Int. J. Chem. Sci. : 2 (2), 2004, 251–258

DIELECTRIC RELAXATION AND THERMODYNAMIC PARAMETERS OF AMINE–TRIGOL IN 1, 4–DIOXANE USING MICROWAVE TECHNIQUE

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ABSTRACT

The dielectric relaxation (τ) and dipole moment (μ) for binary mixtures of diethylene triamine (DETA) and trigol (TG) in 1, 4–dioxane solution are calculated using frequency concentration variational method at 10.7 GHz frequency and at temperatures 22, 30, 40 and 50°C. Thermodyanamic parameters have also been calculated for dielectric relaxation and viscous flow process. Debye factor (C) and Kalman factor (C') are also calculated. The non–linear variation of τ with mole fraction of DETA in mixture confirms the presence of solute–solute molecular association and is maximum at 45 mole % of DETA in the mixture. The non–linear variation of excess inverse relaxation time with mole fraction of DETA in mixtures also confirms the solute–solvent interaction, which produces a field such that effective dipole rotate slowly.

Key words : Dielectric relaxation, Amine, Trigol, Microwave, Dioxane

INTRODUCTION

The study of dielectric relaxation of polar molecules in non–polar solvents from microwave absorption studies have been frequently attempted[1–5]. Dipolar behaviour of organic compounds[6,7] is understood by estimation of dielectric parameters of polar compounds in non–polar solvents. The study also gives indication about different types of molecular interactions such as solute–solute, solute–solvent and self association in the solution. Diethylene triamine (DETA) and trigol (TG) are chosen for the present study for the dielectric behaviour of their mixtures in 1, 4–dioxane solution. The measurements are done at 10.7 GHz frequency and at temperatures 22–50°C.

EXPERIMENTAL

The liquids were procured from M/s S.d. fine chemicals (A. R. grade) and used without further purification. X–band microwave bench was used to measure the wave length[8] 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 + TG) in 1, 4–dioxane were prepared. The dielectric constant $\in'$ of dilute solutions of binary mixtures of (DETA + TG) in 1, 4–dioxane at different (22 to 50 °C) were calculated using Heston *et al.* technique[9]. The temperature of the solution was controlled by circulating thermostated water around the dielectric cell. Dielectric relaxation time τ for different mole fraction of DETA in (DETA + TG) mixtures and dipole moment (μ) for DETA and TG were calculated following the single frequency concentration variational method of Gopal Krishna[10]

Determination of molecular parameters : The dielectric constant ($\in'$) and dielectric loss ($\in''$) were calculated by the method of Heston[9] at 22, 30, 40 and 50°C by following equations

$$\in' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \qquad ...(1)$$

and $$\in'' = \frac{2}{\pi}\left(\frac{\lambda_0}{\lambda_d}\right)^2\left(\frac{\lambda_g}{\lambda_d}\right)\frac{d\rho}{dn} \qquad ...(2)$$

where $\lambda_0, \lambda_c, \lambda_d$ and λ_g are the free space wavelength, cut–off wavelength, wavelength in the wave guide filled with solution and guide wavelength, respectively. ρ is the inverse of VSWR and $d\rho/dn$ is slope of ρ versus n where n = 1, 2, 3...... such that $n\frac{\lambda_d}{2}$ represents the length of the dielectric filled waveguide.

Gopal Krishna[10] fixed frequency method was used to estimate the relaxation time (τ) and dipole moment (μ). The energy parameters free energy (ΔF_τ), enthalpy (ΔH_τ) and the entropy of activation (ΔS_τ) for dielectric relaxation process and the corresponding parameters for viscous flow (ΔF_n, ΔH_n and ΔS_n) have been calculated using Eyrings[11] equations.

The Debye equation for dielectric relaxation time in terms of viscosity (η) of the solvent is given by

$$\tau = \left(\frac{C}{T}\right)\eta \text{ or } C = \left(\frac{\tau T}{\eta}\right) \qquad ...(3)$$

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

$$\tau = \left(\frac{C'}{T}\right)\eta^x \text{ or } C' = \left(\frac{\tau T}{\eta^x}\right) \qquad ...(4)$$

where $x = \left(\frac{\Delta H_\tau}{\Delta H_\eta}\right)$ and C' is called Kalman's factor. The Debye factor (C) and Kalman's factor C' are reported in Table 2.

The theoretical relation for determining the values of relaxation times of these systems for non–associated behaviour is given by[12]

$$\tau_{m} = C_1\tau_1 + (1 - C_1)\tau_2 \qquad ...(5)$$

where τ_1 and τ_2 are relaxation times of pure solutes 1 and 2, respectively and C_1 is the mole fraction of first solute in their mixtures. A theoretical relation proposed by Madan[13] to represent the molecular behaviour in binary mixtures can be written as

$$\frac{1}{\tau_m} = \left(\frac{C_1\mu_1^2}{[C_1\mu_1^2 + (1 - C_1)\mu_2^2]\,\tau_1} + \frac{(1 - C_1)\mu_2^2}{[C_1\mu_1^2 + (1 - C_1)\mu_2^2]\,\tau_2} \right) \qquad ...(6)$$

where C_1 = Mole fraction of first solute in the mixture,

μ_1 = dipole moment of first solute,

τ_1 = relaxation time of first solute,

μ_2 = dipole moment of second solute and

τ_2 = relaxation time of second solute

The excess inverse relaxation time can be found from the following equation

$$\left(\frac{1}{\tau}\right)^e = \left(\frac{1}{\tau_m}\right) - \left[X_1\left(\frac{1}{\tau_1}\right) + X_2\left(\frac{1}{\tau_2}\right)\right] \qquad ...(7)$$

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 $\left(\frac{1}{\tau}\right)^e = 0$, means there is no change in dynamics of solute – solvent interactions.

If $\left(\frac{1}{\tau}\right)^e < 0$, means that the solute – solvent interactions produces a field such that the effective dipole rotate slowly, that is the field will resist the rotation.

If $\left(\frac{1}{\tau}\right)^e > 0$, then it indicates that the solute – solvent interaction produces a field such that the dipole will rotate faster, that is the field will co–operate in rotation of the dipoles.

RESULTS AND DISCUSSION

The values of $\in'$ and $\in''$ obtained for DETA, TG and their mixtures for different concentrations in 1, 4–dioxane and at different temperatures are reported in Table 1. The value of relaxation time (τ) are also reported in Table 1. From Table 1, it is seen that both dielectric constant $\in'$ and loss factor $\in''$ increase as the weight fraction increases and decreases with the increase of temperatures. It is also seen that the relaxation time increases with mole fraction of

Table 1. Values of $\in'$, $\in''$ and $\in$ for DETA + TG mixtures containing (I) 0, (II) 24, (III) 45, (IV) 65, (V) 83 and (VI) 100 mole % DETA in 1, 4–dioxane at different temperatures

Temp.	22°C			30°C			40°C			50°C		
Wt. fraction of solute in 1, 4–dioxane	ε′	ε″	τ	ε′	ε″	τ	ε′	ε″	τ	ε′	ε″	τ
I												
0.52	3.72	0.25	4.26	3.71	0.23	3.94	3.70	0.22	3.32	3.67	0.21	2.92
0.098	3.98	0.50		3.96	0.47		3.96	0.46		3.94	0.46	
0.141	4.63	0.73		4.55	0.66		4.54	0.59		4.35	0.55	
0.179	4.81	0.91		4.77	0.84		4.71	0.78		4.63	0.74	
II												
0.051	3.92	0.33	4.86	3.79	0.31	4.20	3.74	0.30	3.77	3.67	0.28	3.08
0.096	3.96	0.44		3.93	0.39		3.90	0.37		3.87	0.33	
0.140	4.54	0.65		4.48	0.61		4.42	0.57		4.10	0.49	
0.170	4.97	0.75		4.40	0.68		4.38	0.64		4.27	0.59	
III												
0.049	3.85	0.35	7.14	3.83	0.33	6.30	3.81	0.30	5.99	3.77	0.28	5.68
0.094	4.08	0.51		4.05	0.50		4.01	0.49		3.98	0.47	
0.130	4.27	0.58		4.20	0.55		4.15	0.52		4.10	0.49	
0.170	4.46	0.75		4.40	0.68		4.38	0.64		4.77	0.59	
IV												
0.048	3.87	0.39	6.30	3.85	0.36	4.96	3.83	0.33	3.15	3.77	0.29	2.82
0.091	4.22	0.53		4.17	0.46		4.15	0.44		4.00	0.39	
0.130	4.27	0.62		4.22	0.58		4.20	0.55		4.03	0.49	
0.170	4.46	0.72		4.38	0.64		4.32	0.60		4.22	0.56	
V												
0.046	3.77	0.28	3.05	3.73	0.26	2.83	3.71	0.25	2.25	3.67	0.24	1.92
0.088	4.05	0.52		4.03	0.49		3.98	0.47		3.94	0.43	
0.126	4.46	0.68		4.41	0.63		4.40	0.60		4.38	0.56	
0.160	4.48	0.74		4.46	0.70		4.35	0.61		4.22	0.56	
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	1.47
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		4.25	0.47	
0.219	5.00	0.80		4.84	0.70		4.79	0.68		4.68	0.58	

DETA in mixture, which indicates the solute–solute interactions. With further increase in mole fraction of DETA, the relaxation time decreases, which indicates the disruption of associates in the mixture and change to the structure of self association. Similar behaviour is found for different temperatures.

The non–linear variation of relaxation time (τ) with mole fraction of DETA in the mixture shows the presence of solute – solute association in the mixture[8]. The value of 'τ' is found to be maximum at 45 mole % of DETA, which shows that the molecular association is maximum at 45 mole % of DETA.

The values of free energies of activation (ΔF_τ, ΔF_η), enthalpies of activation (ΔH_τ, ΔH_η) entropies of activation (ΔS_τ, ΔS_η), Debye factor (C), Kalman's factor (C') and dipole moment (μ) are reported in Table 2 for DETA, TG and binary mixture containing 45 mole % of DETA. It is seen that ΔF_τ is less than ΔF_η and this may be explained on the basis that the dielectric relaxation process involves rotation of molecules, whereas the viscous flow involves both rotational and translational motion of the molecules. It is also seen that ΔH_τ is less than ΔH_η and their ratio is less than 0.55, which shows that the solid rotator phase may exist. The orderly

Table 2. Values of free energies of activation (ΔFτ, ΔFη), enthalpies of activation (ΔHτ, ΔHη), entropies of activation (ΔSτ, ΔSη), Debye factor (C), Kalman's factor (C') and dipolement (μ) for (I) DETA, (II) TG and (III) DETA+TG containing 45 mole % of DETA in 1, 4–dioxane

Temp. K	ΔF_τ Kcal/mole	ΔH_τ Kcal/mole	ΔS_τ Kcal/mole	ΔF_η Kcal/mole	$\Delta H\eta$ Kcal/mole	$\Delta S\eta$ Kcal/mole	C 10^{-8}	C' 10^{-8}	μ
				I					
295	1.72	1.337	–1.298	3.33	4.425	3.61	6.20	0.28	2.21
303	1.77		– 1.432	3.21		3.44	6.22	0.25	2.23
313	1.83		– 1.581	3.20		3.38	7.04	0.25	2.27
323	1.90		– 1.734	3.14		3.46	7.34	0.21	2.30
				II					
295	1.90	1.823	–0.27	3.33	4.425	3.61	10.49	0.77	2.75
303	1.92		–0.34	3.21		3.44	12.07	0.80	2.79
313	1.91		–0.26	3.20		3.38	12.76	0.75	2.81
323	1.90		–0.25	3.14		3.46	14.99	0.76	2.85
				III					
295	2.21	0.98	–4.17	3.33	4.425	3.61	15.79	0.56	
303	2.21		–4.10	3.21		3.44	19.32	0.53	
313	2.27		–4.13	3.20		3.38	23.03	0.54	
323	2.33		–4.19	3.14		3.46	29.17	0.56,	

Table 3. Values of experimental relaxation time (τ), theoretical relaxation times; (τ^5) using equation (5); (τ^6) using equation (6) and excess inverse relaxation time $(1/\tau)^e$ for binary mixtures of (DETA + TG) in 1, 4–dioxane

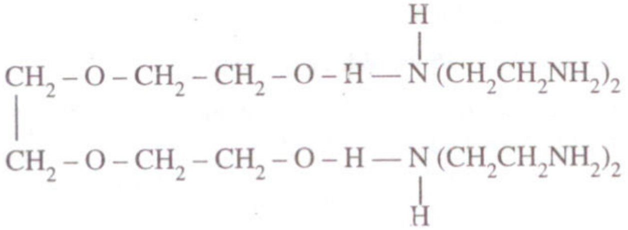
Mole fraction of DETA in 1, 4–dioxane	Temp. 22°C				Temp. 30 °C				Temp 40 °C				Temp. 50 °C			
	τ P.S.	τ_5 P.S.	τ_6 P.S.	$\left(\frac{1}{\tau}\right)^e$	τ P.S.	τ_5 P.S.	τ_6 P.S.	$\left(\frac{1}{\tau}\right)^e$	τ P.S.	τ_5 P.S.	T_6 P.S.	$\left(\frac{1}{\tau}\right)^e$	τ P.S.	τ_5 P.S.	τ_6 P.S.	$\left(\frac{1}{\tau}\right)^e$
1.00	2.52	2.52	2.52	0.00	2.03	2.03	2.03	0.00	1.83	1.83	1.83	0.00	1.43	1.43	1.43	0.00
0.83	3.05	2.82	2.80	–0.04	2.83	2.35	2.29	–0.10	2.25	2.08	2.05	–0.11	1.92	1.68	1.63	–0.12
0.65	6.30	3.13	3.10	–0.18	4.96	2.70	2.64	–0.21	3.15	2.35	2.30	–0.14	2.85	1.95	1.86	–0.22
0.45	7.14	3.48	3.44	–0.17	6.30	3.08	2.98	–0.20	5.99	2.65	2.59	–0.25	5.68	2.25	2.14	–0.19
0.24	4.80	3.84	3.82	–0.07	4.20	3.48	3.40	–0.07	3.77	2.96	2.91	–0.10	3.08	2.56	2.48	–0.10
0.00	4.26	4.26	4.26	0.00	3.94	3.94	3.94	0.00	3.32	3.32	3.32	0.00	2.92	2.92	2.92	0.00

nature of the system is decided by the entropy of the system. The negative values of the change in entropy for the activated process indicates the cooperative environment of the system and that the activated state is stable. The positive change in entropy values indicates the non–cooperative environment of the system and that the activated state is unstable. In the present study, the change in entropy for dielectric process is negative and for viscous flow process, it is positive.

From Table 2, it is seen that the Debye factor (C) varies considerably with temperature whereas Kalman's factor remains almost constant. This indicates that Kalman's equation (4) for the dielectric relaxation time as a function of viscosity is superior to the Debye's equation (3) and the quantity η^x is a better representation of the inner friction coefficient to the macroscopic viscosity (η)[14]

From Table 3, it is seen that the values of relaxation times calculated by equation (5) and (6) are less than the experimental values of relaxation times, which indicates the behaviour of the molecular association between DETA + TG through inter molecular interaction. Similar kind of behaviour has been found earlier in the case of aniline and nitrobenzene mixture in benzene solution[15]. The variation of excess inverse relaxation times with mole fraction of DETA are reported in Table 3. The values are negative and show that the solute–solvent interaction produces field such that the effective dipoles rotate slowly, that is the field will resist the rotation of molecule.

The mechanism of complex formation between TG and DETA is explained using Pauling[16] scale of electronegativity of nitrogen, oxygen and hydrogen in order of N (3.4) > O (3) > H (2). The complex formation is favored in case $H^{\delta+}$ of alcohol and $\dot{N}^{\delta-}$ of amine in the manner as shown.



$$\begin{array}{l}
CH_2-O-CH_2-CH_2-O-H \text{ — } \overset{\displaystyle H}{\overset{|}{N}}(CH_2CH_2NH_2)_2 \\
| \\
CH_2-O-CH_2-CH_2-O-H \text{ — } \underset{\displaystyle H}{\underset{|}{N}}(CH_2CH_2NH_2)_2
\end{array}$$

Because of presence of nitrogen of amine and hydrogen of alcohol in the chain, charge distribution between them is likely to be favored. Since the nitrogen atom is sp^3 hydridized and shape of amine is pyramidal, there is a lot of space on the outside of the apex of pyramid for the OH to penetrate and enter into complexation.

ACKNOWLEDGEMENT

The authors are thankful to the Principal, Science College, Nanded, the Chairman Dr. V.R. Kabde and Secretary, S.O. Patil for encouragement and support. One of them (G.M.K.) is indebted to the University Grants Commission, Western Regional Office, Ganesh Khind, Pune for a Minor Research Project.

REFERENCES

1. N. Srinyashiki, S. Sudo, W. Abe and S. Yoghara, J. Chem. Phys., **109**, 22 (1998).
2. A. Sharma and D. R. Sharma, Indian J. Pure Appl. Phys., **31**, 814 (1993).
3. Nagesh Thakur and D. R. Sharma, Indian J. Pure Appl. Phys., **31**, 721, (1993).
4. T. Telgmann and U. Kantze, J. Phys. Chem. A., **21**, 2000 (2000).
5. N. Poul, Indian J. Phys., **71B**, 711, (1997).
6. C. August, "Dielectric Physics", Elsevier, Amsterdam, (1980).
7. N. E. Hill, W. E. Waughan, A. H. Price and M. "Devices, Dielectric Properties and Molecular Behaviour", Van Nostrand, Reinhold, London (1969).
8. G. M. Kalamse and M. J. Nimkar, Asian J. Chem., **4**, 1474 (2002).
9. Heston (Jr.), W. M. Franklim and A. D. Hennelly, J. Am. Chem. Soc., **72**, 3443 (1950).
10. K.V. Gopal Krishna, Trans. Faraday Soc., **33**, 167 (1957).
11. H. Eyring, S. Glasstone and K. J. Laidler, "The Theory of Rate Process", Mc Graw Hill, New York (1947).
12. B. M. Suryawanshi, Thesis submitted to Dr. B.A.M.U., Aurangabad (1987).
13. M. P. Madan, Canad. J. Phys., **58**, 20 (1980)
14. M. Khatri and J. M. Gandhi, J. Mol. Liq., **30**, 63 (1986).
15. J. Prakash and B. Rai, Indian J. Pure Appl. Phys., **24**, 187 (1986).
16. M. V. George, J. Mahanty and P. T. Narasimhan (Eds.) "A Hand Book of Chemistry and Physics", East West Press Pvt. Ltd., New Delhi (1970) p.228.

Accepted : 19.4.2004