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

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Abstract : Dielectric relaxation times (τ) and the dipole moments (μ) of the binary mixtures of different molar concentrations of acetone (CH_3COCH_3) in the binary mixtures of acetone and N-methylformamide (NMF) in benzene solutions have been calculated by using standard standing wave microwave techniques and Gopala Krishna's single frequency (9 88 GHz) concentration variational method at different temperatures (25°C, 30°C, 35°C, 40°C). The dielectric relaxation process have been found to be an activated process. The energy parameters (ΔH_ϵ, ΔF_ϵ, ΔS_ϵ) for the dielectric relaxation process of binary mixtures containing 50% mole-fraction of acetone 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. Solute-solute and solute-solvent molecular associations have been predicted.

Keywords : Dielectric relaxation binary mixtures (acetone + NMF), microwave absorption.

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Dielectric relaxation studies of polar molecules in non-polar solvents using microwave absorption methods have been attempted by many research workers [1–6]. Acetone (CH_3COCH_3) is a dipolar, aprotic solvent having dielectric constant [7] $\varepsilon' = 20.7$ and dipole-moment [7] $\mu = 2.84D$ in the vapour phase. N-methylformamide (NMF) is an important non-aqueous amide with a large value of dielectric constant [8] ($\varepsilon' = 182.4$ at 25°C) and possessing a dipole-moment [8] $\mu = 4.0D$ approximately. It is possible to prepare binary mixtures of given dielectric constant value lying between that of acetone and NMF 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 acetone and NMF in order to understand the molecular association in the whole concentration range of acetone in the binary mixtures. 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 [9–11]. This is because of the capability of the microwaves to detect the weak molecular interactions. Dielectric relaxation of the binary mixtures of acetone and NMF have been studied in the whole concentration range of acetone in the binary mixtures using standard microwave standing wave techniques and single frequency (9.88 GHz) concentration variation method of Gopala Krishna [12]. The measurements have been made for the binary mixtures of different mole-fractions of acetone (0.0, 0.3, 0.5, 0.7, 1.0) at four different temperatures (25°C, 30°C, 35°C, 40°C). The dielectric relaxation process has been found to be an activated process. The energy parameters have been calculated for the binary mixtures having 0.5 mole-fraction of acetone. From the experimental observations, it is found that the dielectric relaxation process is a rate process like that of the viscous flow process. Solute-solute

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and solute-solvent types of the molecular associations for NMF have been proposed.

Pure samples of acetone (AR Grade) from SISCO Research Laboratories Pvt. Ltd., Mumbai (India) and N-methylformamide (GC Grade) from Fluka, Germany were dried with 4Å molecular sieves for about 10 hours with occasional shakings. The pure sample of acetone was distilled through a long vertical fractionating column and the middle fraction was collected for use. The pure sample of NMF was distilled through a long vertical fractionating column under the reduced pressure and the middle fraction of distilled NMF was used. The X-band microwave bench (freq 9.88 GHz) was used. By mixing acetone with NMF in the calculated proportions, the binary mixture of required mole-fraction was made. Set of dilute solutions of the binary mixtures in the benzene solutions were made. Using microwave techniques of Heston et al [13], the dielectric constant (ε') and the dielectric loss (ε'') of dilute solutions of binary mixtures of acetone and NMF in benzene solution at different temperatures were calculated. The temperature of the solution was controlled by circulating thermostated water around the dielectric cell. Dielectric relaxation time (τ) and dipole moment of molecular entities in the benzene solutions were calculated following the single frequency concentration variational method of Gopala Krishna [12].

Table 1 shows the dielectric relaxation time (τ) and dipole-moment (μ) for different mole-fractions of (acetone + NMF) binary mixtures at different temperatures in the benzene solution. The values of the dipole-moments for pure acetone and NMF calculated in this table are very close to the literature values of the dipole-moment. This shows that pure acetone and pure NMF exist in the monomer form in the benzene solution. The values of the relaxation time (τ) vary non-linearly with the increase in the mole-fraction of acetone in the binary mixtures (acetone + NMF) 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 mixture. 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 mixture. In the

Table 1. Dielectric relaxation time (τ) and dipole-moment (μ) for different mole-fractions of (acetone + NMF) mixture in benzene solution at different temperatures.

Temperature (°C)	Mole Fraction of acetone in binary mixture	$\dfrac{\tau}{10^{-12}}$ sec	μ (Debye)
25	0.00	4.29	4.04 (μ_{NMF})
	0.30	4.82	
	0.50	5.36	
	0.70	3.24	
	1.00	2.04	2.78 ($\mu_{acetone}$)
30	0.00	4.20	3.98 (μ_{NMF})
	0.30	4.76	
	0.50	5.25	
	0.70	3.15	
	1.00	1.85	2.76 ($\mu_{acetone}$)
35	0.00	4.11	3.95 (μ_{NMF})
	0.30	4.69	
	0.50	5.14	
	0.70	3.06	
	1.00	1.69	2.76 ($\mu_{acetone}$)
40	0.00	4.02	3.91 (μ_{NMF})
	0.30	4.63	
	0.50	5.03	
	0.70	2.96	
	1.00	1.52	2.76($\mu_{acetone}$)

present case, the non-linear variation of the relaxation time with the change in mole-fraction of acetone in the binary mixture at 25°C (Figure 1) shows the presence of solute-solute molecular associations. The solute-solute
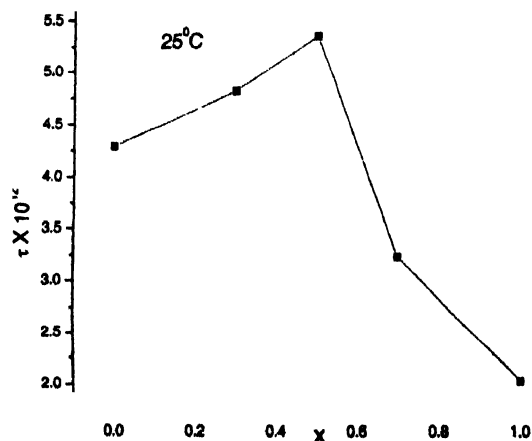
Figure 1. Variation of relaxation time with mole fraction of acetone in [NMF + acetone] mixture in benzene solution at 25°C.

molecular association arising from the interaction of the fractional negative charge on the oxygen atom of acetone and fractional positive charge on the hydrogen atoms of NMF molecule may be proposed (Figure 2). It is found
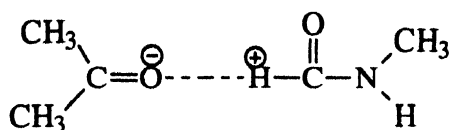

Figure 2. Solute-solute association of NMF molecule in benzene.

that there is a small variation in the dipole-moment values of binary mixtures of acetone and NMF in benzene solution with the rise in temperature (Table 1). This could be explained on the basis of the solvent-effects [14]. The value of the dipole-moment of acetone (binary mixture with 1.00 mole-fraction of acetone in the mixture at all temperatures) does not depend on the temperature. This indicates the absence of solute-solvent association for pure acetone in benzene solution. The value of the dipole-moment of NMF (binary mixture with 0.00 mole-fraction of acetone in the binary mixture) is found to change slightly with the rise of temperature. This predicts the solute-solvent type of molecular association for NMF in the benzene solution. NMF molecule shows the resonance hybrid structure. The molecular association arising because of the interaction of +ve fractional charge at the sight of N-atom in NMF and π-delocalized electron cloud in the benzene ring of benzene molecule is shown in the Figure 3.
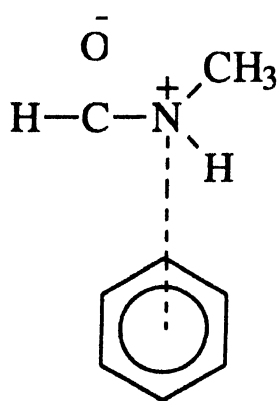

Figure 3. Solute-solvent association of NMF molecule in benzene.

For binary mixtures (50% mole-fraction of acetone in the binary mixture of acetone + NMF), it is found that the variation of log τT versus $10^3/T$ is straight line. This indicates that the dielectric relaxation process can be

treated as a rate process. The energy parameters (ΔH_ε, ΔF_ε, ΔS_ε) for the dielectric relaxation process have been calculated using Eyring rate equations [15]. The energy parameters for the viscous flow (ΔH_η, ΔF_η, ΔS_η) have also been calculated treating the viscous flow as the rate process. These two sets of the energy parameters have been compared as shown in Table 2. It is found that the dielectric relaxation process can be treated as the rate process just like the viscous flow.

Table 2. Relaxation time (τ), free energies of activation (ΔF_ε, ΔF_η in kcal mole⁻¹), enthalpies of activation (ΔH_ε, ΔH_η in kcal mole⁻¹) and entropies of activation (ΔS_ε, ΔS_η in cal mole⁻¹ deg⁻¹) for (acetone + NMF) mixture containing 50 mole% of acetone in benzene solution.

Temp. (°C)	$\frac{\tau}{10^{-12}}$ sec	ΔF_ε	ΔH_ε	ΔS_ε	ΔF_η	ΔH_η	ΔS_η
25	5.36	2.08	1.79	−0.097	2.92	2.63	−0.9631
30	5.25	2.11	1.79	−0.106	2.92	2.63	−0.9703
35	5.14	2.14	1.79	−0.114	2.93	2.63	−0.9773
40	5.03	2.17	1.79	−0.121	2.94	2.63	−0.9872

The observations show 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 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 involves the breaking of bonds with the neighbouring molecules in a different way and to a different extent. The 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 cooperative like that of the activated viscous flow state.

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