

## Dielectric Relaxation of Binary Mixtures of Diethylene Triamine + 2-Ethoxy ethanol in 1,4-Dioxane from Microwave Absorption Studies

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Single frequency concentration variational method of Gopal Krishna has been used to obtain dielectric relaxation time ( $\tau$ ) and dipole moment ( $\mu$ ) for dilute solutions of binary mixtures of diethylene triamine and 2-ethoxy ethanol in 1,4-dioxane at different temperatures (22–50°C). Energy parameters ( $\Delta H$ ,  $\Delta F$ ,  $\Delta S$ ) for dielectric relaxation process of diethylene triamine + 2-ethoxy ethanol mixtures containing 0, 37, 57, 78 and 100% diethylene triamine have also been calculated. Comparison has been made with corresponding energy parameters for viscous flow. Debye's factor ( $C$ ), Kalman's factor ( $C'$ ) and excess inverse relaxation time were computed. The variation of relaxation time and excess relaxation time with weight fraction of diethylene triamine in the mixtures confirms the solute-solute and solute-solvent interactions.

**Key Words:** Dielectric relaxation, Binary mixtures, Diethylene triamine, 2-Ethoxy ethanol, 1,4-dioxane.

### INTRODUCTION

Dielectric relaxation studies of the polar molecules in non-polar solvent from microwave absorption studies have been frequently attempted<sup>1–6</sup>. Dielectric relaxation data obtained from microwave absorption studies may provide information regarding the presence of solute-solute and solute-solvent interactions. Solvents like 2-ethoxy ethanol (EE) are widely used as components of solvents, co-emulsifiers and stabilizers of emulsions, dyes and lacquers<sup>7</sup>. Their molecules contain both hydroxylic and ether groups. Wide applications of 2-ethoxy ethanol (EE) in different fields motivated us to study the dielectric relaxation behaviour of binary mixtures of (DETA + EE) in 1,4-dioxane.

In the present paper microwave techniques<sup>8</sup> have been used to measure dielectric constant ( $\epsilon'$ ), loss factor ( $\epsilon''$ ), relaxation time ( $\tau$ ), excess relaxation time ( $\tau^e$ ) for dilute solutions of diethylene triamine (DETA), 2-ethoxy ethanol (EE) and their binary mixtures (DETA + EE) in 1,4-Dioxane at different temperatures. Energy parameters  $\Delta H_\tau$ ,  $\Delta F_\tau$ ,  $\Delta S_\tau$  have been calculated for 37, 57 and 78% weight fractions of DETA in the binary mixture. These parameters have been used to throw light on the dynamic characteristics of molecular association in these binary mixtures of polar liquids.

## EXPERIMENTAL

The compounds used were procured from M/s. S.D. Fine Chemicals of AR grade and used without further purification. X-band microwave bench was used to measure the wavelength of e.m. waves in the waveguide filled with dielectric. The liquids were mixed according to their proportions by volume. To hold liquid 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. A set of dilute solutions of (DETA + EE) in 1,4-dioxane were prepared. The dielectric constant ( $\epsilon'$ ) and loss factor ( $\epsilon''$ ) at 10.7 GHz microwave frequency were computed by the method of Heston and Smyth<sup>8</sup> for different temperatures (22–50°C). Circulating thermostated water around the dielectric cell controlled the temperature of the solution.

### Determination of molecular parameters

The dielectric parameters ( $\epsilon'$ ,  $\epsilon''$ ) for different concentrations and temperatures were calculated for different temperatures (22–50°C) by using the following equations<sup>8–10</sup>.

$$\epsilon' = (\lambda_0/\lambda_c)^2 + (\lambda_0/\lambda_d)^2 \quad (1)$$

and

$$\epsilon'' = (2/\pi)(\lambda_0/\lambda_d)^2(\lambda_g/\lambda_d)(d\rho/dn) \quad (2)$$

where  $\lambda_0$ ,  $\lambda_c$ ,  $\lambda_d$  and  $\lambda_g$  are the free space wavelength, cut-off wavelength, wavelength in waveguide filled with solution and guide wavelength respectively.  $\rho$  is the inverse of VSWR and  $(d\rho/dn)$  is slope of  $\rho$  vs.  $n$  where  $n = 1, 2, 3, \dots$  such that  $n(\lambda_d/2)$  represents the length of the dielectric filled waveguide. The energy parameters, free energy ( $\Delta F_\tau$ ), enthalpy ( $\Delta H_\tau$ ) and entropy ( $\Delta S_\tau$ ) for dielectric relaxation process and the corresponding parameters for viscous flow ( $\Delta F_\eta$ ,  $\Delta H_\eta$ ,  $\Delta S_\eta$ ) have been calculated by using Eyring's equations<sup>11</sup>

$$\tau = (h/kT) \exp(\Delta F_\tau/RT) \quad (3)$$

$$\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \quad (4)$$

$$\eta = (hN/V) \exp(\Delta F_\eta/RT) \quad (5)$$

and

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

The Debye equation for dielectric relaxation<sup>9</sup> time in terms of viscosity ( $\eta$ ) of the solvent is

$$\tau = (C/T)\eta \quad (7)$$

were used to calculate Debye factor ( $C$ ). Again using Kalman and Smith's<sup>12</sup> equation

$$\tau = (C'/T)\eta^x \quad (8)$$

Kalman's factor ( $C'$ ) is calculated where  $x = (\Delta H_\tau/\Delta H_\eta)$ .

The values of relaxation time ( $\tau$ ) of the binary mixtures in 1,4-dioxane have been determined by using Gopal Krishna's<sup>13</sup> method. The theoretical relation for

calculating the values of relaxation times for non-associated behaviour<sup>14</sup> is given by

$$\tau_m = C_1\tau_1 + (1 - C_1)\tau_2 \quad (9)$$

where  $\tau_1$  and  $\tau_2$  are the relaxation time of pure solutes 1 and 2 respectively.  $C_1$  is the weight fraction of first solute in the mixture. Another theoretical relation proposed by Madan<sup>15</sup> to represent the weightcular behaviour in binary mixtures is given by

$$\frac{1}{\tau_m} = \left\{ \frac{C_1\mu_1^2}{[C_1\mu_1^2 + (1 - C_1)\mu_2^2]\tau_1} + \frac{(1 - C_1)\mu_2^2}{[C_1\mu_1^2 + (1 - C_1)\mu_2^2]\tau_2} \right\} \quad (10)$$

where  $\mu_1$  and  $\mu_2$  are the dipole moments of 1 and 2 solutes respectively.

The excess inverse relaxation time  $(1/\tau)^e$  can be calculated by using the following equation<sup>14, 15</sup>:

$$(1/\tau)^e = (1/\tau_m) - [(1/\tau_1)X_1 + (1/\tau_2)X_2] \quad (11)$$

The symbols  $m$ , 1, and 2 are related to the mixture, liquid 1 and liquid 2, in the mixture respectively. The excess inverse relaxation time provides the quantitative information regarding the dynamic solute-solvent interactions as follows:

- If  $(1/\tau)^e = 0$  there is no change in dynamics of solute-solvent interactions.
- If  $(1/\tau)^e < 0$  the solute-solvent interaction produces a field such that the effective dipoles rotate slowly, *i.e.*, the field will resist the rotation.
- If  $(1/\tau)^e > 0$  the solute-solvent interaction produces a field such that the dipole will rotate faster, *i.e.*, the field will co-operate in rotation of the dipole.

## RESULTS AND DISCUSSION

The values of dielectric parameters ( $\epsilon'$ ,  $\epsilon''$ ) and relaxation time ( $\tau$ ) for diethylene triamine (DETA), 2-ethoxy ethanol (EE) and their mixtures in 1,4-dioxane for different temperatures and weight fraction are listed in Table-1. It is seen that both  $\epsilon'$  and  $\epsilon''$  increase as weight fraction increases and decrease with the increase of temperature. The variation of relaxation time ( $\tau$ ) with the increase in weight fraction of DETA attains maximum value at about 18% weight fraction of DETA and then falls towards the value of pure DETA in 1,4-dioxane. The nonlinear variations of the relaxation time with the change in weight fraction of DETA in the binary mixtures shows the presence of solute-solute molecular associations. The maximum value of ( $\tau$ ) at 18% weight fraction of DETA in the mixture indicates that the molecular association is maximum at 1 : 4 weight fraction of DETA and EE in the mixture. In the DETA rich region, the fall of relaxation time indicates the presence of solute-solvent association.

TABLE-I  
VALUES OF  $\epsilon'$ ,  $\epsilon''$  AND  $\tau$  FOR DETA + EE MIXTURES CONTAINING (I) 0, (II) 18,  
(III) 37, (IV) 57, (V) 78 AND (VI) 100 WEIGHT % DETA IN 1,4-DIOXANE AT  
DIFFERENT TEMPERATURES

Wt. fraction of solute in 1,4-Dioxane	Temperature											
	22°C			30°C			40°C			50°C		
	$\epsilon'$	$\epsilon''$	$\tau$ (PS)	$\epsilon'$	$\epsilon''$	$\tau$ (PS)	$\epsilon'$	$\epsilon''$	$\tau$ (PS)	$\epsilon'$	$\epsilon''$	$\tau$ (PS)
(I)												
0.043	3.57	0.15	5.78	3.55	0.14	5.34	3.53	0.13	4.85	3.52	0.13	4.53
0.083	3.85	0.34		3.83	0.33		3.79	0.30		3.77	0.30	
0.120	4.30	0.57		4.27	0.54		4.25	0.52		4.22	0.51	
0.150	4.57	0.74		4.54	0.70		4.51	0.65		4.48	0.62	
(II)												
0.044	3.59	0.21	9.46	3.57	0.20	8.11	3.55	0.17	8.03	3.53	0.16	7.89
0.084	3.81	0.37		3.79	0.34		3.77	0.32		3.75	0.30	
0.120	4.05	0.49		3.98	0.47		3.96	0.44		3.94	0.42	
0.150	4.32	0.67		4.30	0.56		4.27	0.56		4.22	0.53	
(III)												
0.044	3.67	0.23	6.53	3.63	0.21	6.45	3.57	0.21	6.31	3.55	0.20	5.35
0.084	3.96	0.41		3.94	0.39		3.92	0.38		3.83	0.36	
0.120	4.20	0.53		4.15	0.48		4.12	0.47		4.05	0.44	
0.160	4.84	0.69		4.35	0.64		4.27	0.60		4.22	0.57	
(IV)												
0.044	3.65	0.22	5.09	3.63	0.22	5.09	3.61	0.21	4.94	3.59	0.19	4.16
0.084	4.05	0.39		3.98	0.37		3.90	0.35		3.75	0.31	
0.120	4.30	0.51		4.20	0.49		4.10	0.45		4.03	0.42	
0.160	4.68	0.76		4.63	0.72		4.54	0.68		4.51	0.59	
(V)												
0.044	3.61	0.27	4.42	3.57	0.25	4.14	3.55	0.23	3.94	3.51	0.21	3.85
0.084	3.85	0.41		3.83	0.39		3.81	0.37		3.79	0.35	
0.120	4.22	0.52		4.12	0.46		4.08	0.43		4.03	0.41	
0.160	4.43	0.63		4.40	0.61		4.32	0.58		4.22	0.54	
(VI)												
0.031	3.73	0.27	2.52	3.65	0.25	2.03	3.55	0.23	1.83	3.48	0.20	1.43
0.093	4.12	0.38		4.07	0.35		4.05	0.34		3.94	0.31	
0.155	4.48	0.55		4.44	0.54		4.40	0.51		4.28	0.47	
0.220	5.00	0.80		4.84	0.70		4.79	0.68		4.68	0.58	

Values of energy parameters for the dielectric relaxation process and the corresponding energy parameters for viscous flow are presented in Table-2. It is found that the free energy of activation ( $\Delta F_{\tau}$ ) for dielectric relaxation process is less than the free energy of activation ( $\Delta F_{\eta}$ ) for the viscous flow process. It may be explained on the basis of the fact that dielectric relaxation process involves the rotation of participating molecules and the viscous flow involves both the rotational and translational motions of the molecule. The enthalpy of activation

TABLE-2  
 VALUES OF FREE ENERGIES OF ACTIVATION ( $\Delta F_{\tau}$ ,  $\Delta F_{\eta}$ ) ENTHALPY OF  
 ACTIVATION ( $\Delta H_{\tau}$ ,  $\Delta H_{\eta}$ ) ENTROPY OF ACTIVATION ( $\Delta S_{\tau}$ ,  $\Delta S_{\eta}$ ),  
 DEBYE CONSTANT (C), KALMAN FACTOR (C') AND DIPOLE MOMENT ( $\mu$ )  
 FOR DETA + EE MIXTURES CONTAINING (I) 0, (II) 37, (III) 57, (IV) 78  
 AND (V) 100 WEIGHT % DETA IN 1,4-DIOXAN AT DIFFERENT TEMPERATURES

Temp. (°C)	$\Delta F_{\tau}$ (kcal/mol)	$\Delta H_{\tau}$ (kcal/mol)	$\Delta S_{\tau}$ (cal/mol)	$\Delta F_{\eta}$ (kcal/mol)	$\Delta H_{\eta}$ (kcal/mol)	$\Delta S_{\eta}$ (cal/mol)	C $\times 10^{-8}$	C' $\times 10^{-8}$	$\mu$ (D)
<b>I</b>									
22	2.080	0.950	-3.84	3.33	4.425	3.61	14.24	0.44	2.16
30	2.110		-3.21	3.21		3.44	16.38	0.44	2.18
40	2.140		-3.20	3.20		3.38	18.65	0.42	2.18
50	2.180		-3.14	3.14		3.46	23.26	0.43	2.22
<b>II</b>									
22	2.156	1.139	-3.45	3.33	4.425	3.61	16.09	0.60	
30	2.223		-3.58	3.21		3.44	19.78	0.64	
40	2.303		-3.72	3.20		3.38	24.26	0.68	
50	2.302		-3.60	3.14		3.46	27.47	0.64	
<b>III</b>									
22	2.010	1.440	-1.93	3.33	4.425	3.61	12.55	0.49	
30	2.080		-2.11	3.21		3.44	15.61	0.53	
40	2.151		-2.27	3.20		3.38	18.99	0.56	
50	2.130		-2.14	3.14		3.46	21.37	0.62	
<b>IV</b>									
22	1.927	0.396	-5.19	3.33	4.425	3.61	10.89	0.19	
30	2.957		-5.15	3.21		3.44	12.69	0.19	
40	2.011		-5.16	3.20		3.38	15.16	0.19	
50	2.081		-5.22	3.14		3.46	17.79	0.19	
<b>V</b>									
22	1.720	1.340	-1.30	3.33	4.425	3.61	6.20	0.28	2.20
30	1.770		-1.43	3.21		3.44	6.22	0.25	2.23
40	1.830		-1.58	3.20		3.38	7.04	0.25	2.27
50	1.900		-1.73	3.14		3.46	7.34	0.21	2.30

for dielectric process ( $\Delta H_{\tau}$ ) is less than the enthalpy for viscous flow process ( $\Delta H_{\eta}$ ). The difference in values of enthalpy of activation indicates that the enthalpy depends on the local environment of the molecules. Entropy of a system is a measure of the orderly nature of the system. For co-operative environment of the system the change in entropy becomes negative and for non-cooperative environment of the system the change in entropy becomes positive and activated state is unstable. In our case it is observed that the change in entropy for dielectric

process is negative indicating the stable state, while the positive values for viscous flow process indicate that the activated states of viscous flow are unstable.

The values of Debye factor (C), Kalman's factor (C') and the dipole moment ( $\mu$ ) are listed in Table-2. It is found that the Debye factor (C) varies considerably with temperature, whereas the Kalman's factor (C') remains nearly same at all temperatures. This indicates that, the Kalman's equation is better over Debye's equation for the dielectric relaxation time as a function of viscosity. The quantity ( $\eta^*$ ) is a better representation of the inner friction coefficient for dipole rotation as compared to the macroscopic viscosity  $\eta$ . The small variations in the values of dipole moment with rise in temperature may be due to the possible solute-solvent molecular association.

The values of relaxation time ( $\tau$ ), calculated theoretically and experimentally are listed in Table-3. It is found that the values of relaxation time calculated theoretically are less than the values obtained experimentally for mixtures. The difference in values indicates the behaviour of molecular association between DETA and EE through intermolecular interactions. The values of excess inverse relaxation time are negative which shows that the solute-solvent interaction produces a field such that the effective dipoles rotate slowly, *i.e.*, the field will resist the rotation of the molecule.

TABLE-3  
VALUES OF EXPERIMENTAL RELAXATION TIME ( $\tau$ ), THEORETICAL RELAXATION TIMES ( $\tau_1$ ) USING EQUATION (9), ( $\tau_2$ ) USING EQUATION (10) AND EXCESS INVERSE RELAXATION TIME ( $(1/\tau)^e$ ) FOR (DETA + EE) MIXTURES IN 1,4-DIOXANE

Weight fraction of DETA in 1,4-Dioxane	Temp. 22°C				Temp. 30 °C			
	$\tau$	$\tau_1$	$\tau_2$	$(1/\tau)^e$	$\tau$	$\tau_1$	$\tau_2$	$(1/\tau)^e$
1.00	2.52	2.52	2.52	0.00	2.03	2.03	2.03	0.00
0.78	4.42	3.24	2.87	-0.12	4.14	2.76	2.34	-0.18
0.57	5.09	3.92	3.30	-0.10	5.09	3.45	2.74	-0.17
0.37	6.53	4.57	3.88	-0.10	6.45	4.12	3.29	-0.15
0.18	9.46	5.19	4.66	-0.11	8.11	4.74	4.09	-0.12
0.00	5.78	5.78	5.78	0.00	5.34	5.34	5.34	0.00
Weight fraction of DETA in 1,4-Dioxane	Temp 40°C				Temp 50°C			
	$\tau$	$\tau_1$	$\tau_2$	$(1/\tau)^e$	$\tau$	$\tau_1$	$\tau_2$	$(1/\tau)^e$
1.00	1.83	1.83	1.83	0.00	1.43	1.43	1.43	0.00
0.78	3.94	2.49	2.10	-0.22	3.86	2.11	1.67	-0.34
0.57	4.94	3.13	2.46	-0.20	4.16	2.76	1.99	-0.25
0.37	6.31	3.73	2.95	-0.18	5.35	3.38	2.46	-0.21
0.18	8.03	4.31	3.68	-0.14	7.89	3.97	3.40	-0.18
0.00	4.85	4.85	4.85	0.00	4.53	4.53	4.53	0.00

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