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Dielectric Behaviour of Diethylene Triamine + Trigol Mixtures Using Microwave Techniques

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In the present paper we have obtained the values of dielectric constant (ε′) and loss factor (ε″) experimentally by using Serber's method, for the binary mixtures of diethylene triamine (DETA) and trigol (TG) at 10.7 GHz microwave frequency and 20°C temperature. Molar polarization, apparent polarization and the excess values of permitivities (Δε′, Δε″), square of refractive index (Δn_D^2), viscosity (Δη) and activation energy (ΔE_a) of viscous flow estimated from the measured dielectric data. We have used these parameters to explain the nature of complex formation. The results suggest the strong interactions between the molecules of amine and trigol.

Key Words: Dielectric behaviour, Diethylene triamine, Trigol, Microwave techniques.

INTRODUCTION

Experimental investigation of dielectric properties of organic compounds is of great value in understanding the nature of complex formation between the molecules. The knowledge of dielectric properties and thermodynamic properties, of organic compounds and their mixtures at microwave frequencies helps in their characterization and applications. More investigations may lead to proper understanding of the behaviour of the liquid mixtures. In case of binary mixtures the dielectric parameters, thermodynamic parameters, refractive index and viscosity do not vary linearly[1–3]. The deviation from linearity of these parameters is called as excess parameters. These excess parameters are useful to understand the nature of bonding between the two constituents of the mixture. Trigol (TG) is used for determining saponification values of oils and also employed as an air disinfectant and as a solvent for nitrocellulose. Thus the investigation on dipolar behaviour is important for deciding their uses. The present work aims at the estimation of dielectric behaviour of diethylene triamine (DETA)-trigol (TG) binary mixture by studying the change in the dielectric constant (ε′) and loss factor (ε″) of DETA + TG mixture at room temperature.

EXPERIMENTAL

The X-band microwave bench is used to measure the wavelength in the dielectric. To hold the liquid sample in the cell, a thin mica window, whose VSWR and attenuation were neglected, is introduced between the cell and the rest of the microwave-bench. The dielectric constant (ε′) and the loss factor (ε″) were measured using Serber's technique[4–6] of measuring the reflection co-efficient from the air-dielectric boundary of the liquid.

The movable short in the dielectric cell is coupled to a moving mechanism (sliding carriage) which is mounted above the vertical brass bed. The sliding carriage is further coupled to the vertical threading rod, with the help of box nut. The threading rod is directly coupled to the axle of the stepper motor. The movements of the stepper motor entirely controlled by the computer programming. Thus by employing stepper motor, computer and other electronic devices (Stepping Motor control card PCL-839, Amplifire and Multiplexer PCLD-789D A-D Card and Driver Card etc. purchased from Dynalog India Ltd., Pune) we can move the short plunger in the dielectric cell filled with liquid sample. When short plunger moves up, the length of the liquid column changes slowly and the corresponding output from the crystal detector is recorded in the computer.

Dielectric parameters

Serber[4, 5] has derived the following relations for the dielectric parameters ε′, ε″, D and $\alpha_d\lambda_d$.

$$\varepsilon' = (\lambda_0/\lambda_c)^2 + (\lambda_0/\lambda_d)^2[1 - \tan^2(1/2 \tan^{-1} D)] \quad (1)$$

$$\varepsilon'' = 1/\pi(\lambda_0/\lambda_d)^2\alpha_d\lambda_d \quad (2)$$

$$D = \tan [2 \tan^{-1}(\alpha_d\lambda_d)/2\pi] \quad (3)$$

where, λ_0 is the free space wavelength, λ_c is the cut-off wavelength for the waveguide, α_d is the attenuation constant due to dielectric, λ_d is the wavelength of e.m. waves in the waveguide filled with dielectric, ε′ is the real part, associated with the ability of the dielectric material to store electric energy, ε″ is the imaginary part associated with the losses occurring in the dielectric, $\alpha_d \lambda_d$ is the attenuation per wavelength. Now the parameters to be measured experimentally are λ_d and $\alpha_d\lambda_d$. The dissipation factor D for the system may be computed analytically as follows:

Defining a factor M_n such that

$$M_n = |\Gamma_n|^2/|\Gamma_\infty|^2 = I_n/I_\infty \quad (4)$$

where n = 1, 2, 3 . . . $|\Gamma_n|$ is the reflection coefficient by the liquid column of length L = n (λ_d/2) and Γ_∞ is the reflection coefficient for the liquid column of infinite length. I_n and I_∞ represent the corresponding current values. According to Serber[4] attenuation per wavelength is given by

$$\alpha_d\lambda_d = l/n\ l_n\ [k_1\{1 + (1 + k_2)^{1/2}\}] \quad (5)$$

where $$K_1 = (1 - M_nY^2)/y(M_n - 1) \quad (6)$$

$$K_2 = (M_n - 1)(1 - M_nY^4)/(1 - M_nY^2)^2 \quad (7)$$

$$Y = (1 - \lambda_d/\lambda_g)/(1 + \lambda_d/\lambda_g) \quad (8)$$

Thus measuring $(\alpha_d\lambda_d)$, λ_0, λ_c and λ_d the values of dielectric parameters ε', ε'' and D can be calculated by using the above equations.

The density and viscosity of pure components and their mixtures were measured by using the pyknometer and Ostwald's viscometer[7] respectively. Refractive indices for sodium D-line were measured by using Abbe's refractometer.

The free energy of activation E_a of the viscous flow for the pure liquids and their mixtures is obtained by using the following equation:[1, 8–10]

$$\eta = (hN/V) \exp (E_a/RT) \tag{9}$$

where η is viscosity and V is molar volume of the liquids. Other symbols have their usual meaning.

RESULTS AND DISCUSSON

The values of dielectric constant (ε') with increasing mole fraction (x) of DETA are given in Table-1 and the variation of (ε') with mole fraction of DETA in the mixture is shown in Fig. 1. A minima at $x = 0.45$ indicates the formation of complex in the binary mixture as observed by other workers[1, 11]

The values of tan δ with increasing mole fraction (x) of DETA are given in Table-1 and the variation of tan δ with mole fraction of DETA is shown in Fig. 2. A minima in the curve at $x = 0.45$ shows that there is a decrease in relaxation time in the mixture for dilute solutions of a polar liquid in a nonpolar solvent. This can be explained on the basis of Debye's equation[6, 8] for tan δ.

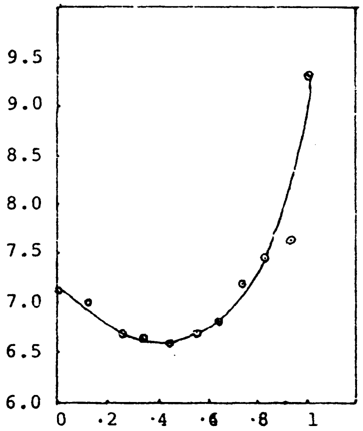

Fig. 1. Variation of ε' *vs.* x of DETA in the mixture

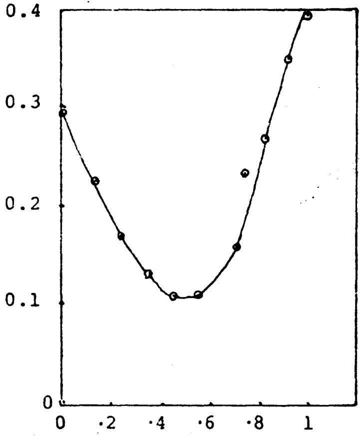

Fig. 2. Variation of tan δ *vs.* x of DETA in the mixture

The values of viscosity (η) with increasing mole fraction (x) of DETA are listed in Table-1 and the variation of viscosity with mole fraction of DETA is shown in Fig. 3. A maxima in the curve at $x = 0.35$ shows increase in the mutual viscosity of the TG and DETA molecules as provided by the Andrade's theory.[8]

TABLE-1
VALUES OF MOLE FRACTION (X) OF DETA, VISCOSITY (η), SQUARE OF THE REFRACTIVE INDEX (n_D^2), DIELECTRIC CONSTANT (ε′), DIELECTRIC LOSS (ε″), LOSS TANGENT (tan δ), ACTIVATION ENERGY (E_a) AND MOLAR POLARIZATION (P_{12}) FOR DETA + TG SYSTEM AT 20°C

X	η (cp)	N_D^2	ε′	ε″	tan δ	E_a (kcal/mole)	P_{12} (cm³/mole)
0.0000	5.120	2.097	7.114	1.962	0.2926	4.316	90.11
0.1201	59.097	2.117	7.023	1.522	0.2300	5.776	86.99
0.2350	97.341	2.129	6.706	1.083	0.1720	6.073	83.20
0.3450	122.538	2.146	6.658	0.810	0.1294	6.223	80.90
0.4502	91.364	2.152	6 595	0.718	0.1160	6.036	78.78
0.5513	68.877	2.161	6.732	0.719	0.1140	5.868	77.91
0.6483	51.165	2.167	6.816	1.013	0.1590	5.690	76.74
0.7414	32.119	2.173	7.166	1.611	0.2380	5.402	76.89
0.8309	18.293	2.179	7.452	1.907	0.2710	5.077	76.77
0.9170	11.020	2.182	7.610	2.570	0.3570	4.774	76.08
1.0000	7.062	2.184	9.320	3.496	0.3920	4.512	79.73

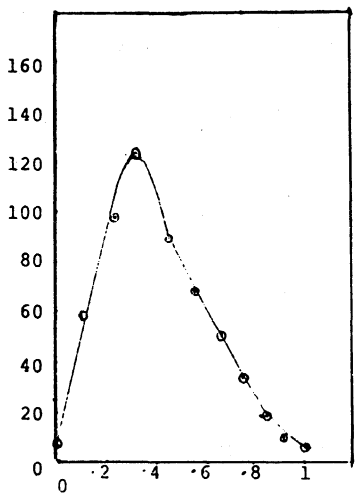

Fig. 3. Variation of η *vs.* x of DETA in the mixture

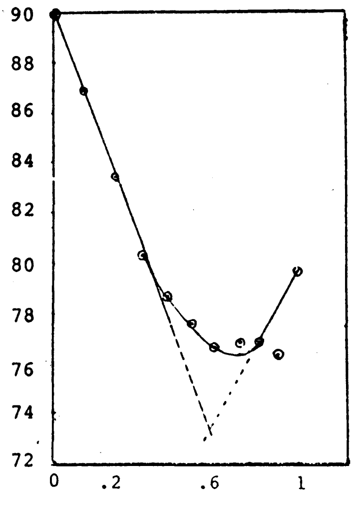

Fig. 4. Variation of P_{12} *vs.* x of DETA in the mixture

The values of polarization of the mixture were obtained using the formula

$$P_{12} = (\varepsilon' - 1/\varepsilon' + 2)(X_1M_1 + X_2M_2)/d \quad (10)$$

where M_1 and M_2 are the molecular weights, X_1 and X_2 the molar concentration of the constituents of the mixture and d is the density of the mixture. The values of P_1 and P_2 were calculated by using the following equation:

$$P_{12} = X_1P_1 + X_2P_2 \quad (11)$$

where P_2 is the appaerent polarization of each liquid in the mixture P_1 is the polarization of the other component of the mixture in the pure liquid state. The values of molar polarization (P_{12}) are listed in Table-1 and the variation of P_{12} with mole fraction of DETA in the mixture is shown in Fig. 4. The intersection of the straight lines at $X = 0.65$ representing separate region of high and low concentrations of DETA can be interpreted as the point of maximum concentration of the complex[1]. This result supports our earlier conclusion made from Fig. 1 for ε' *vs.* mole fraction X.

Fig. 5 represents the variation of apparent polarization (P_2) for trigol with mole fraction of TG. The flat portion of the curve clearly indicates the formation of complex in DETA + TG mixtures. The more pronounced the flat portion, the more stable is the complex. Our results matched with the results obtained by Combs[11] for alcohol + *o*-dichlorobenzene mixtures.

Excess parameters

The variation of excess values of dielectric constant, loss factor, viscosity, square of refractive index and activation energy with mole fraction are presented in Fig. 6 to 10. The excess values are calculated by using the following equation[1]

$$\Delta y = y_m - (x_1 y_1 + x_2 y_2) \qquad (12)$$

where Δy is any excess parameter and y refers to the above mentioned quantities. The subscripts m, 1 and 2 used are for the mixture, component 1 and component 2, x_1 and x_2 are the mole fractions of two components in the mixtures. The excess values were fitted through least squares with all points equally weighted by using Redlich-Kister equation[1]

$$\Delta y = x_1 x_2 \sum_j A_j (x_1 - x_2)^j \qquad (13)$$

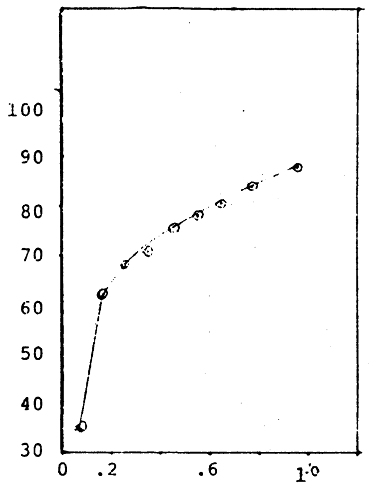

Fig. 5. Variation of P_2 *vs.* x of trigol in the mixture

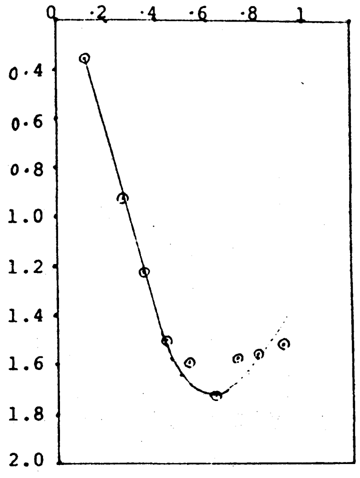

Fig. 6. Variation of $\Delta\varepsilon'$ *vs.* x of deta in the mixture

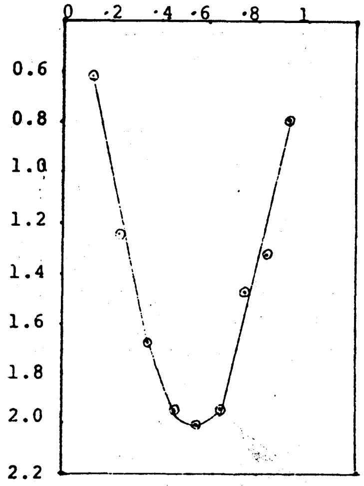

Fig. 7. Variation of $\Delta\varepsilon''$ *vs.* x of deta in the mixture

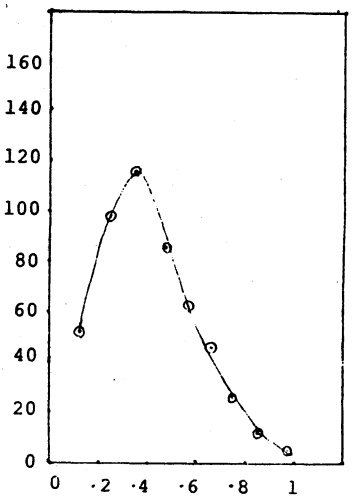

Fig. 8. Variation of $\Delta\eta$ versus x of deta in the mixture

where y is any physical parameter and x_1 and x_2 are the concentrations of the two constituents. For better fitting curve we have used six coefficients in the expansion. The values of coefficients A_j's for j = 0 to 5 are listed in Table-2 along with the standard deviation σ. By using these A_j values excess parameters Δy are calculated and used them as guidelines to draw smooth curves in Fig. 6 to 10.

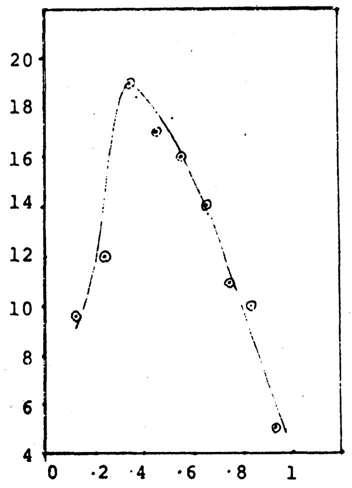

Fig. 9. Variation of Δn_D^2 *vs.* x of deta in the mixture

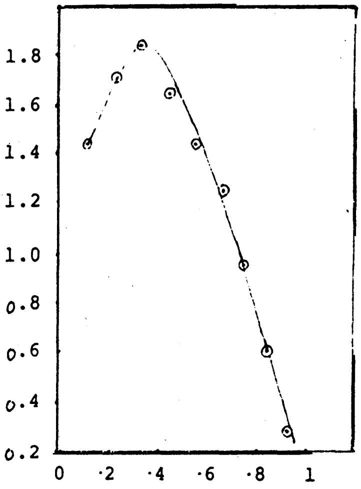

Fig. 10. Variation of ΔE_a *vs.* x of deta in the mixture

TABLE-2

VALUES OF COEFFICIENT A_j's AND STANDARD DEVIATION (σ) IN VARIOUS EXCESS PARAMETERS FOR DETA + TRIGOL SYSTEM AT 20°C.

Physical parameters Δy	A_0	A_1	A_2	A_3	A_4	A_5	σ
$\Delta\varepsilon'$	–7.644	–40.300	6.039	229.96	–6.144	–289.76	0.4145
$\Delta\varepsilon''$	–8.242	–15.428	4.399	85.35	–1.641	–104.78	0.4834
$\Delta\eta$	216.130	–920.200	146.59	3196.467	–219.58	–3360.67	36.66
Δn_D^2	0.066	–0.0574	0.027	0.242	–0.0055	–1.275	0.0041
ΔE_a	6.389	–4.01	1.375	–0.215	4.976	–6.526	0.4984

The excess dielectric constant ($\Delta\varepsilon'$) and excess loss ($\Delta\varepsilon''$) are negative. The minima in the $\Delta\varepsilon'$ and $\Delta\varepsilon''$ curves occur at 0.65 and 0.55 mole fraction of DETA respectively at which we expect the formation of complexes on the basis of ε', tan δ and η curves given in Fig. 1 to 3.

The excess viscosity ($\Delta\eta$), square refractive index (Δn_D^2) and activation energy (ΔE_a) are positive, indicating strong interactions between trigol and amine molecutes. For all these parameters the maxima occur at 0.35 mole fraction of DETA.

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REFERENCES

1. P.J. Singh and K.S. Sharma, *Pramana. J. Phys.*, **46**, 259 (1996)
2. S.M. Puranik, S.N. Helambe and S.C. Mahrotra, *Indian J. Pure and Appl. Phys.*, **29**, 255 (1991).
3. R.H. Fattepur *Pramana. J. Phys.*, **44**, 33 (1995).
4. W.H. Sarber, *J. Appl. Phys.*, **19**, 514 (1948).
5. M.L. Sisodia and G.S. Raghuvanshi, Basic Microwave Techniques and Lab Manual, Wiley Eastern Ltd. (1990).
6. A. Chelkowski, Dielectric Physics, Elsevier Scientific Publishing Company, New York (1980).
7. V.V. Nadkarny, A.N. Kothare and Y.V. Lawande, Practical Physical Chemistry, Popular Prakashan, Bombay.
8. N.E. Hill, W.E. Vaughan, A.H. Price and M. Davies, Dielectric Properties and Molecular Behavior, Van Nostrand Reinhold, London (1968).
9. H. Eyring, S. Glasstone and K.J. Laidler, The Theory of Rate Processes, McGraw-Hill, New York (1941).
10. S.S. Nalwad, M.J. Nimkar and G.M. Kalamse, *Asian J. Chem.*, **13**, 1175 (2001).
11. L.L. Combs *J. Phys. Chem.*, **75**, 2133 (1971).

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