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Thermodynamic Parameters and Related Studies of Amine-Diol Mixtures in 1,4-Dioxane Using Microwave Technique

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Single frequency concentration variational method has been used to calculate dielectric relaxation time (τ) and dipole moment (μ) for binary mixtures of diethylene triamine (DETA) and ethane diol (ED) in 1,4-dioxane solution. These measurements have been made at 10.7 GHz frequency and at temperatures 22, 30, 40 and 50°C. Thermodynamic parameters have also been calculated for the dielectric relaxation process and for viscous flow process. The values of relaxation time (τ) used to calculate the dipole moment (μ), Debye factor (c) and Kalman's factor (C'). The nonlinear variation of τ with the change in mole fraction of DETA in the binary mixture shows presence of solute-solute molecular association and which is maximum at 44 mole % of DETA in the mixture.

Key Words: Thermodynamic parameters, Diethylene triamine, Ethane diol, Microwave technique.

INTRODUCTION

Dielectric relaxation studies of polar molecules in non-polar solvents from microwave absorption studies have been frequently attempted[1–6]. Experimental investigation of dielectric properties of organic compounds in non-polar solvents is of great value in understanding the dipolar behaviour[7–10] of the substances. Dielectric relaxation studies of liquid mixtures in the microwave region has been recognized to characterize different types of molecular interactions[7–10] such as solute-solute, solute-solvent and self-association in the solution. Diethylene triamine (DETA) and ethanediol (ED) is chosen to study the dielectric behaviour of their mixture in 1,4-dioxane in solution.

Ethanediol (ED) is a dihydric alcohol with two hydroxyl groups. The presence of two OH groups gives rise to extensive H-bonding. The present work aims at an insight into the molecular interactions in dilute solution of DETA, ED, and their mixture in 1,4-dioxane from microwave absorption measurements at 10.7 GHz in 22–50°C temperature range.

EXPERIMENTAL

Pure samples of diethylene triamine, ethanediol and 1,4-dioxane were procured from M/s S.D. Fine Chemicals, AR grade and used without further purification. X-band microwave bench was used to measure the wavelength in the dielectric (λd) and voltage standing wave ratio (VSWR) using a short circuit plunger[11, 12]. The dieiectric cell has an adjustable short. To hold the liquid sample in the cell, a thin mica window whose VSWR and attenuation were neglected was introduced between the cell and the rest of the microwave bench . The length of the liquid column in the cell could be adjusted to an accuracy of 0.001 cm by means of a micrometer plunger drive. IN21 crystals were used for detection, The temperature was maintained within ±0.5°C by circulating water of constant temperature around the cell. The measurements of dielectric constant (ε') and dielectric loss (ε'') for different concentrations and temperatures were made at a fixed frequency of 10.7 GHz . The measurements were carried out at 22, 30, 40, and 50°C in a dielectric cell by circulating constant temperature water. The use of the dilute solution helps to minimize the effect of viscosity, molecular interactions, internal field and other factors.

Molecular Parameters

The dielectric constant (ε') and the loss values (ε'') for different concentrations and at different temperatures have been utilised in evaluating the relaxation time (τ) and the dipole moment (μ), following Gopalkrishna's[11] fixed frequency method for dielectric solutions employing the following relations:

$$X = (\varepsilon'^2 + \varepsilon' + \varepsilon''^2 - 2)/(\varepsilon' + 2)^2 + \varepsilon''^2 \quad (1)$$

$$Y = (3\varepsilon'')/(\varepsilon' + 2)^2 + \varepsilon''^2 \quad (2)$$

$$\tau = (\lambda_0/2\pi C)(dy/dx) \quad (3)$$

$$\mu = [(9KTM)/(4\pi Nd) \times \{1 + (dy/dx)^2(dx/dw)\}]^{1/2} \quad (4)$$

where C is the velocity of electromagnetic waves, K is the Boltzmann's constant, N is Avogadro's number, M is the molecular weight of the solute, d is the density of the solvent, T is the absolute temperature and W is the weight fraction of the solute. Factors X and Y were computed from the measured values of (ε') and (ε''). The slope of the line drawn between X and Y was used for determining the value of the relaxation time (τ) and the slope of the line X *vs*. W was used for calculating the dipole moment (μ).

The energy parameters, free energy (ΔF_τ), enthalpy (ΔH_τ) and the entropy of activation (ΔS_τ) for the dielectric relaxation process and the corresponding parameters for the viscous flow (ΔF_η), (ΔH_η) and (ΔS_η) have been calculated by using the Eyring's equations.[7–10]

$$\tau = (h)/(KT) \exp (\Delta F_\tau)/(RT) \quad (5)$$

$$\Delta F_\tau = \Delta H_\tau - T\,\Delta S_\tau \quad (6)$$

$$\eta = (hN)/(V) \exp (\Delta F_\eta)/(RT) \quad (7)$$

and

$$\Delta F_\eta = \Delta H_\eta - T\,\Delta S_\eta \quad (8)$$

in which V is molar volume, η is the viscosity of the pure solvent and K is Boltzmann's constant. The Debye equation for the dielectric relaxation time in terms of the viscosity (η) of solvent is given by[7]

$$\tau = (C/T)\eta \quad \text{or} \quad C = (\tau T)/\eta \quad (9)$$

where C is called Debye factor. Again Kalman and Smyth derived another equation using the rate process equation which is given by

$$\tau = (C'/T)\eta* \quad \text{or} \quad C' = (\tau T)/\eta* \quad (10)$$

where $x = (\Delta H_\tau)/(\Delta H_\eta)$and C′ is called Kalman's factor. Using equations (9) and (10) we have calculated Debye's factor (C) and Kalman's factor (C′) and are reported in Table-2.

RESULTS AND DISCUSSION

The values of ε' and ε'' obtained for DETA, ED and their mixtures for different concentrations and temperatures are reported in Table-1. From the data obtained it is clear that the dielectric constant (ε') and the loss factor (ε'') both increase as the weight fraction increases and decreases with the increase of temperature for DETA, ED and their mixtures in 1,4-dioxane.

TABLE-1
VALUES OF $\varepsilon', \varepsilon''$ AND τ FOR DETA + ED MIXTURES CONTAINING (I) 0, (II) 12 (III) 25 (IV) 44 (V) 67 AND (VI) 100 MOLE % OF DETA IN 1,4-DIOXANE AT DIFFERENT TEMPERATURES

Temp.(°C)	22			30			40			50		
Wt. fraction of solute in 1,4-dioxane	ε'	ε''	τ_{ps}	ε'	ε''	τ_{ps}	ε'	ε''	τ_{ps}	ε'	ε''	τ_{ps}
					I							
0.036	4.38	0.38	2.36	4.32	0.34	2.28	4.17	0.34	2.17	4.10	0.33	1.43
0.107	4.87	0.60		4.82	0.54		4.79	0.49		4.75	0.44	
0.177	5.82	0.37		5.73	0.86		5.60	0.79		5.42	0.69	
0.247	7. 54	1.75		6.56	1.30		6.32	1.13		5.81	0.96	
					II							
0.035	4.01	0.35	2.98	4.00	0.33	2.83	3.98	0.31	2.76	3.94	0.29	2.80
0.088	4.54	0.54		4.57	0.52		4.49	0.48		4.43	0.42	
0.183	5.38	0.87		5.20	0.77		5.13	0.72		5.01	0.64	
0.244	6.021	1.148		5.91	1.08		5.70	0.98		5.53	0.89	
					III							
0.035	4.22	0.48	4.03	4.20	0.44	3.60	4.17	0.37	3.10	4.14	0.33	3.01
0.104	4.38	0.54		4.37	0.51		4.22	0.45		4.15	0.43	
0.172	4.78	0.74		4.71	0.67		4.59	0.66		4.55	0.59	
0.241	5.23	0.88		5.15	0.75		5.01	0.70		4.97	0.67	
					IV							
0.034	3.57	0.18	3.56	3.48	0.16	3.50	3.44	0.15	3.19	3.31	0.13	3.01
0.100	4.01	0.44		4.01	0.43		3.98	0.40		3.44	0.38	
0.168	4.63	0.71		4.52	0.67		4.48	0.58		4.46	0.54	
0.235	4.99	0.86		4.93	0.82		4.80	0.71		4.60	0.62	
					V							
0.033	3.65	0.22	3.50	3.61	0.22	3.40	3.58	0.21	3.15	3.52	0.19	2.78
0.097	4.02	0.45		3.98	0.39		3.95	0.37		3.87	0.35	
0.162	4.55	0.62		4.52	0.59		4.48	0.54		4.45	0.50	
0.228	5.27	0.87		5.02	0.77		4.81	0.71		4.75	0.65	
					VI							
0.031	3.73	0.26	2.52	3.65	0.25	2.03	3.55	0.23	1.83	3.48	0.2	1.43
0.093	4.12	0.38		4.08	0.35		4.05	0.34		3.74	0.31	
0.155	4.49	0.61		4.49	0.54		4.40	0.51		4.42	0.47	
0.219	4.99	0.8		4.84	0.70		4.79	0.69		4.47	0.57	

TABLE-2

VALUES OF FREE ENGERIES OF ACTIVATION (ΔF_τ, ΔF_η, kcal mol^{-1}) ENTHALPIES OF ACTIVATION (ΔH_τ, ΔH_η, kcal mol^{-1}), ENTROPIES OF ACTIVATION (ΔS_τ, ΔS_η, kcal mol^{-1}), DEBYE FACTOR (C), KALMAN'S FACTOR (C′), RELAXATION TIME (τ) AND DIPOLE MOMMENT (μ) FOR (I) DETA (II) ED AND (III) DETA + ED CONTAINING 44 MOLE % OF DETA IN 1,4-DIXONE

T_k^0	ΔF_τ	ΔH_τ	ΔS_τ	ΔF_η	ΔH_η	ΔS_η	C (10^{-8})	C′ (10^{-8})	τ_{ps}	μ (debye)
					I					
295	1.720	1.337	−1.298	3.329	4.425	3.610	6.20	0.280	2.52	2.21
303	1.771		−1.432	3.203		3.438	6.22	0.248	2.03	2.24
313	1.832		−1.581	3.198		3.378	7.04	0.245	1.83	2.28
323	1.897		−1.734	3.464		3.464	7.34	0.214	1.43	2.31
					II					
295	1.721	0.28	−4.88	3.329	4.425	3.610	5.81	0.0921	2.36	1.71
303	1.768		−4.91	3.203		3.438	6.99	0.0925	2.28	1.73
313	1.827		−4.94	3.198		3.378	8.34	0.092	2.17	1.76
323	1.897		−5.01	3.464		3.464	7.34	0.063	4.43	1.79
					III					
295	1.801	1.37	−1.46	3.329	4.425	3.610	8.77	0.413	3.56	
303	1.856		−1.604	3.203		3.438	10.73	0.443	3.50	
313	1.880		−1.63	3.198		3.378	12.26	0.442	3.19	
323	1.923		−1.384	3.464		3.464	3.464	0.466	3.01	

The values of relaxation time (τ) for DETA, ED and their mixtures in 1,4-dioxane for different temperatures are also reported in Table-1. The increase of mole fraction of DETA in the mixture indicates solute-solute interactions. The decrease of relaxation time (τ) with further increase in mole fraction leads to the conclusion that we may expect the disruption of associates in the mixture and change to the structure of self-association. Similar type of behaviour is found over the entire temperature range selected.

Solute-solute association in the mixture may be considered as absence if there is a linear variation of the relaxation time (τ) from its value corresponding to the one constituent to the value corresponding to the other constituent with mole fraction variation of the other constituent. On the other hand, the nonlinear variation of relaxation time with the mole fraction of one of the constituents is to be considered as possible solute-solute molecular association in the binary mixture. In our case the nonlinear variation of τ shows the presence of solute-solute molecular association. The value of (τ) is found to be maximum at 44 mole % of DETA; thus the molecular association is maximum at this concentration of DETA.

The values of free energies of activation (ΔF_τ, ΔH_η), entropies of activation (ΔS_τ, ΔS_η), Debye factor (C), Kalman's factor (C′), relaxation time (τ) and dipole moment (μ) are reported in Table-2 for DETA, ED, binary mixture containing 44 mole % of DETA. If we compare free energies of activation $\Delta F_\tau \Delta F_\eta$ it is clear that ΔF_τ is less than ΔF_η. This may be explained on the basis of the fact that, dielectric relaxation process involves rotation of the molecules whereas viscous flow involves both rotational and translational motion of the molecules. Again if we compare the enthalpies of activation $\Delta H_\tau, \Delta H_\eta$ it is clear that ΔH_τ is less than 0.55. which shows that the solid rotator phase may exist.

The entropy of a system is a measure of the orderly nature of the system[7, 8]. The negative values of change in entropy for activated process indicate the cooperative environment of the system and activated state is stable. The positive values of the change in entropy indicate the non-cooperative environment of the system and activated state is unstable. In our case it is found that the change in entropy for dielectric process is negative and for viscous flow process it is positive.

From Table-2 it is also clear that the Debye factor (C) varies considerably with temperature. The Kalman's factor (C′) remains nearly constant at all the temperatures. This indicates that the Kalman's equation (10) for the dielectric relaxation time as a function of viscosity is superior to the Debye's equation (9) and the quantity η^* is a better representation of the inner friction coefficient for dipole rotation as compared to the macroscopic viscosity η; our results matched with Singh *et al.*[4]

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