DIELECTRIC BEHAVIOUR OF BINARY MIXTURES OF PROPANE DIOL WITH ETHYLENE DIAMINE

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ABSTRACT

Density, viscosity, refractive index, dielectric constant (ϵ') and dielectric loss (ϵ'') of propane diol, ethylene diamine and their mixtures for different mole fraction of ethylene diamine have been measured at 9.84 GHz and temperature 22°C. From the experimental data, molar polarization (P_{12}), apparent polarization (P_2) and the excess values of permittivities ($\Delta\epsilon'$, $\Delta\epsilon''$) square refractive index (n_D2), viscosity ($\Delta\eta$) and activation energy (ΔE_a) of viscous flow are estimated. These parameters have been used to explain the formation of complexes in the system.

Key words : Dielectric constant, Polarization, Excess parameters, Propane diol,

INTRODUCTION

Attempts have been made by several workers[1–7] to study the dielectric properties of binary mixtures of liquids. The study of dielectric behaviour of binary mixtures of polar molecules under varying conditions of compositions has evoked considerable interest. Much work[1–7] has been carried out in this field through different problems, even then more work is expected to continue on the dielectric study. Propane diol (PD) is classified as a dihydric alcohol and the presence of two OH groups gives rise to extensive H–bonding. Propane diol (PD) is used as a solvent in the extraction of crude drugs and in the preparation of solution of alkaloids, volatile oils, steroids and dyes. It is a useful vehicle for antihistamines, some vitamins and paracetomol. It is also used as a humectant and solvent for flavorings in the food industries. Thus because of its large applications in various fields, it is hoped that the study of dielectric behaviour of PD + EDA (Ethylene diamine) binary mixture may provide useful information.

EXPERIMENTAL

The dielectric constant (ϵ') and loss factor (ϵ'') were measured by using Serber's[8] technique of measuring the reflection co–efficient from the air dielectric boundary of the liquid in the microwave X–band at 9.84 GHz frequency. In this technique, the heart of the measurement centers around the dual three arm directional couplers, which are placed back to back. Since there is a direct relationship between the VSWR and the reflection co–efficient of a wave–guide, by measuring the ratio of relative amplitudes of reflected and incident reflection co–efficients, VSWR can be measured. This method of measuring VSWR is superior to slot line

measurements because it measures the ratio of the two dissimilar magnitudes of voltages while latter measures the ratio of nearly equal magnitudes. Further the slot line measuring system is insensitive to power fluctuations and slot errors. In this method the attenuation per wavelength $(\alpha_d\lambda_d)$ is found by computing variation in the reflected power when the length of the sample is varied by moving a short plunger through a dielectric filled in the cell. The experimental set up and procedure employed for the present investigation is the same as used by Singh and Sharma[9].

Ethylene diamine (EDA) and Propane diol (PD) (both A.R. grade) were procured from M/s. S.D. fine chemicals and used without further purification. The two liquids, according to their proportions by volume were mixed well and kept to ensure good thermal equilibrium. The density (ρ), viscosity (η) of pure components and their mixtures were measured by Pyknometer and Oswalds Viscometer, respectively. Refractive indices for sodium D–lines were measured by Abbe's refractometer.

Dielectric parameters

Serber[8] has derived the following relations for the dielectric parameters $\in'$, $\in''$, D, and $\alpha_d\lambda_d$.

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

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

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

where, $\lambda_0 = c/f$ is free space wavelength, $\lambda_c = 2a$ is the cut–off wavelength for the wave guide, $\alpha_d\lambda_d$ is the attenuation per wavelength, λ_d is the wavelength of e.m. waves in the wave guide filled with dielectric and D is the dissipation factor. According to Serber[8], attenuation per wavelength is given by

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

where, $\qquad k_1 = \frac{(1 - M_nY^2)}{Y(M_n - 1)}, \; k_2 = \frac{(M_n - 1)(1 - M_nY^4)}{(1 - M_nY^2)^2}, \; Y = \frac{\left(1 - \dfrac{\lambda_d}{\lambda_g}\right)}{\left(1 + \dfrac{\lambda_d}{\lambda_g}\right)},$

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

$n = 1,2,3.....$ $|\Gamma_n|$ is the reflection co–efficient by the liquid column of length $L = n\left(\dfrac{\lambda_d}{2}\right)$ and Γ_∞ is the reflection co–efficient for the liquid column of infinite length. I_n and I represent the corresponding current values. Thus measuring λ_0, λ_g, λ_c, λ_d and $\alpha_d\lambda_d$ the values of dielectric constant ($\in'$), loss factor ($\in''$) can be calculated by using equations (1) – (3).

The value of molar polarization of the mixtures were obtained by using the relation[9–11]

$$P_{12} = \left[\frac{(\in' - 1)}{(\in' + 2)}\right]\left[\frac{x_1M_1 + x_2M_2}{d}\right] = x_1P_1 + x_2P_2 \qquad ...(5)$$

where, M_1 and M_2 are the molecular weights, x_1 and x_2 are the molar concentrations of the 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 free energy of activation (E_a) of the viscous flow for the pure liquids and their mixtures obtained by using the following equations[9–12]

$$\eta = \left(\frac{hN}{V}\right)\exp\left(\frac{E_a}{RT}\right) \qquad ...(6)$$

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

The excess values of permittivity $\Delta\in'$ and $\Delta\in''$, excess viscosity ($\Delta\eta$) excess square refractive index (n^2_D) and the excess activation energy (ΔE_a) for PD + EDA system are calculated using the relation of the form[4,9]

$$\Delta Y = Y_m (x_1y_1 + x_2y_2) \qquad ...(7)$$

where, ΔY is the excess parameters 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 and x_1 and x_2 are the mole fraction of the two components in the liquid mixture.

RESULTS AND DISCUSSION

The values of density (ρ), viscosity (η), square refractive index (n^2_D), dielectric constant ($\in'$), loss factor ($\in''$), loss tangent (tan δ), activation energy (E_a) and molar polarization (P_{12}) with increasing mole fraction (x) of EDA in the binary mixtures of (PD + EDA) are listed in Table–1.

The variation of dielectric constant ($\in'$) with mole fraction (x) of EDA in the mixture is depicted in Fig. 1. A minima is observed in the curve at x = 0.27, which indicates the formation of complex in the binary system (PD + EDA) as observed by Singh and Sharma[9] for ethylene diamine with ethyl methyl ketone and methyl isobutyl ketone.

The variation of tan δ versus mole fraction (x) of EDA in the mixture is depicted in Fig. 2. The binary system PD + EDA exhibit two peaks of absorption.

Table 1. Values of mole fraction (x) of EDA, density (ρ), viscosity (η), square of refractive index (n²_D), dielectric constant (∈'), loss factor (∈''), loss tangent (tan δ), activation energy (E_a) and molar polarization (P₁₂) for binary liquid system of (EDA + PD) at 25°C

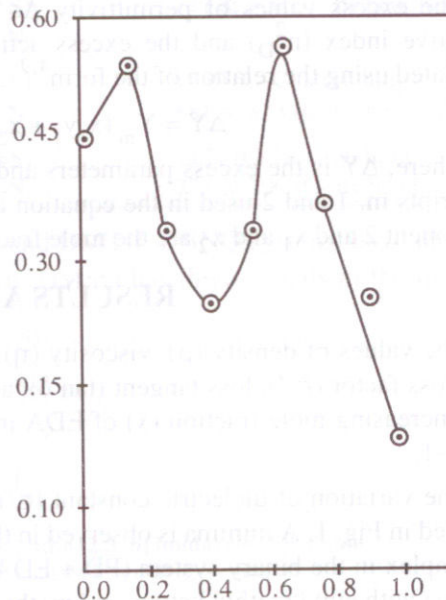| x	ρ	η (CP)	n^2_D	$\in'$	$\in''$	tan δ	E_a Kcal/mole	P12
0.000	1.036	24.270	2.059	5.284	2.306	0.452	7.653	43.258
0.134	1.026	27.786	2.079	5.045	2.467	0.506	7.734	41.361
0.266	1.016	28.448	2.099	5.045	1.637	0.345	7.748	40.592
0.395	1.003	22.486	2.114	5.111	1.194	0.251	7.609	40.196
0.521	0.985	13.397	2.125	5.400	1.714	0.336	7.302	40.882
0.645	0.964	6.656	2.131	6.222	3.211	0.518	6.888	43.300
0.766	0.942	3.275	2.134	7.536	2.726	0.371	6.468	46.417
0.884	0.919	1.828	2.131	10.550	2.764	0.268	6.122	51.283
1.000	0.892	1.082	2.131	12.530	1.588	0.130	5.812	53.468

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 = 0.27 mole fraction of EDA in the mixture. The increase in viscosity may be due to the mutual viscosity of the propane diol (PD) and ethylene diamine (EDA) molecules as provided by the Andrades theory[9].
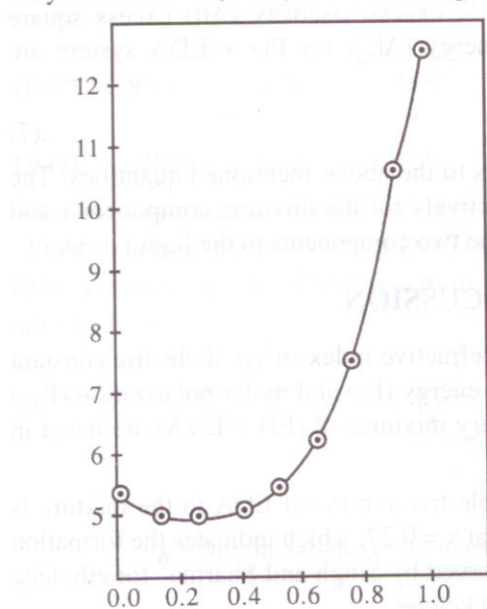
Variation of ∈' versus x of EDA in the mixture

Fig. 1
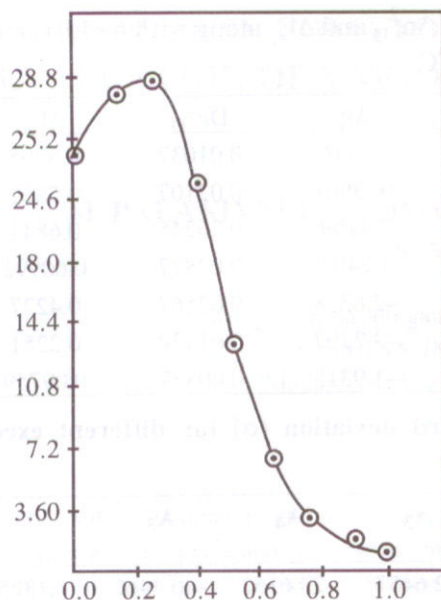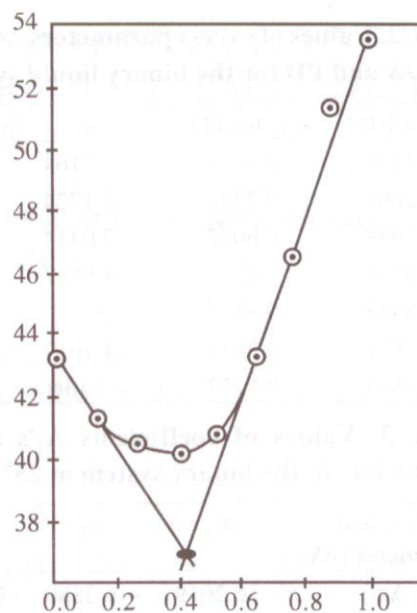
Variation of tan δ versus x of EDA in the mixture

Fig. 2

Variation of η versus x of EDA in the mixture

Fig. 3

Variation of P_{12} versus x of EDA in the mixture

Fig. 4

The values of molar polarization (P_{12}) with mole fraction (x) of EDA 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 the 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 ($\Delta\in'$), loss factor ($\Delta\in''$), viscosity ($\Delta\eta$), square refractive index (Δn^2_D) and activation energy (ΔE_a) for PD + EDA system are presented in Table 2. The excess values were fitted through least squares by Redlich–Kister equation. The values of co–efficient Aj's, for J = 0 to 5 are presented in Table 3 along with the standard deviation (σ). It is found that the excess permitivities ($\Delta\in'$) are negative. The minima for $\Delta\in'$ occurs at x = 0.4 mole fraction of EDA, where one expects the formation of complex on the basis of P_{12} curve (Fig. 4). The excess dielectric permitivity 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 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^2_D) and activation energy (ΔE_a) are positive. This includes strong interactions between propane diol (PD) and ethylene diamine (EDA) molecules.

Table 2. Values of excess parameters $\Delta\epsilon$ ',$\Delta\epsilon$ ", $\Delta\eta$, Δn^2_D and ΔE_a along with mole fraction of EDA and PD for the binary liquid system at $25^\circ C$

x_1 for EDA	x_2 for PD	$\Delta\epsilon'$	$\Delta\epsilon''$	$\Delta\eta$	Dn^2_D	ΔE_a
0.1349	0.8651	−1.2164	0.25788	6.6816	0.01037	0.3295
0.2668	0.7332	−2.1724	−0.47723	10.3961	0.02107	0.5862
0.3958	0.6042	−3.0414	−0.82800	7.4199	0.26245	0.6844
0.5219	0.4781	−3.6667	−0.216626	1.2497	0.02877	0.60992
0.6453	0.3547	−3.739	1.368266	−2.6358	0.02567	0.4227
0.7661	0.2339	−3.3017	0.969829	−3.2207	0.01470	0.2251
0.8843	0.1157	−1.136	1.09311	−1.9315	0.00837	0.09759

Table 3. Values of coefficients A_j's and standard deviation (σ) for different excess parameters of the binary system at $25^\circ C$

Physical parameter (ΔY)	A_0	A_1	A_2	A_3	A_4	A_5	α
$\Delta\epsilon'$	−16.2019	−16.3869	23.4838	52.6457	−28.6352	−46.4460	1.1325
$\Delta\epsilon''$	−1.8438	9.8496	26.7763	6.6337	−22.6773	−26.8625	0.7710
$\Delta\eta$	15.3434	78.0321	−27.4016	−13.739	64.4367	107.0288	4.9736
Δn^2_D	0.1875	−0.0278	−0.9846	0.2465	1.4589	−0.4376	0.0156
ΔE_a	3.1856	1.482	−11.0552	−22.6177	15.9660	31.1053	0.0652

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