Solute-solvent association can be interpreted because of the molecular association arising from the interaction of fractional positive charge at the sight of *C*-atom in NMA molecules and π-delocalized electron cloud in the benzene ring of benzene molecule is shown in the Fig. 4.

The observation shows that, the free energy of activation (ΔF_ε) for the dielectric relaxation process is less than the free energy of activation (ΔF_η) for the viscous flow process. This may be explained on the basis that the dielectric relaxation process involves the

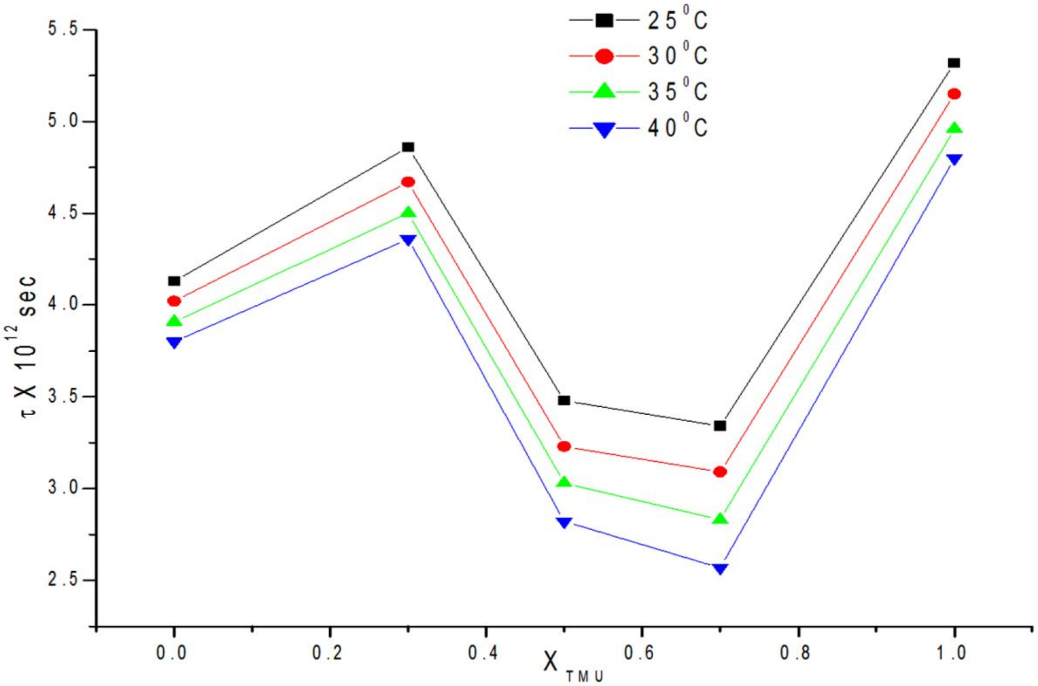

Fig. 2 – Plot of relaxation time (τ) versus mole fraction of TMU (X_{TMU}) in NMA+TMU mixtures in benzene solution at different temperatures.

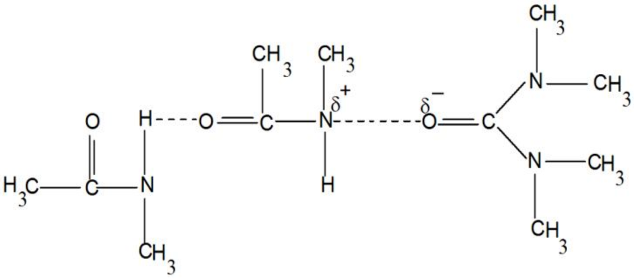

Fig. 3 – Solute-solute associations between NMA and TMU.

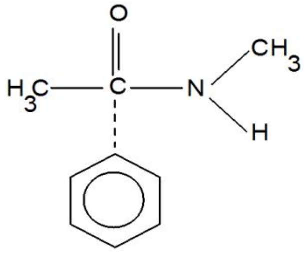

Fig. 4 – Solute-solvent association of NMA molecule in benzene.

rotation of molecular entities whereas in the viscous flow process, the rotational as well as the translational motion of the molecules is involved. It is found that the enthalpy of activation for the dielectric relaxation process (ΔH_ε) 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 neighbouring molecules in a different way and to a different extent. Entropy of a system is the 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 (ΔS_ε) becomes –ve. Whereas the +ve value of the change in the entropy (ΔS_ε) 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.

4 Conclusions

The values of dielectric relaxation parameters and thermodynamics parameters have been reported for the binary mixtures. These studies suggests the solute-solute (dimer) and solute-solvent (monomer) molecular association in the mixture through hydrogen bonding.

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