

Dielectric Behaviour of Binary Mixture of Diethylene Triamine with 2-Ethoxy Ethanol

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Densities, viscosities, refractive indices, dielectric constant (ϵ') and dielectric loss (ϵ'') of 2-ethoxy ethanol, diethylene triamine and their mixtures for different mole fractions of diethylene triamine have been measured at 10.7 GHz microwave frequency. The values of dielectric parameters (ϵ' and ϵ'') have been used to evaluate the molar polarization, apparent polarization and the excess permittivities. Excess refractive index, viscosity and activation energy of viscous flow have also been estimated. These parameters have been used to explain the formation of complexes in the system. The excess values have been fitted through least squares with all points equally weighted by using the Redlich-Kister equation, to estimate the binary coefficient and standard deviations (σ).

Key Words: 2-Ethoxy ethanol, Binary mixtures, Dielectric constant, Dielectric loss.

INTRODUCTION

In case of binary mixture refractive index, viscosity, density, dielectric parameters and thermodynamic parameters do not vary linearly. The deviation from linearity of these parameters is called excess parameters. These excess parameters help to explain the dielectric behaviour of the binary mixtures of two liquids.

2-Ethoxy ethanol (EE) commercially known as “cello solves” is widely used as components of solvents, coemulsifiers and stabilizers of emulsions, dyes and lacquers. In the past several workers¹⁻⁸ have made dielectric studies of liquid mixtures. However, limited information appears for the alcohol + amine mixtures. As such, it was felt that the present studies may provide useful information regarding the molecular interactions and the formation of complexes in the binary mixture of diethylene triamine (DETA) + 2-ethoxy ethanol (EE).

EXPERIMENTAL

The measurements of dielectric constant (ϵ') and dielectric loss (ϵ'') were carried out from the x-band microwave bench⁸⁻¹¹ of oscillating frequency 10.7 GHz at 20°C temperature. The densities and viscosities of the pure compo-

nents and their mixtures were measured by using pycnometer and Oswald's viscometer respectively. Refractive indices for sodium D-lines were measured by using Abbe's refractometer. The chemicals used were of AR grade supplied by M/S S.D. Fine Chemicals. The two liquids according to their proportions by volume were mixed well and kept for 6 h in well stoppered bottles to ensure good thermal equilibrium. The experimental technique for the measurement of wavelength in dielectric (λ_d), attenuation per unit length ($\alpha_d \lambda_d$), dielectric constant (ϵ') and dielectric loss (ϵ'') were the same as reported earlier^{5,8}.

The dielectric parameters (ϵ' and ϵ'') were measured by using Serber's technique^{11,12} of measuring the reflection coefficient from the air-dielectric boundary of the liquid. Serber's technique for medium and high loss liquids permits rapid measurements of VSWR. Serber has derived the following relations for the dielectric parameters ϵ' , ϵ'' , D and $\alpha_d \lambda_d$.

$$\epsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \left[1 - \tan^2\left(\frac{1}{2} \tan^{-1} D\right)\right] \quad (1)$$

$$\epsilon'' = \frac{1}{\pi} \left(\frac{\lambda_0}{\lambda_d}\right)^2 \alpha_d \lambda_d \quad (2)$$

and

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

where λ_0 is the free-space wavelength, λ_c is the cut-off wavelength for the wave guide, $\alpha_d \lambda_d$ is the attenuation per unit length due to dielectric, λ_d is the wavelength of e.m. waves in the waveguide filled with dielectric. According to Surber¹², attenuation per wavelength is given by

$$\alpha_d \lambda_d = \frac{1}{n} \ln [k_1 \{1 + (1 + k_2)^{1/2}\}] \quad (4)$$

where $k_1 = \frac{(1 - M_n Y^2)}{Y(M_n - 1)}$, $k_2 = \frac{(M_n - 1)(1 - M_n Y^4)}{(1 - M_n Y^2)^2}$, $Y = \frac{(1 - \lambda_d/\lambda_g)}{(1 + \lambda_d/\lambda_g)}$,

and

$$M_n = \frac{|\Gamma_n|^2}{|\Gamma_\infty|^2} = \frac{I_n}{I_\infty}$$

where $n = 1, 2, 3, \dots$; $|\Gamma_n|$ is the reflection coefficient for the liquid column length $l = n(\lambda_d/2)$ and $|\Gamma_\infty|$ is the reflection coefficient for the liquid column of infinite length; I_n and I_∞ represent the corresponding current values.

Thus, measuring $\alpha_d \lambda_d$, λ_0 , λ_c and λ_d , the values of dielectric constant ϵ' , dielectric loss ϵ'' and dissipation factor D can be calculated. The free energy of activation (E_a) of the viscous flow for the pure liquids and their mixture obtained by using the following equation⁹:

$$\eta = \left(\frac{hN}{V}\right) \exp\left(\frac{E_a}{RT}\right) \quad (5)$$

where η is the viscosity and V is the molar volume and other symbols have their usual meaning.

The values of molar polarization of the mixtures were obtained by using the relation^{9, 10}.

$$P_{12} = \left[\left(\frac{\epsilon' - 1}{\epsilon' + 2} \right) \right] \left[\left(\frac{X_1 M_1 + X_2 M_2}{d} \right) \right] = X_1 P_1 + X_2 P_2 \quad (6)$$

where M_1 and M_2 are the molecular weights, X_1 and X_2 are the molar concentrations of constituents of the mixtures. P_2 is the apparent polarization of each liquid in the mixture, if P_1 is the polarization of the other component of the mixture in the pure liquid state.

The excess values of permittivity ($\Delta\epsilon'$ and $\Delta\epsilon''$), excess viscosity ($\Delta\eta$), excess square refractive index (Δn_D^2) and the excess activation energy (ΔE_a) for EE + DETA system are calculated by using the relation of the form

$$\Delta Y = Y_m(X_1 Y_1 + X_2 Y_2) \quad (7)$$

where ΔY is the excess parameter and Y refers to the above mentioned quantities. The subscripts m , 1 and 2 used in the equation are respectively for the mixture, component 1 and component 2. X_1 and X_2 are the mole fractions of the two components in the liquid mixture.

RESULTS AND DISCUSSION

The values of density (ρ), viscosity (η), square of refraction index (n_D^2), dielectric constant (ϵ'), loss factor (ϵ''), loss tangent ($\tan \delta$), activation energy (E_a) and molar polarization (P_{12}) and apparent polarization (P_2) with increasing mole fraction (X) of DETA in the binary mixtures of EE + DETA are listed in Table-1.

The variation of the dielectric constant (ϵ') with mole fraction (X) of DETA in the mixture is depicted in Fig. 1. A minima is observed in the curve at $X = 0.35$, which indicates the formation of complex in the binary mixture of EE + DETA, as observed by Comb *et al.*¹³ for the alcohol + *o*-dichlorobenzene mixture Fig. 2 illustrates the variation of $\tan \delta$ with mole fraction X of DETA. A minima in the $\tan \delta$ curve occurs at $X = 0.35$ mole fraction of DETA in the mixtures. It is clear from the figure that the absorption in the mixture is less than that in the pure liquids. This may be explain by assuming Debye's¹⁴ equation for $\tan \delta$, for dilute solution of polar liquids. The Debye's equation suggests that the absorption in the mixture increases if the dipole moment (μ) and relaxation time (τ) increases. Assuming the approximate validity of the Debye's equation, the formation of complex may be leading to decrease in dipole moment (μ) and relaxation time (τ). When viscosity (η) is plotted against the mole fraction of DETA, the curve shows maxima (Fig. 3) at $X = 0.50$ mole fraction of DETA in the mixture. The increase in viscosity (η) may be due to the mutual viscosity of

the 2-ethoxy ethanol and amine molecules as provided by the Andrade's theory⁹.

TABLE-1
VALUES OF MOLE FRACTION (X) OF DETA, DENSITY (ρ), VISCOSITY (η), SQUARE REFRACTIVE INDEX (n_D^2), DIELECTRIC CONSTANT (ϵ'), DIELECTRIC LOSS (ϵ''), LOSS TANGENT ($\tan \delta$), ACTIVATION ENERGY (E_a), MOLAR POLARIZATION (P_{12}) FOR THE BINARY LIQUID SYSTEM AT 20°C

X	ρ	η (cp)	n_D^2	ϵ'	ϵ''	$\tan \delta$	E_a (kcal/mole)	P_{12}
0.000	0.926	1.985	1.985	9.477	3.524	0.388	3.753	77.844
0.090	0.932	3.771	2.002	8.664	2.772	0.335	4.135	70.339
0.182	0.983	4.744	2.031	7.761	2.422	0.312	4.272	68.244
0.276	0.944	5.841	2.051	7.935	2.262	0.300	4.396	69.289
0.372	0.946	6.576	2.073	7.941	2.219	0.294	4.467	70.096
0.471	0.946	6.811	2.091	7.957	2.275	0.301	4.488	71.069
0.571	0.947	7.146	2.111	8.151	2.530	0.326	4.516	72.575
0.657	0.947	6.833	2.131	8.387	2.729	0.341	4.490	74.231
0.780	0.948	6.772	2.152	8.637	2.933	0.356	4.484	75.969
0.889	0.948	6.632	2.172	8.764	3.046	0.364	4.472	77.330
1.000	0.950	6.530	2.184	9.319	3.503	0.393	4.463	79.758

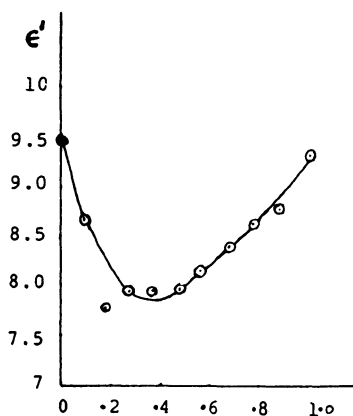


Fig. 1. Variation of ϵ' vs. X of DERA in the mixture

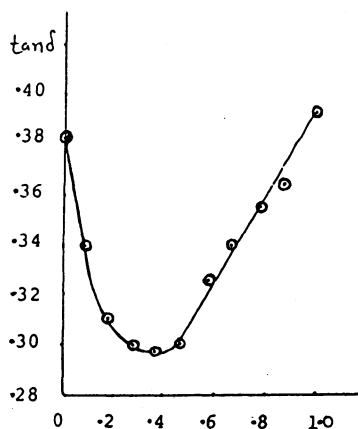


Fig. 2. Variation of $\tan \delta$ vs. X of DETA in the mixture

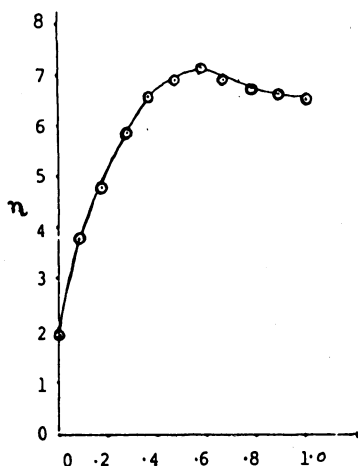


Fig. 3. Variation of η vs. X of DETA in the mixture

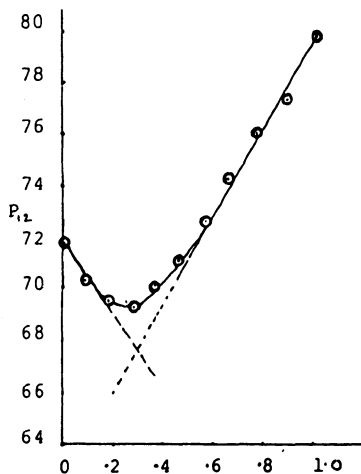


Fig. 4. Variation of P_{12} vs. X of DETA in the mixture

The values of molar polarization (P_{12}) as a function of mole fraction (X) of DETA in the mixture are depicted in (Fig. 4). The minima in the curve is caused by the presence of a complex and the amount of complex present is responsible for the shape of the polarization curve. The intersection of the straight lines represents two regions of high and low DETA concentration. The intersection point at $X = 0.35$ can be interpreted as the point of maximum concentration of complex which corresponds to 1 : 2 complex for the system. This result regarding the formation of complex is supported by our earlier conclusions made for (ϵ') vs. (X) curve (Fig. 1).

The values of apparent polarization (P_2) vs. mole fraction (X_{EE}) of 2-ethoxyethanol are depicted in Fig. 5. The flat portion of this curve indicates the formation complex in the mixture. The more flat portion indicates more stable complex¹³

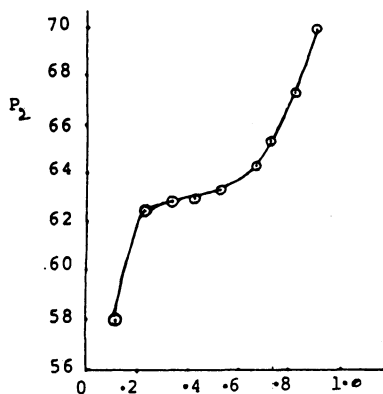


Fig. 5. Variation of P_2 vs. X of EE in the mixture

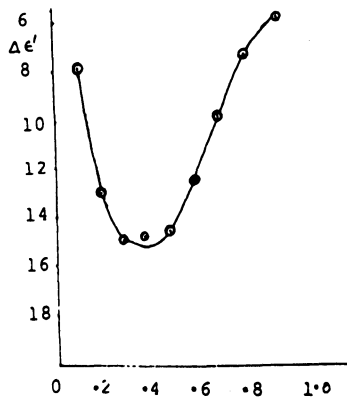


Fig. 6. Variation of $\Delta\epsilon'$ vs. X of DETA in the mixture

The excess values of permittivity ($\Delta\epsilon'$, $\Delta\epsilon''$), excess viscosity ($\Delta\eta$), excess square refractive index (Δn_D^2) and excess activation energy (ΔE_a) for EE + DETA system are presented in Figs. 6–10. The excess values were fitted through least squares by using Redlich-Kister¹⁵ equation (Figs. 6–10). To get better curve fitting, six coefficients in the expansion have been chosen. The values of coefficients A_j 's for $J + 0$ to 5 are presented in Table-2 along with the standard deviation (σ). Using A_j values, excess parameters calculated are used as guidelines to draw smooth curve in Figs. 6–10. The values of excess parameters show deviations only up to 4% from the experimental data were observed.

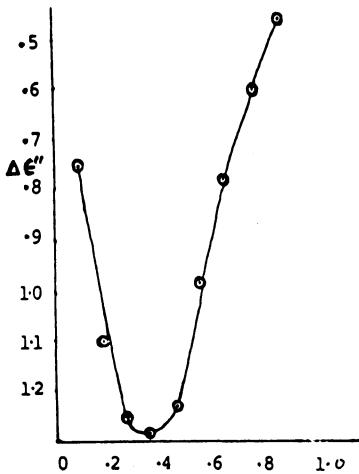


Fig. 7. Variation of $\Delta\epsilon''$ vs. X of DETA in the mixture

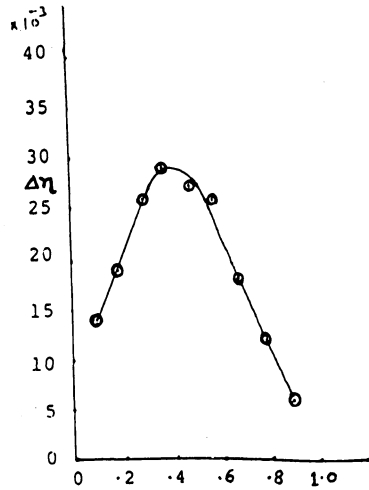


Fig. 8. Variation of $\Delta\eta$ vs. X of DETA in the mixture

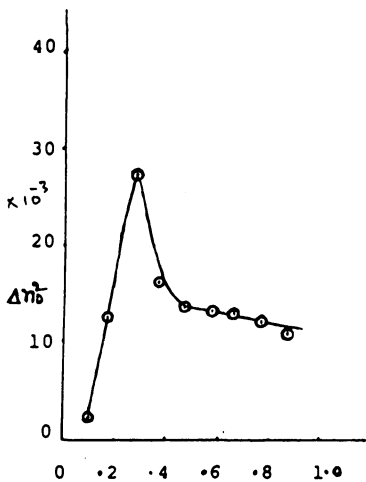


Fig. 9. Variation of Δn_D^2 vs. X of DETA in the mixture

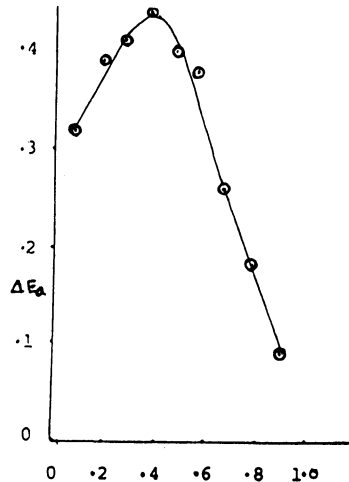


Fig. 10. Variation of ΔE_a vs. X of DETA in the mixture

TABLE-2
VALUES OF COEFFICIENT A_j 's AND STANDARD DEVIATION (σ) IN VARIOUS
EXCESS PARAMETERS FOR THE BINARY LIQUID SYSTEM AT 20°C

Physical parameter	A_0	A_1	A_2	A_3	A_4	A_5	σ
$\Delta\epsilon'$	-5.173	1.625	-6.880	19.800	3.280	28.813	0.378
$\Delta\epsilon''$	-5.879	3.763	0.066	-2.918	-5.586	1.531	0.288
$\Delta\eta$	0.111	-0.029	-0.067	-0.136	0.113	0.133	0.007
Δn_D^2	0.062	1.494	-0.256	-9.813	0.723	12.168	0.006
ΔE_a	1.617	-0.950	-0.091	0.284	0.539	-3.943	0.144

It is found that the excess dielectric constant ($\Delta\epsilon'$) and excess loss ($\Delta\epsilon''$) are negative. The minima in the $\Delta\epsilon'$ and $\Delta\epsilon''$ curves occur at $X = 0.35$ mole fraction of DETA at which the formation of complex on the basis of P_{12} curve were expected (Fig. 4). The excess dielectric permittivity is associated with the polarization and loss is regarded due to the molecular motions, which are governed by the complex forces of molecular interaction. Thus, the excess loss may be regarded as a parameter, which reflects the entropy change in a binary system. The excess viscosity ($\Delta\eta$), square refractive index (n_D^2) and activation energy (ΔE_a) are positive. This indicates the strong interactions between 2-ethoxy ethanol and amine molecules.

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