Dielectric Relaxation of Binary Mixtures of Tetrahydrofuran and N-Methylformamide in Benzene Solution Using Microwave Absorption Studies

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Using standard standing wave microwave X-band technique and following Gopala Krishna's single frequency (9.90 GHz) concentration variational method, the dielectric relaxation times τ and the dipole moments μ of dilute solutions of Tetrahydrofuran (THF), N-methylformamide (NMF), and THF+NMF binary mixtures in benzene solutions have been calculated 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 for the THF+NMF binary mixture containing 30 mol% THF have been calculated at 25 °C, 30 °C, 35 °C, 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 a rate process. From relaxation time behaviour of THF and NMF binary mixture in benzene solution, solute-solute types of the molecular association has been proposed.

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

1. Introduction

Tetrahydrofuran (THF) is a non-aqueous dipolar aprotic solvent [1]. It has a low dielectric constant $\varepsilon' = 7.58$ at 25 °C and a low dipole moment $\mu = 1.75$ D [1]. It can be made either by catalytic hydrogenation of furan or by intermolecular removal of water from butane 1,4-diol [2]. THF is an important solvent, used in reduction with lithium aluminium hydride in the preparation of aryl magnesium chlorides and in hydroboration. It is used as starting material for the manufacture of nylon [2]. THF has also been used as the important constituent of binary mixture of the required characteristics. N-methylformamide (NMF) is an important non-aqueous amides with a large value of dielectric constant $\varepsilon' = 182.4$ at 25 °C and a dipole moment $\mu = 3.83$ D [3]. From solvent point of view, it is possible to have binary mixtures of THF and NMF having dielectric constant and dipole moment values in between that of THF and NMF. This motivated the authors to undertake the experimental work concerning the dielectric relaxation process in the binary mixture of THF and NMF in order to understand the molecular association in the whole concentration range of THF 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 [4 – 8]. In order to obtain some information about the behaviour of THF+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.

2. Experimental Details

The reagent of THF (Merck, Merck Limited, Worli, Mumbai) was dried with $4A^0$ molecular sieves for about 48 hours with occasional shaking and then distilled through long vertical fractionating column. N-methylformamide (GC Grade) from Fluka, Germany, was dried with $4A^0$ molecular sieves for 10 hours

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with occasional shakings and then distilled through a long vertical fractionating column. The middle fractions were collected for use. Benzene (A. R. 99.7% pure, from Central Drug House Pvt. Ltd, New Delhi) was dried by refluxing over freshly cut sodium metal for 6 – 8 hours and distilled through a long vertical fractionating column. The middle fraction of the distilled benzene was used. The X-band microwave bench was used to measure the wavelength in the dielectric medium and the voltage standing wave ratio (VSWR) using a short-circuiting plunger. The set up was tuned at the microwave frequency 9.90 GHz. The experimental techniques of Arrawatia et al. used by Sharma and Sharma [9] for microwave measurements were used. 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). The whole equipment was standardized with the help of standard materials like methanol and pyridine.

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

3. Results and Discussions

Using standard standing wave microwave techniques and following the method of Heston et al. [10], the dielectric constant ε' and the dielectric loss ε'' of the dilute solutions of THF, NMF, and THF+NMF binary mixtures containing 30, 50, and 70 mol% THF in benzene solutions at 25 °C were calculated and are given in Table 1.

Using following equations

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

and

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_o}{\lambda_d}\right)^2 \cdot \frac{\lambda_g}{\lambda_d}\left(\frac{\mathrm{d}\rho}{\mathrm{d}n}\right), \tag{2}$$

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 the voltage standing wave ratio (VSWR) and $\mathrm{d}\rho/\mathrm{d}n$ is the slope of the curve of ρ versus n, where n is an integer $(1,2,3,4,\ldots)$ such that $(n\lambda_d/2)$ represents the length of the dielectric filled waveguide. The values of ε' and ε'' were reproducible within ±0.5% and ±1.67%, respectively.

Table 1. Dielectric constant ε', dielectric loss ε'', relaxation time τ, and dipole moment μ of different mole fractions of THF in (THF+NMF) binary mixture in benzene at temperature of 25 °C.

Mole fraction of THF in binary mixture	Weight fraction of solute in benzene	ε' (±0.5%)	ε'' (±1.67%)	$\frac{\tau}{10^{-12}}$ sec	μ (Debye)
0.00	0.00204	2.324	0.0134	4.85	3.77 μ_{NMF}
	0.00343	2.351	0.0233		
	0.00430	2.376	0.0301		
	0.00511	2.394	0.0374		
	0.00639	2.424	0.0476		
0.30	0.00249	2.296	0.0120	5.57	
	0.00341	2.306	0.0158		
	0.00539	2.334	0.0270		
	0.00643	2.346	0.0318		
	0.00757	2.361	0.0386		
0.50	0.00374	2.276	0.0138	4.58	
	0.00518	2.286	0.0175		
	0.00699	2.310	0.0248		
	0.00858	2.327	0.0301		
	0.0011	2.348	0.0376		
0.70	0.00291	2.273	0.00945	2.58	
	0.00520	2.296	0.0134		
	0.00684	2.313	0.0168		
	0.00837	2.330	0.0194		
	0.0126	2.369	0.0273		
1.00	0.00531	2.266	0.00532	1.29	1.85 μ_{THF}
	0.00873	2.283	0.00649		
	0.0120	2.303	0.00807		
	0.0196	2.341	0.0134		
	0.0266	2.374	0.0147		

Following the Gopala Krishna's single frequency concentration variational method [11], the dielectric relaxation time τ and the dipole moment μ have been calculated. The procedure is outlined in the previous publication [12].

It is found that the dipole moment for pure THF and NMF in benzene solution is very close to the literature values of the dipole moment. This shows that pure THF and pure NMF exist in the monomer form in the benzene solution. The energy parameters (ΔH_ε, ΔF_ε, ΔS_ε) for the dielectric relaxation process for THF+NMF binary mixture containing 30 mol% THF in benzene at 25 °C, 30 °C, 35 °C, and 40 °C and the corresponding energy parameters (ΔH_η, ΔF_η, ΔS_η) for the viscous flow have been calculated by using the from Eyring et al. [13] mentioned relations for the rate process. Following relations were used:

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

Table 2. Relaxation time τ, free energies of activation ΔF_ε, ΔF_η (in kcal mole^{-1}), enthalpies of activation $\Delta H_\varepsilon, \Delta H_\eta$ (in kcal mole^{-1}), and entropies of activation $\Delta S_\varepsilon, \Delta S_\eta$ (in cal mole^{-1} deg^{-1} K^{-1}) for THF+NMF mixture containing 30 mol% of THF in benzene solutions.

Temp (°C)	$\frac{\tau}{10^{-12}}$ sec	ΔF_ε	ΔH_ε	ΔS_ε	ΔF_η	ΔH_η	ΔS_η
25	5.57	2.102	−0.0858	−7.340	2.917	2.608	−1.036
30	5.49	2.138	−0.0858	−7.139	2.924	2.608	−1.043
35	5.41	2.174	−0.0858	−7.338	2.930	2.608	−1.045
40	5.33	2.210	−0.0858	−7.335	2.945	2.608	−1.076

Table 3. Dielectric relaxation time τ and dipole moment μ for different mole-fractions of (THF+NMF) mixtures in benzene solution at different temperatures.

Temperature (°C)	Mole fraction of THF in binary mixtures	$\frac{\tau}{10^{-12}}$ sec	μ (Debye)
25	0.00	4.85	3.77 μ_{NMF}
	0.30	5.57	
	0.50	4.58	
	0.70	2.58	
	1.00	1.29	1.85 μ_{THF}
30	0.00	4.71	3.61 μ_{NMF}
	0.30	5.49	
	0.50	4.47	
	0.70	2.52	
	1.00	1.23	1.76 μ_{THF}
35	0.00	4.56	3.58 μ_{NMF}
	0.30	5.41	
	0.50	4.36	
	0.70	2.46	
	1.00	1.17	1.71 μ_{THF}
40	0.00	4.43	3.50 μ_{NMF}
	0.30	5.33	
	0.50	4.25	
	0.70	2.40	
	1.00	1.12	1.66 μ_{THF}

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

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

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 plots 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 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 time τ for THF+NMF binary mixtures containing 30 mol% THF in benzene solution at 25 °C, 30 °C, 35 °C, and 40 °C have been summarized in Table 2.

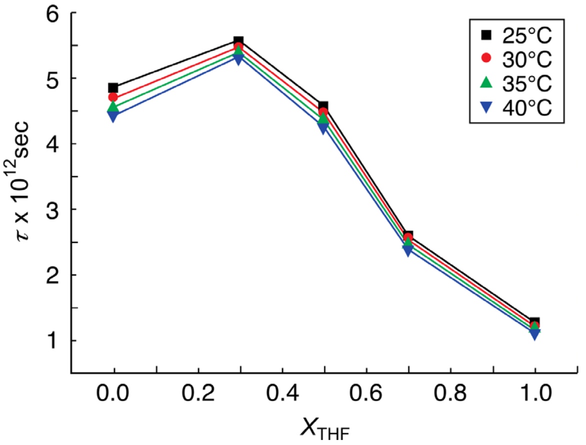

Fig. 1. Plot of relaxation time τ versus mole fraction of THF (X_{THF}) in THF+NMF in benzene solution at different temperatures.

Table 3 represents the values of the dielectric relaxation time τ and dipole moment μ for THF+NMF binary mixtures in the benzene solution at different temperatures (25 °C, 30 °C, 35 °C, and 40 °C) for different mole fractions of THF in the binary mixtures. The nonlinear variation of relaxation time values with the increase in the mole fraction of THF in the binary mixtures (THF+NMF) at all temperatures has been observed (Fig. 1). 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, nonlinear variation of the relaxation time with the mole fraction is interpreted as the possible solute-solute molecular association in the binary mixtures.

The variation of the relaxation time τ first increase with the increase in mole fraction of THF in THF+NMF binary mixture and attains a maximum value at 30 mol% of THF in the mixture. Then, with the further increase in the mole fraction of THF in the mixture, there is seen a sharp decrease in the relaxation time and falls towards the value of pure THF in benzene solution. This behaviour indicates solute-solute type of molecular association between THF and NMF. This shows that the molecular association is maximum at 30 mol% THF in THF+NMF binary mixture. 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 is found that the above results are reproducible within the experimental accuracy range. The binary mixture of THF and NMF was prepared by mixing THF and NMF in required proportions. And then by mixing this binary solution in the benzene solvent, dilute solutions of binary mixtures in benzene were made. In view of above results, it is proposed that in the binary mixtures of THF and NMF, NMF exists in the dimer structure resulting because of the H-bonding and this dimer structure of THF interacts with the NMF molecules to give the maximum value of relaxation time at 30 mol% THF binary mixture. 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 NMF molecule and π-delocalized electron cloud in the benzene molecule.

It is found that the free energy of activation ΔF_ε for the dielectric relation 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 rotation of molecular entities where as in the viscous flow process the rotation as well as the translation motion of the molecule is involved. It is found that the enthalpy of activation for the dielectric relaxation process ΔH_ε is less than the enthalpy 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 the viscous flow process involves breaking of bonds with the neighbouring molecule in a different way and to a different extent.

The entropy of a system is a measure of orderly nature of the system. If the environment of the system is co-operative for the activated process, the change in entropy becomes negative. The positive value of the change in entropy for activated process indicates the non co-operative environment of the system and the activated state is unstable. In the present case, it is observed that the change in entropy for the dielectric relaxation process is negative indicating that the environment of the system is co-operative like that of the activated viscous flow state.

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