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DIELECTRIC BEHAVIOUR OF ETHYLENE DIAMINE, 2–ETHOXY ETHANOL AND THEIR BINARY MIXTURES AT MICROWAVE FREQUENCIES

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ABSTRACT

Using Surber's technique of measuring reflection coefficient from air dielectric boundary of the liquid, the dielectric constant (ε'), dielectric loss (ε") of 2–ethoxy ethanol (EE), ethylene diamine (EDA) and their binary mixtures for different mole fractions of ethylene diamine in the mixture have been measured at 9.8 GHz frequency. The density (ρ), viscosity (η) and squared refractive index (n_D2) 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 values of dielectric constant (Δε'), loss factor (Δε"). The excess square of refractive index (Δn_D^2), viscosity (Δη), and activation energy (ΔEa) of viscous flow have also been estimated. The computed results have been fitted to the Redlich–Kister relation to estimate the binary coefficients and standard deviations (σ). The results suggest a strong interaction between 2–ethoxy ethanol and amine molecules.

Key words : Dielectric constant, Polarization, Excess parameters, 2–Ethoxy ethanol

INTRODUCTION

The viscosity, density, refractive index, thermodynamic parameters and dielectric parameter of solutions containing interacting solutes do not vary linearly. The deviation from linearity of these parameters is termed as excess parameters. In the field of dielectrics much work has been carried out, through different problems, even then more work is expected to continue on the dielectric study. Though the information in this field is being regularly enriched by large number of workers[1–6], the problem of binary mixtures becomes increasingly intricate where complex formation takes place. Alcohols have found numerous applications in pharmaceutical and other fields. 2–Ethoxy ethanol is a monohydric alcohol having one OH group attached to carbon atom in a carbon chain. 2–Ethoxy ethanol is used in the manufacture of lacquers and printing inks. Investigation on molecular complexes of phenol with ketones and aldehydes have been made by several workers.[7–8] Sarojani and Narasimha Murthy[9] studied the H–bonded complexes in certain amines and cresols by dielectric method. With this background information, the present investigation is aimed to study the dielectric behaviour of binary

mixtures of 2–ethoxy ethanol and ethylene diamine which may provide useful information regarding the molecular interactions and the formation of complexes in the mixture.

EXPERIMENTAL

Ethylene diamine (EDA) and 2–ethoxy ethanol (EE) (both A.R. Grade; S.D. Fine) were used without further purification. Samples of binary mixtures with different mole fractions of ethylene diamine in the mixture were prepared and kept for six hours in well-stoppered bottles to ensure good thermal equilibrium. The density (ρ) and viscosity (η) of pure components and their mixtures were measured by Pyknometer and Oswald's viscometer, respectively. The refractive indices for sodium D–lines were measured by 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[10] technique of measuring reflection coefficient from the air–dielectric boundary of the liquid. The dielectric parameters of binary mixtures of 2–ethoxy ethanol with ethylene diamine at 22°C were calculated. The experimental set up and the procedure employed for the measurement of dielectric constant (ε'), loss factor (ε") etc. is the same as earlier[11].

RESULTS AND DISCUSSION

The value of density (ρ), viscosity (η), square of refractive index (n^2_D), dielectric constant (ε'), dielectric loss (ε"), loss tangent (tan δ), activation energy (Ea)and molar polarization (P_{12}) with increasing mole fraction (X) of EDA in the binary mixtures of EE + EDA are presented in Table 1.

Table 1. Values of mole fraction (X) of EDA, density (ρ), viscosity (η), square of refractive index (n^2_D), dielectric constant (ε'), loss factor (ε"), loss tangent (tan δ), activation energy (E_a) and molar polarization (P_{12}) for binary liquid system of EDA + EE at 25°C

X	ρ	η(CP)	n^2_D	ε'	ε"	tan δ	E_a(kcal/ mole)	P_{12}
0.0000	0.9262	1.425	1.974	6.097	1.788	0.316	5.935	61.245
0.1710	0.9293	1.895	1.993	5.798	1.795	0.335	6.103	56.270
0.3249	0.9296	2.175	2.022	6.028	2.024	0.335	6.184	54.146
0.4642	0.9264	2.109	2.039	6.727	2.111	0.336	6.165	53.967
0.5908	0.9211	1.903	2.047	7.957	2.281	0.303	6.105	54.903
0.7065	0.9149	1.668	2.070	9.001	2.317	0.271	6.027	54.719
0.8125	0.9095	1.471	2.085	9.944	2.094	0.221	5.953	54.116
0.9099	0.9019	1.312	2.102	11.029	1.917	0.181	5.886	53.601
1.0000	0.8920	1.133	2.131	12.098	1.433	0.118	5.800	53.036

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 = 0.25, which indicates the formation of a complex in the binary mixture of EE + EDA as observed by Singh and Sharma[12] for ethyl methyl ketone + ethylene diamine and methyl isobutyl ketone + ethylene diamine.

The variation of tan δ versus mole fraction (X) of EDA in the mixture is depicted in Fig. 2. From the figure, it is clear that the absorption in the mixture at X = 0.35 mole fraction of EDA is maximum and greater than that in pure liquids. The Debye[12,13] equation for tan δ suggest that the absorption in the mixture increases, if the dipole moment of the complex increases. In the H–bonding of the complexes, a redistribution of electron density can occur due to electrostatic, polarization, and charge transfer interactions. In this case, the polarization effect may yield large change in the dipole moment, which is responsible for the increase in absorption.

Fig. 1 Variation of dielectric constant V/s X of EDA

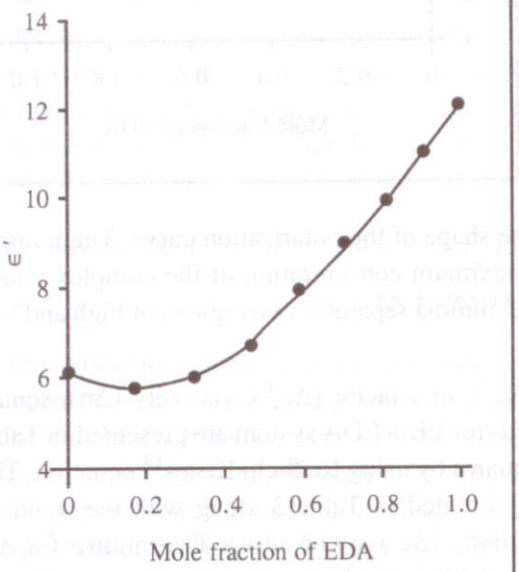
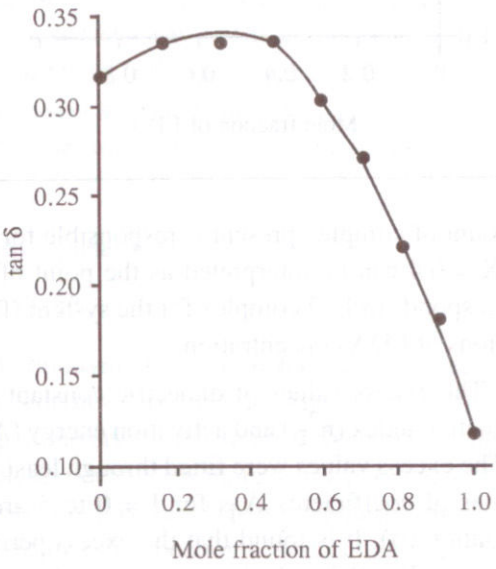


Fig. 2 Variation of loss tangent V/s X of EDA



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 = 0.35 mole fraction of EDA in the mixture. The increase in viscosity may be due to the mutual viscosity of the 2–ethoxy ethanol and ethylene diamine molecules as provided by the Andrades[13–15] theory.

The values of molar polarization (P_{12}) with mole fraction (X) of EDA in the mixture depicted in Fig. 4. The minima in the curve is caused by the presence of a complex and the

Fig. 3 Variation of viscosity V/s X of EDA

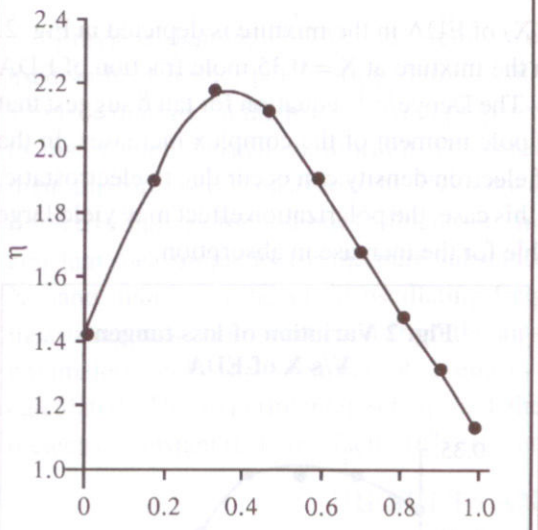
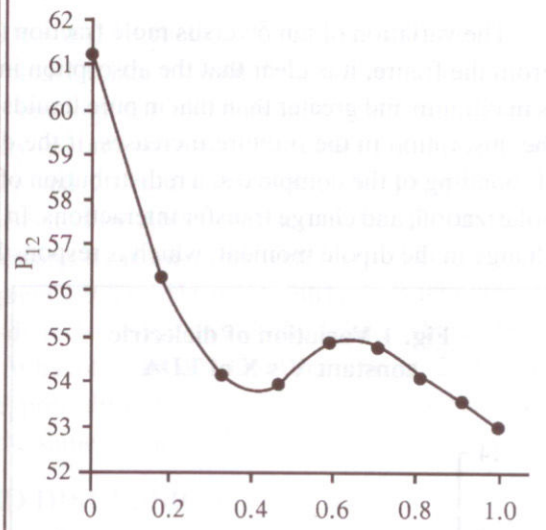


Fig. 4 Variation of molar polarigation V/s X of EDA



amount of complex present is responsible for the shape of the polarization curve. The minima at X = 0.4 can be interpreted as the point of maximum concentration of the complex which corresponds to 1 : 2 complex for the system. The minima separates two regions of high and low regions of EDA concentration.

The excess values of dielectric constant ($\Delta\epsilon'$), loss factor ($\Delta\epsilon''$), viscosity ($\Delta\eta$), square refractive index (n^2_D) and activation energy (ΔEa) for EE + EDA system are presented in Table 2. The excess values were fitted through least squares by using Redlich–Kister[14] equation. The values of coefficients $A'_j s$ for J = 0 to 5 are presented in Table 3 along with the standard deviation (σ). It is found that the excess permittivity ($\Delta\varepsilon'$) are negative. The minima for $\Delta\varepsilon'$ occurs at X = 0.33 which is close mole fraction of EDA at which we expect the formation of complex on the basis of P_{12} curve (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 the excess loss may be regarded as a parameter, which reflects the entropy change in a binary system. The excess values of loss factor ($\Delta\varepsilon''$), viscosity ($\Delta\eta$) activation energy (ΔEa) are positive and maxima occurs at X = 0.46 of EDA, which indicates a strong interaction between the molecules of EE + EDA. Similarly the excess square refractive index (n^2_D) are negative and a minima occurs at X = 0.46.

Table 2. Values of excess parameters $\Delta\varepsilon'$, $\Delta\varepsilon''$, $\Delta\eta$, Δn^2_D and ΔE_a along with mole fraction of EDA and EE in the binary system at 25°C

X_1 for EDA	X_2 for EE	$\Delta\varepsilon'$	$\Delta\varepsilon''$	$\Delta\eta$	$\Delta\eta_p 2$	ΔE_a
0.1710	0.8290	–1.3249	0.068	0.519	–0.007	0.191
0.3249	0.6751	–2.1579	0.357	0.844	–0.003	0.292
0.4642	0.5358	–2.1558	0.487	0.819	–0.007	0.293
0.5908	0.4092	–1.6851	0.702	0.650	–0.019	0.249
0.7065	0.2935	–1.3350	0.779	0.449	–0.014	0.188
0.8125	0.1875	–1.0289	0.594	0.283	–0.016	0.128
0.9099	0.0901	–0.5278	0.451	0.152	–0.014	0.074

Table 3. Values of coefficients A_js and standard deviation (σ) for the binary liquid system at 25°C

Physical parameter	A_0	A_1	A_2	A_3	A_4	A_5	σ
$\Delta\varepsilon'$	–7.9313	4.5215	–1.6798	–5.5736	4.0654	0.1639	0.5213
$\Delta\varepsilon''$	1.8772	6.0549	11.4661	–32.3680	–25.6919	55.3655	0.2364
$\Delta\eta$	3.1427	–2.5552	–0.6037	2.7123	–0.6296	0.0101	0.2412
Δn^2_D	–0.0512	–0.1136	0.1197	0.1517	–0.4471	–0.0072	0.0051
ΔE_a	1.1449	–0.6435	–0.1405	0.6167	0.0816	0.0045	0.0764

CONCLUSION

The molar polarization and excess dielectric parameters have been reported for EE + EDA binary systems containing different mole fraction of EDA. These studies suggest strong interactions between the alcohol and amine molecules and the molar polarization curve suggests formation 1 : 2 complexes in the mixtures of EE + EDA system.

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