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Studies of Alcohol-Amine Complexation by Dielectric Measurements

REKHA PANDE and G.M. KALAMSE*
Department of Physics, Science College, Nanded-431 605 India
E-mail: nnd_princsn@sancharnet.in

Using Surber's technique of measuring reflection coefficient from the air-dielectric boundary of the liquid, the dielectric constant (ε'), dielectric loss (ε'') of trigol, ethylene diamine, and their binary mixtures for different mole fractions of ethylene diamine in the mixture have been measured at 9.84 GHz. Density, viscosity and square of refractive index of binary mixtures, including those of pure liquids are reported. The values of dielectric parameters (ε', ε'') have been used to evaluate the molar polarization (p_{12}) and the excess permittivities ($\Delta\varepsilon'$, $\Delta\varepsilon''$). Excess square refractive index, viscosity and activation energy of viscous flow have also been estimated. These parameters have been used to explain the nature of complex formation. The computed values of excess parameters have been fitted to the Ridlich-Kister relation to estimate binary coefficient and standard deviation.

Key Words: Trigol, Dielectric constant, Polarization excess parameters.

INTRODUCTION

The refractive index, viscosity, density, thermodynamic parameters and dielectric parameters of solutions containing interaction solutes, do not vary linearly. The deviation from linearity of these parameters is termed as excess parameters. Several workers[1–6] have studied the excess parameters in the liquid mixtures to explain the nature of bonding between the two liquids.

Trigol (TG) is a hygroscopic liquid. It is used as a solvent for resins, oils, and many organic compounds. It has been used in brake fluids and in antifreeze solutions. It is employed as a plasticiser and as a humectant for tobacco, cork, printing ink and glue. Because of its high bactericidal potency, trigol is an ideal chemical for aerial disinfection in sterile filling units. Thus, because of its wide applications in various fields, the present study may provide useful information regarding the molecular interactions and the formation of complex in the mixtures of trigol and ethylenediamine.

EXPERIMENTAL

Ethylene diamine and trigol, both AR grade, were procured from M/s. S.D. Fine Chemicals and were used without further purification. Samples of binary

mixtures with different mole fractions of ethylene diamine in the mixture were prepared and kept for 6 h in well-stoppered bottles to ensure good thermal equilibrium. The density (ρ), viscosity (η) of pure components and their mixtures were measured by using pyknomter and Oswald's viscometer, respectively. The refractive indices for sodium D-lines were measured by using Abbe's refractometer.

The dielectric constant measurements for the pure substances and their mixtures were carried out from the X-band microwave bench of oscillating frequency 9.84 GHz. Using Surber's technique[7] of measuring reflection coefficient from the air-dielectric boundary of the liquid, the dielectric constant (ε′), loss factor (ε″) of binary mixtures of trigol and performed accordingly as reported ethylene diamine at 22°C were calculated. The experimental set up and the procedure employed for the measurement of dielectric constant (ε′), refractive index, density, etc. is earlier[8].

RESULTS AND DISCUSSION

The values of density (ρ), viscosity (η), square of refractive index (n_D^2), dielectric constant (ε′), loss factor (ε″), loss tangent (tan δ), activation energy (E_a) and molar polarization (P_{12}) with increasing mole fraction (X) of ethylenediamine (EDA) in the binary mixtures of TG + EDA are listed in Table-1.

TABLE-1
VALUES OF MOLE FRACTION (X) OF EDA, DENSITY (ρ), VISCOSITY (η), SQUARE OF REFRACTIVE INDEX (n_D^2), DIELECTRIC CONSTANT (ε′), LOSS FACTOR (ε″), LOSS TANGENT (tan δ) ACTIVATION ENERGY (E_a) AND MOLAR POLARIZATION (P_{12}) FOR BINARY LIQUID SYSTEM OF TRIGOL + ETHYLENE DIAMINE AT 25°C

X	ρ	η (CP)	n_D^2	ε′	ε″	tan δ	E_a (kcal/mol)	P_{12}
0.0000	1.1196	23.990	2.1374	5.432	1.519	0.279	7.647	79.978
0.2214	1.1011	28.296	2.1462	5.212	1.289	0.247	7.745	69.071
0.3988	1.0800	28.878	2.1491	5.360	1.080	0.201	7.757	62.668
0.5443	1.0519	18.645	2.1521	5.878	1.212	0.206	7.498	59.537
0.6655	1.0250	10.323	2.1462	6.775	1.794	0.264	7.148	57.931
0.7681	0.9935	5.5530	2.1433	7.545	2.017	0.267	6.781	56.642
0.8567	0.9618	3.0030	2.1374	8.721	2.757	0.316	6.416	54.666
0.9331	0.9322	1.8780	2.1374	10.576	2.627	0.248	6.138	54.259
1.0000	0.8920	1.0820	2.1316	12.543	1.433	0.114	5.812	53.478

The variation of dielectric constant (ε′) with mole fraction (X) of EDA in the mixture is depicted in Fig. 1. A minima is observed in the curve at $X = 0.3$, which indicates the formation of complex in the binary system of TG + EDA as observed by Singh and Sharma[9] for ethylene diamine with ethyl methyl ketone and methyl isobutyl ketone. The absorption of microwave energy in the binary system of TG + EDA is depicted in Fig. 2. A minima at X = 0.4 and maxima at X = 0.8 mole fraction of EDA in the mixture obtained.

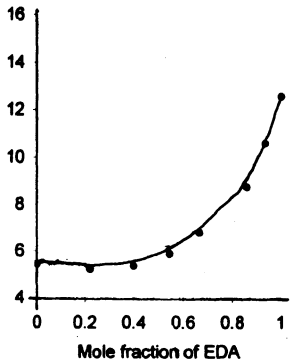


Fig. 1. Variation of dielectric constant *vs.* X of EDA

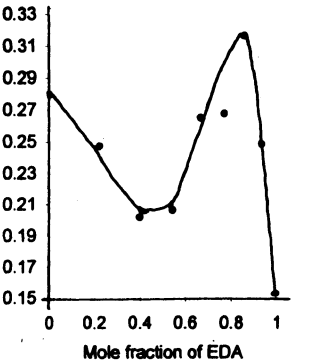


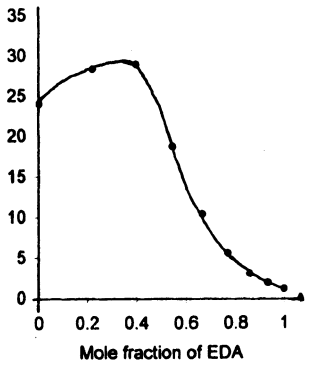
Fig. 2. Variation of loss tangent *vs.* X of EDA

According to Price[10], the dipole moment of the complex may be greater or less than that of the polar constituents. The overall decrease or increase of the dipole moment of the complex arises from geometry of the complex. In the complex the dipole moment can be taken as $(\mu_1 + \mu_2)$, where μ_1 and μ_2 are the dipole moments of the constituent molecules.

For n molecules of each liquid forming the complex, the absorption would be proportional to $n(\mu_1 + \mu_2)^2$. In present case, the minimum and maximum absorption of microwave energy indicates that the dipoles of the two polar liquids in the mixture align such that the overall dipole moment of the complex reduces at X = 0.4 and increases at X = 0.8 mole fraction of EDA in the mixture.

The variation of viscosity (η) with mole fraction (X) of EDA in the mixture is presented in Fig. 3. The viscosity curve shows a maxima at X = 0.4 mole fraction of EDA in the mixture. The increase in viscosity may be due to the mutual viscosity of the trigol and ethylene diamine molecules as provided by the Andrades theory[10]. To explain the maximum in the viscosity curve at X = 0.4 mole fraction of EDA, it seems reasonable to assume that the formation of associates composed of trigol and ethylene diamine in this composition range is held together by stronger intermolecular dipole-dipole interaction. Beyond the mole fraction 0.4 of EDA the value of viscosity decreases. This may be due to

the disruption of TG + EDA associates with the increase of EDA component in the mixture.



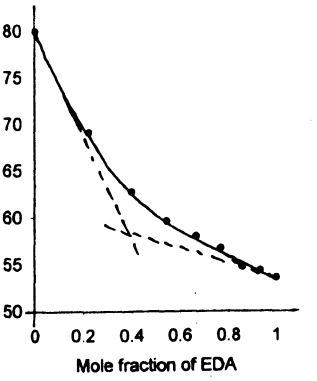


Fig. 3. Variation of viscosityt *vs.* X of EDA Fig. 4. Variation of $P_{1/2}$ *vs.* X of EDA

The values of molar polarization (P_{12}) with mole fraction (X) of EDA in the mixture are depicted in Fig. 4. The amount of complex present in the mixture is responsible for the shape of the polarization curve. The intersection of the straight lines represents two regions of high and low EDA concentration. The intersection point at X = 0.4 can be interpreted as the point of maximum concentration of complex.

The excess values of dielectric constant ($\Delta\varepsilon'$), loss factor ($\Delta\varepsilon''$), viscosity ($\Delta\eta$), square refractive index (Δn_D^2) and activation energy (ΔE_a) for TG + EDA system are presented in Table-2. The excess values were fitted through least squares by using Redlich-Kister equation[11]. The values of coefficient A_j's for j = 0 to 5 are presented in Table-3 along with the standard deviation (σ). It is found that the values of excess permittivity ($\Delta\varepsilon'$) are negative and the minima for $\Delta\varepsilon'$ occurs at X ≈ 0.5 mole fraction of EDA at which the formation of complex on the basis of P_{12} curve is expected (Fig. 4). The excess dielectric permittivity is associated with polarization and loss is regarded due to the molecular motions which are governed by the complex forces of molecular interaction. Thus, excess loss may be regarded as a parameter which reflects the entropy change in a binary system. In present case, the excess loss is negative in high region of EDA and it is positive in low region of EDA. The excess values of viscosity ($\Delta\eta$) are positive in the high region of EDA and negative in the low region of EDA. The excess values of square refractive index (Δn_D^2) and activation energy (ΔE_a) are positive, which indicates the strong interactions between trigol and ethylene diamine molecules.

TABLE-2
VALUES OF EXCESS PARAMETERS $\Delta\varepsilon'$, $\Delta\varepsilon''$, $\Delta\eta$, Δn_D^2 AND ΔE_a ALONG WITH MOLE FRACTION OF EDA AND TRIGOL (TG) IN THE BINARY SYSTEM.

X_1 for EDA	X_2 for trigol	$\Delta\varepsilon'$	$\Delta\varepsilon''$	$\Delta\eta$	Δn_D^2	ΔE_a
0.2274	0.7786	–1.7944	–0.2115	9.3773	0.0100	0.5040
0.3988	0.6012	–2.9076	–0.4044	14.024	0.0140	0.8417
0.5443	0.4557	–3.4244	–0.2606	7.1232	0.0178	0.8496
0.6655	0.3345	–3.3894	0.3326	1.5776	0.0126	0.7218
0.7681	0.2319	–3.3787	0.5641	–0.8409	0.0103	0.5429
0.8567	0.1433	–2.8024	1.3114	–1.3623	0.0050	0.3413
0.9331	0.0689	–1.5016	1.1848	–0.7373	0.0011	0.1881

TABLE-3
VALUES OF COEFFICIENTS A_j^s AND STANDARD DEVIATION (σ) IN VARIOUS EXCESS PARAMETERS FOR THE BINARY LIQUID SYSTEM AT 25°C.

Physical parameter	A_0	A_1	A_2	A_3	A_4	A_5	σ
$\Delta\varepsilon'$	–12.86270	–8.6334	0.0475	–6.2800	–24.6983	30.0643	0.5437
$\Delta\varepsilon''$	–1.17290	6.3508	2.2427	–1.5068	24.8983	–2.0758	0.4454
$\Delta\eta$	41.17620	–33.6028	–143.4320	–72.5630	293.9770	–62.9797	5.1990
Δn_D^2	0.07360	0.1341	–0.3259	–0.4785	0.8679	–0.1865	0.0066
ΔE_a	3.06500	0.3808	–2.6192	–2.0339	2.2301	2.2434	0.2062

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