Dielectric Relaxation Studies of Binary Mixtures of *N*-Methylformamide and Tetramethylurea in Benzene Using Microwave Absorption Data

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The dielectric relaxation time (τ) and dipole moment (μ) of binary mixtures of different molar concentrations of *N*-methylformamide (NMF) in binary mixtures of NMF and tetramethylurea (TMU) in benzene have been calculated at 25, 30, 35 and 40 °C using standard standing wave microwave techniques and following the single frequency (9.885 GHz) concentration variational method of Gopala Krishna. The energy parameters (ΔH_ε, ΔF_ε, ΔS_ε) for the dielectric relaxation process of binary mixtures containing 30 mol% of NMF have been calculated at different temperatures, and comparison has been made with the corresponding energy parameters (ΔH_η, ΔF_η, ΔS_η) for the viscous flow process. Based on these studies, it was inferred that the dielectric relaxation process can be treated as a rate process just like the viscous flow process. Solute-solvent and solute-solute molecular associations have been proposed.

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

1. Introduction

N-Methylformamide (NMF) is an important non-aqueous amide. It has a high dielectric constant ($\varepsilon' = 182.4$) and high dipole moment ($\mu = 3.82$ D) [1]. The investigation of the structure of NMF is interesting for biochemists because the molecule contains a peptide linkage, and a study of its hydrogen bonding yields insight into the nature of protein structures [2, 3]. NMF is also of considerable medical interest since it possesses antitumour activities [4]. Tetramethylurea (TMU) is an important non-aqueous solvent with a dielectric constant ε' of (23.45 ± 0.06) and a dipole moment μ of 3.37 D [5]. The combination of a high dipole moment, moderate dielectric constant, low viscosity and low specific conductance makes TMU a useful solvent for studying the behaviour of electrolytes in solution [5]. Dielectric relaxation studies of polar molecules in non-polar solvents by microwave absorption have frequently been attempted [6 – 12]. From the solvent point of view it is possible to prepare binary mixtures of NMF and TMU having a dielectric constant between that of NMF and TMU. This motivated us to study the dielectric relaxation of (NMF+TMU) mixtures in order to understand the molecular association in the system.

Dielectric relaxation studies in the microwave region provide information about various types of molecular associations [13], because microwaves allow to detect even weaker molecular interactions. Standard standing wave microwave techniques have been used to measure the dielectric constant ε' and dielectric loss ε'' of dilute solutions of (NMF+TMU) binary mixtures in benzene. Gopala Krishna's [14] single frequency concentration variational method has been used to calculate the dielectric relaxation time τ and dipole moment μ. The measurements have been made on different mole fractions of NMF (0, 0.3, 0.5, 0.7, 1.0) in (NMF+TMU) binary mixtures at different temperatures (25, 30, 35, and 40 °C). The energy parameters ΔH_ε, ΔF_ε, ΔS_ε for the dielectric relaxation process have been calculated for a binary mixture having 30 mol% NMF and compared with the corresponding energy parameters for the viscous flow process. It was found that the dielectric relaxation process is a rate process like the viscous flow process. Solute-solute and solute-solvent molecular associations have been proposed for NMF and TMU.

2. Experimental

NMF GC grade (Fluka, Germany) was dried with 4 Å molecular sieves for about 10 h and then distilled under reduced pressure using a long vertical fractionating column. The middle fraction was collected for

Table 1. Dielectric constant (ε') and dielectric loss (ε'') for (NMF+TMU) mixtures containing 0, 30, 50, 70 and 100 mol% of NMF in benzene solution at different temperatures.

Mole fraction of NMF in binary mixture	Weight fraction of solute in benzene	25 °C		30 °C		35 °C		40 °C	
		ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
0.00	0.0026	2.334	0.0111	2.317	0.0105	2.305	0.0098	2.292	0.0094
	0.0044	2.348	0.0167	2.332	0.0156	2.317	0.0146	2.313	0.0143
	0.0063	2.367	0.0232	2.353	0.0214	2.339	0.0201	2.332	0.0189
	0.0082	2.387	0.0294	2.371	0.0279	2.355	0.0260	2.348	0.0248
	0.0103	2.405	0.0380	2.389	0.0360	2.378	0.0336	2.369	0.0319
0.30	0.0021	2.331	0.0106	2.317	0.0102	2.305	0.0093	2.293	0.0089
	0.0038	2.350	0.0154	2.331	0.0143	2.320	0.0134	2.307	0.0126
	0.0056	2.364	0.0224	2.348	0.0211	2.338	0.0198	2.327	0.0187
	0.0078	2.387	0.0328	2.369	0.0307	2.360	0.0296	2.348	0.0279
	0.0098	2.403	0.0416	2.389	0.0394	2.380	0.0372	2.369	0.0351
0.50	0.0020	2.339	0.0104	2.310	0.0097	2.293	0.0089	2.283	0.0085
	0.0038	2.360	0.0168	2.331	0.0155	2.317	0.0148	2.303	0.0139
	0.0059	2.383	0.0264	2.355	0.0246	2.343	0.0237	2.331	0.0225
	0.0077	2.405	0.0363	2.380	0.0348	2.364	0.0332	2.353	0.0319
	0.0094	2.424	0.0451	2.398	0.0433	2.385	0.0403	2.378	0.0391
0.70	0.0020	2.319	0.0105	2.302	0.0098	2.293	0.0094	2.288	0.0086
	0.0038	2.351	0.0188	2.336	0.0173	2.329	0.0162	2.319	0.0141
	0.0058	2.391	0.0301	2.378	0.0283	2.369	0.0267	2.351	0.0229
	0.0080	2.433	0.0420	2.413	0.0397	2.409	0.0382	2.385	0.0327
	0.0100	2.465	0.0534	2.455	0.0517	2.448	0.0503	2.418	0.0404
1.00	0.0022	2.362	0.0121	2.339	0.0113	2.325	0.0106	2.315	0.0100
	0.0043	2.407	0.0280	2.391	0.0256	2.376	0.0235	2.366	0.0222
	0.0068	2.465	0.0476	2.446	0.0445	2.437	0.0421	2.427	0.0397
	0.0076	2.488	0.0574	2.463	0.0540	2.454	0.0515	2.446	0.0493
	0.0112	2.566	0.0845	2.550	0.0808	2.544	0.0783	2.538	0.0744

use. TMU (Fluka, Germany) was dried over anhydrous BaO for 48 h and then distilled a long vertical fractionating column, and the middle fraction was used within a week to avoid decomposition. Benzene extra-pure AR (Sisco Research Laboratories Pvt. Ltd., Mumbai, India) was dried by refluxing over freshly cut sodium metal for 6 – 8 h and then distilled using a long vertical fractionating column. The middle fraction of distilled benzene was collected for use. An X-band microwave bench was used to measure the wavelength in the dielectric medium and a short-circuiting plunger to measure the voltage standing wave ratio (VSWR). Microwave techniques of Heston et al. [15] were used to calculate the dielectric constant (ε') and dielectric loss (ε'') of the dilute solutions of binary mixtures of NMF and TMU in benzene at different temperatures. Circulation of thermostated water around the dielectric cell controlled the temperature of the solution within ±0.05 °C. The viscosity and density of benzene at different temperatures were measured with a Ubbelohde viscometer and a pycnometer, respectively. The dielectric relaxation time (τ) for NMF, TMU and different mole fractions of (NMF+TMU) mixtures, and the dipole moment (μ) for NMF and TMU were calculated following the single frequency concentration variational method of Gopala Krishna [14]. Eyring rate equations [16] have been used to calculate the energy parameters for the dielectric relaxation and viscous flow processes treating the viscous flow as a rate process.

3. Results and Discussion

The dielectric constant (ε') and dielectric loss (ε'') for the dilute solutions of NMF, TMU and (NMF+TMU) mixtures containing 30, 50, and 70 mol% NMF in benzene at 25, 30, 35 and 40 °C have been calculated by the method of Heston et al. [15]. The equations

$$\varepsilon' = \left(\frac{\lambda_\mathrm{o}}{\lambda_\mathrm{c}}\right)^2 + \left(\frac{\lambda_\mathrm{o}}{\lambda_\mathrm{d}}\right)^2 \tag{1}$$

and

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_\mathrm{o}}{\lambda_\mathrm{d}}\right)^2 \frac{\lambda_\mathrm{g}}{\lambda_\mathrm{d}}\left(\frac{\mathrm{d}\rho}{\mathrm{d}n}\right) \tag{2}$$

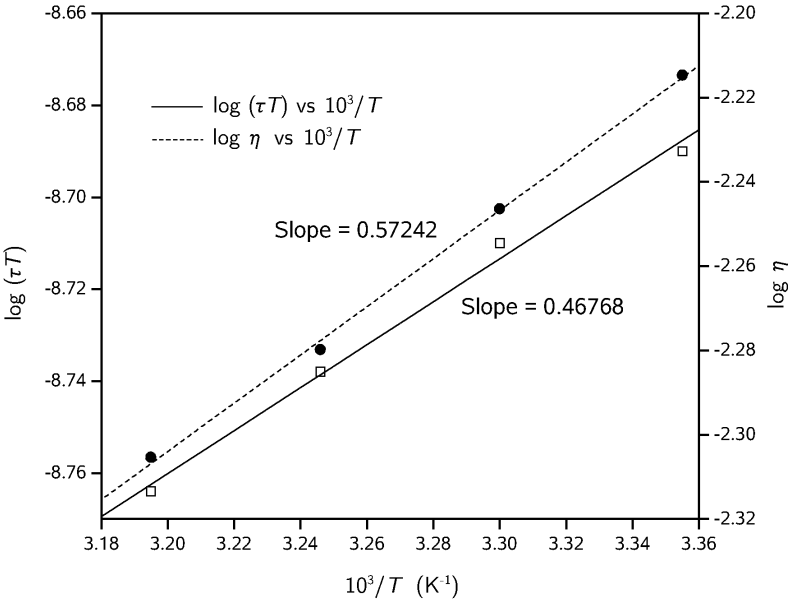

Fig. 1. Plot of $\log(\tau T)$ versus $10^3/T$ for 30 mol% of NMF in the binary mixture (NMF+TMU) and $\log\eta$ versus $10^3/T$.

have been used where λ_o, λ_c, λ_g and λ_d are the free space wavelength, the cut-off wavelength, the waveguide wavelength and the wavelength in the waveguide filled with solution, respectively. ρ is the inverse of the VSWR, and $\mathrm{d}\rho/\mathrm{d}n$ is the slope of the ρ versus n curve, where $n = 1, 2, 3, \cdots$. ε' and ε'' were reproducible within $\pm 0.5\%$ and $\pm 3.8\%$, respectively. The values of ε' and ε'' thus obtained for different mole fractions of NMF in the binary mixture at 25, 30, 35 and 40 °C are reported in Table 1. The relaxation time and dipole moment have been calculated by using the following equations of Gopala Krishna's single frequency concentration variation method [14]:

$$\tau = \left(\frac{\lambda_o}{2\pi c}\right)\frac{\mathrm{d}y}{\mathrm{d}x}, \tag{3}$$

$$\mu^2 = \frac{9kTM}{4\pi N d_o}\left[1 + \left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2\right]\frac{\mathrm{d}x}{\mathrm{d}W}, \tag{4}$$

where

$$x = \frac{\varepsilon'(\varepsilon'+1) + \varepsilon''^2 - 2}{(\varepsilon'+2) + \varepsilon''^2}, \tag{5}$$

$$y = \frac{3\varepsilon''}{(\varepsilon'+2)^2 + \varepsilon''^2}, \tag{6}$$

where d_o is the density of the solvent, M the molecular weight of polar substance, W the weight fraction and N Avogadro's number. k is Boltzmann's constant and T the absolute temperature.

The energy parameters of the dielectric relaxation process and the corresponding energy parameters of the viscous flow process of (NMF+TMU) mixtures containing 30 mol% NMF in benzene have been calculated by using the following equations given by Eyring et al. [16] for the rate process:

$$\tau = \frac{h}{kT}\exp(\Delta F_\varepsilon/RT), \tag{7}$$

$$\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon, \tag{8}$$

$$\eta = \frac{hN}{V}\exp(\Delta F_\eta/RT), \tag{9}$$

$$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta, \tag{10}$$

where ΔF_ε, ΔH_ε and ΔS_ε are the free energy, enthalpy and entropy of activation of the dielectric relaxation process, and ΔF_η, ΔH_η and ΔS_η are the corresponding energy parameters of the viscous flow process. V is the molar volume of the solvent, and all other symbols have their usual meaning. The plots of $\log(\tau T)$ versus $10^3/T$ and $\log\eta$ versus $10^3/T$ (Fig. 1) according to (7) and (9) are found to be linear, which indicates that both, the dielectric relaxation process and the viscous flow process, can be treated as a rate process. 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 $\log\eta$

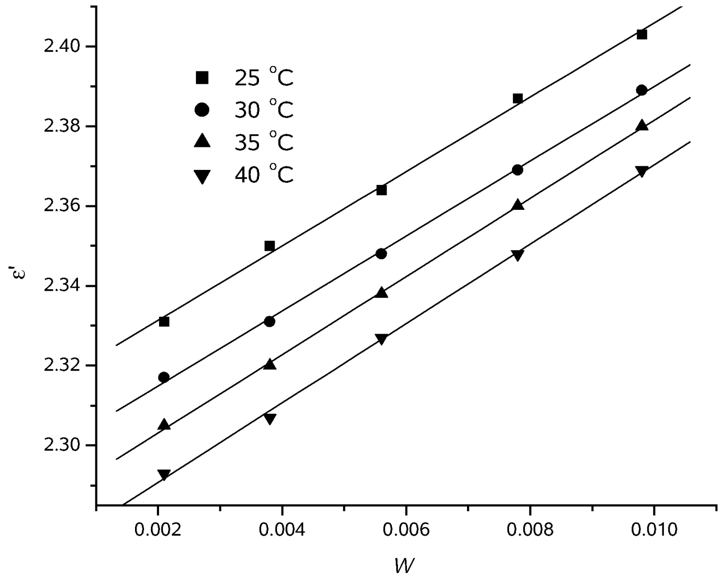

Fig. 2. Variation of dielectric constant (ε') with weight fraction (W) for 30 mol% of NMF in a (NMF+TMU) mixture at different temperatures.

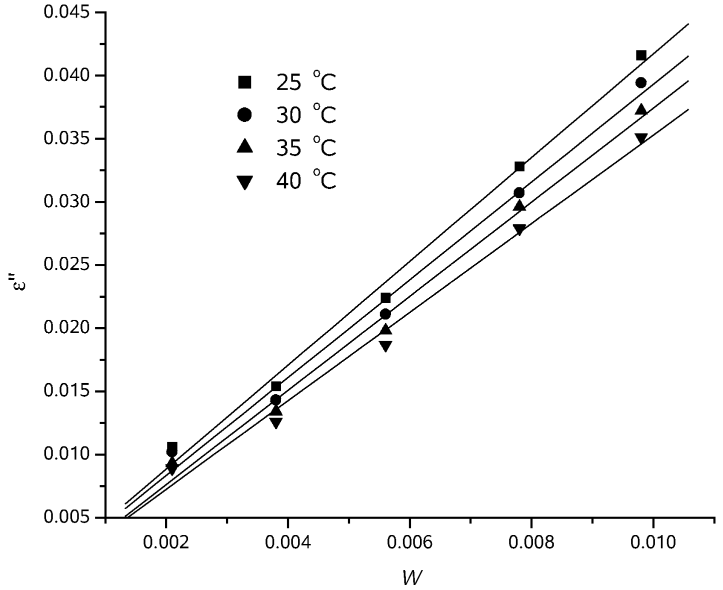

Fig. 3. Variation of dielectric loss (ε'') with weight fraction (W) for 30 mol% of NMF in a (NMF+TMU) mixture at different temperatures.

versus $10^3/T$, respectively, using the relation: slope = $\Delta H/2.303R$.

Table 1 represents the values of ε' and ε'' for NMF, TMU and (NMF+TMU) mixtures containing 30, 50 and 70 mol% NMF in benzene at 25, 30, 35 and 40 °C. It is found that ε' and ε'' vary linearly with the weight fraction of the solute in benzene for all binary mixtures (Figs. 2 and 3). 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 solution. Table 2 represents the values of the relaxation time (τ) of NMF, TMU and their binary mixtures in benzene at different temperatures (25, 30, 35 and 40 °C). The values of the relaxation time are observed to decrease systematically with increase in temperature from 25 to 40 °C for pure components as well as for binary mixtures. This may be due to firstly, the increase in the molar volume and secondly, the increase in the size of the dipole with increase in the temperature. The change in the dipole moment with the temperature may be due

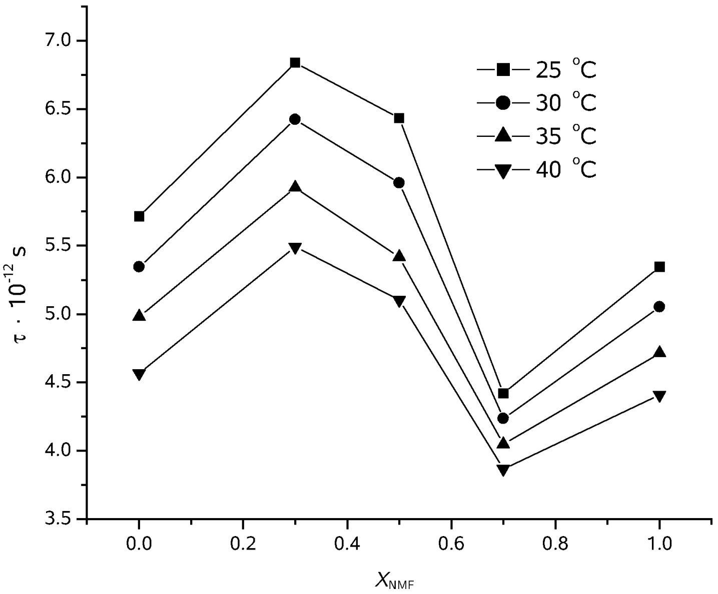

Fig. 4. Variation of relaxation time (τ) with mole fraction of NMF in a (NMF+TMU) mixture in benzene at different temperatures.

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

Temperature (°C)	Mole fraction of NMF in binary mixture	τ (10^{-12} s)	μ (Debye)
25	0.00	5.715	3.296 μ_{TMU}
	0.30	6.840	
	0.50	6.434	
	0.70	4.419	
	1.00	5.346	3.566 μ_{NMF}
30	0.00	5.346	3.345 μ_{TMU}
	0.30	6.425	
	0.50	5.959	
	0.70	4.235	
	1.00	5.052	3.625 μ_{NMF}
35	0.00	4.980	3.374 μ_{TMU}
	0.30	5.925	
	0.50	5.416	
	0.70	4.047	
	1.00	4.715	3.740 μ_{NMF}
40	0.00	4.568	3.437μ_{TMU}
	0.30	5.492	
	0.50	5.103	
	0.70	3.867	
	1.00	4.409	3.805 μ_{NMF}

to the stretching of bond moments and change in bond angles. Figure 4 shows the variation of the relaxation time (τ) with the increase of the mole fraction of NMF in the mixture. It is found that the relaxation time varies nonlinearly with the increase in the mole fraction of NMF in the binary mixture (NMF+TMU) 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 with the mole fraction (mole fraction of one of the constituents of the binary mixture in the whole concentration range) may be taken as the absence of any solute-solute molecular association in the mixture. On the other hand, the nonlinear variation of the relaxation time with the mole fraction of one of the constituents is interpreted as possible solute-solute molecular association in the binary mixtures. In the present study, the non-linear variation of relaxation time with the change in the mole fraction of NMF in the binary mixture predicts the presence of solute-solute molecular associations. From the experimental observations it is observed that the relaxation time first increases with the increase in the mole fraction of NMF in the (NMF+TMU) binary mixture and attains a maximum value at 30 mol% of NMF in the binary mixture. Further, increasing the mole fraction of NMF in the mixture up to 70 mol% the relaxation time decreases sharply, as shown in Figure 4. In the NMF-rich region (i. e. beyond 70 mol% of NMF) the measured value increases to the corresponding value of the NMF molecule. This behaviour indicates solute-solute molecular association between NMF and TMU in the whole concentration range, with the result that the molecular entities become much more voluminous than the individual molecules. In view of the above results, it is proposed that in the binary mixtures of NMF and TMU, NMF exists in a dimer structure, resulting because of the hydrogen bonding, and this dimer structure of NMF interacts with TMU molecules to give the maximum value of the relaxation time at 30 mol% of NMF in the binary mixture.

The values of the dipole moment (μ) of NMF and TMU in benzene (Table 2) are found to increase slightly with increase in temperature and approach the literature value. This shows that both NMF and TMU exist in the monomer form in benzene solution. The small variation in the dipole moment with rise in temperature may be attributed to the possible solute-solvent association [17]. The solute-solvent type of molecular association of NMF in benzene arises because of the interaction of a fractional positive charge at the site of the nitrogen atom of the NMF molecule and a π-delocalized electron cloud in the benzene ring. The variation of the dipole moment with the temperature of TMU indicates the presence of solute-solvent molecular association for TMU in the benzene solution. The molecular association arises because of the interaction of a fractional positive charge at the site of the nitrogen atom of the TMU molecule and a π-delocalized electron cloud in the benzene ring.

The energy parameters (ΔH_ε, ΔF_ε, ΔS_ε) of a dielectric relaxation process and the energy parameters (ΔH_η, ΔF_η, ΔS_η) of a viscous flow process have been compared, as shown in Table 3. It is found 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 the rotation of molecular entities, whereas in the viscous flow process, the rotation as well as the translation of the molecule is involved. It is found that the enthalpy of activation (ΔH_ε) of the dielectric relaxation process is smaller than the enthalpy of activation (ΔH_η) of the viscous flow process. The enthalpy of activation depends upon the local environment of the molecules. Different values of enthalpy of activation indicate that the dielectric relaxation process and the viscous flow process involve the breaking of bonds with neighbouring molecules in a different way and to a different extent. The value of α (the ratio of the enthalpy of the dielectric relaxation process to the enthalpy viscous flow process) is indicative of the solvent environment around the solute molecules. According to the classification of polar liquids, given by Krishnaji and Man Singh [18], molecules with $\alpha > 0.55$ do not behave as solid-phase rotators, and molecules $\alpha < 0.45$ behave as solid-phase rotators. It has been found that many polar liquids show a sudden drop in the static dielectric constant on solidification, indicating that the dipole rotation is prevented by freezing. There are, however, a number of substances for which the dielectric constant increases slightly on solidification, indicating that the dipoles have considerable freedom of rotation even in the solid phase and behave as solid-phase rotators. The value of α for (NMF+TMU) in benzene is 0.82, which is more than 0.55. Hence, according to the above classification, (NMF+TMU) molecules in benzene do not behave as solid-phase rotators. The entropy of a system is a measure of the disorder of the system. According to Branin and Smyth [19], a negative entropy of activation indicates that a comparatively small number of configurations is possible in an activated state, which is more ordered in comparison to the normal state. This again indicates the presence of cooperative orientation of the molecules by the steric forces or strong dipole-dipole interactions with the dipoles being more nearly aligned in an activated state. However, the positive entropy of activation 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 and viscous flow process is negative, indicating that the activated state of both processes is more stable than the ground state.

Table 3. Free energies of activation (ΔF_ε, ΔF_η in kJ mol^{-1}), enthalpies of activation (ΔH_ε, ΔH_η in kJ mol^{-1}), entropies of activation (ΔS_ε, ΔS_η in J mol^{-1} K^{-1}) and α ($= \Delta H_\varepsilon / \Delta H_\eta$) for a (NMF+TMU) mixture containing 30 mol% of NMF in benzene solutions.

Temp. (°C)	ΔF_ε	ΔH_ε	ΔS_ε	ΔF_η	ΔH_η	ΔS_η	α
25	9.2929	8.9589	−1.1206	12.1918	10.964	−4.1194	0.82
30	9.3331	8.9589	−1.2343	12.2202	10.964	−4.1453	0.82
35	9.3214	8.9589	−1.1762	12.2478	10.964	−4.1674	0.82
40	9.3172	8.9589	−1.1444	12.3105	10.964	−4.3012	0.82

4. Conclusion

The presence of solute-solute molecular association is predicted from the nonlinear variation of the relaxation time with the change in the mole fraction of NMF in the binary mixture (NMF+TMU). The variation in the dipole moment of NMF and TMU in benzene with rise of the temperature may be attributed to possible solute-solvent molecular associations. The measured values of the energy parameters of the dielectric relaxation process and their comparison with the energy parameters of the viscous flow process show that the dielectric relaxation process may be treated as a rate process just like the viscous flow process.

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