



Dielectric Study of *Iso*-Butyl Alcohol, Ethylenediamine and their Binary Mixtures at Microwave Frequency.

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ABSTRACT: values of dielectric constant (ϵ'), dielectric loss (ϵ'') of *iso*-butyl alcohol (IBA), ethylenediamine (EDA) and their binary mixtures for different mole fractions of ethylenediamine have been experimentally determined at 9.85 GHz microwave frequency. The values of viscosity (η), density (ρ), square of refractive index (n_D^2) and activation energy (E_a) for viscous flow are also estimated and used to calculate the values of excess viscosity ($\Delta\eta$), excess square refractive index (Δn_D^2) and excess activation energy (ΔE_a). These parameters have been used to explain the formation of complexes in the system.

Keywords: Binary mixture, dielectric parameters, complex formation.

Experimental Details:

Pure samples of *Iso-butyl alcohol* (IBA) and ethylenediamine (EDA) were procured from M/s SD Fine Chemicals, AR Grade and used without further purification. The two liquids were mixed in the required proportions by volume and kept in well-stoppered bottles to ensure good thermal equilibrium.

The viscosities and densities of the pure liquids and their mixtures were measured by using Oswald's Viscometer and Pycnometer respectively. The refractive indices at the sodium-D lines were measured by using Abbe's refractometer. The dielectric constant (ϵ') and dielectric loss (ϵ'') were measured by using Surber's technique⁶ at 9.85 GHz microwave frequency and temperature 29⁰C measured by means of a crystal pickup in the directional coupler. The plunger position (X) and the corresponding reflected output power gives sinusoidal damped waves. The distance between two adjacent minima or maxima of this curve gives wavelength (λ_d) of radiation in the dielectric.


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The experimental set up and the procedure employed for the measurement of the dielectric constant (ϵ') and dielectric loss ϵ'' , were same as reported by Singh and Sharma¹³

Surber⁶ has derived the following relations for the dielectric parameters

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

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

where α_d is the attenuation constant due to dielectric, λ_d is the wavelength of the electromagnetic wave in the wave guide filled with dielectric, λ_c is the cut off wavelength for the wave guide, λ_o is the free space wavelength and $\alpha_d \lambda_d$ is the attenuation per wavelength and D is the dissipation factor. Having determined $\alpha_d \lambda_d$, λ_o , λ_c and λ_d the values of (ϵ') and (ϵ'') may be calculated by using the (1) and (2).

The free energy of activation (E_a) of the viscous flow for pure liquids and their mixtures is obtained by using the relation.¹²

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

The values of polarization of the mixtures were obtained using the formula^{7,9}

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

where M_1 and M_2 are the molecular weights, X_1 and X_2 the molar concentrations of the constituents of the mixture and d the density of the mixture.

Result and Discussion:

The values of viscosity (η), square refractive index (n_D^2), dielectric constant (ϵ'), loss factor (ϵ''), loss tangent ($\tan\delta$), activation energy (E_a) and molar polarization (P_{12}) with increasing mole fraction (X) of *EDA* for the binary mixture of *IBA+EDA* are listed in table.1



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From fig. 1 the values of dielectric constant increases with increase of mole fraction of EDA in the mixture. The graph is non linear and deviation from linearity of this curve indicates complex formation in the mixtures suggested by P. Job⁹. The deviation is maximum at about equimolar ratio of two compounds, hence formation of 1:1 complex in the mixture.

Fig. 2 shows variation of viscosity (η) as a function of mole fraction of EDA in the mixture of IBA+EDA. According to Andrade theory¹² the increase in the viscosity of the mixture is due to collision between two types of molecules in the mixture. In the present case, the solute-solute interaction in the mixture is found around 0.4 mole fraction of EDA. Beyond 0.4 mole fraction of EDA, the viscosity follow reverse trend because of disruption of association in the mixture.

Fig.3 shows variation of $\tan \delta$ versus mole fraction of EDA. Graph indicates that absorption in the mixture is greater than pure liquids. The existence of maxima in $\tan \delta$ curve is at 0.58 mole fraction of EDA, suggesting the large absorption at this concentration. An interaction between IBA and EDA may be responsible for such type of $\tan \delta$ curve. Earlier Degaonkar et al.¹⁰ and Purohit¹¹ observed such marked change in $\tan \delta$ curve.

Excess parameters of a binary mixture are the measure of deviation from ideal behavior of the mixture and found to be highly sensitive towards molecular interaction in the liquid mixture. The values of excess permittivity (ϵ' and ϵ''), excess viscosity ($\Delta\eta$), excess refractive index (Δn_D^2) and excess activation energy (ΔE_a) are shown in table 2. calculated using relation¹³

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

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

All five excess parameters shows deviation in the binary mixture from linearity, indicating interaction between IBA and EDA molecules and complex formation is found to be at equimolar ratio of mole fraction of EDA.



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Conclusion:

The values of dielectric constant (ϵ'), loss tangent ($\tan\delta$), molar polarization (P_{12}) and excess parameters have been reported for *IBA+EDA* binary mixture at various concentration of *EDA*.

$\tan\delta$ curve suggest that the absorption in the mixture is greater than pure compounds.

The non-linear behavior of dielectric constant versus mole fraction of *EDA* suggests formation of complex in the mixture. The increase in the viscosity may be due to the mutual viscosity of the mixture as suggested by Andrade. The deviation from ideal behavior of excess parameters in the mixture indicates solute-solute molecular interaction through hydrogen bonding.

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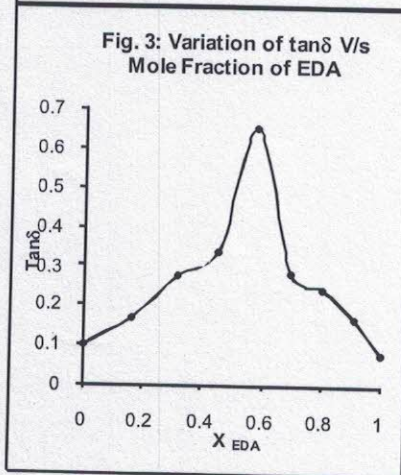
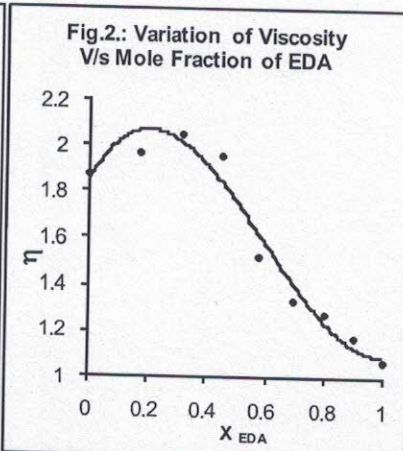
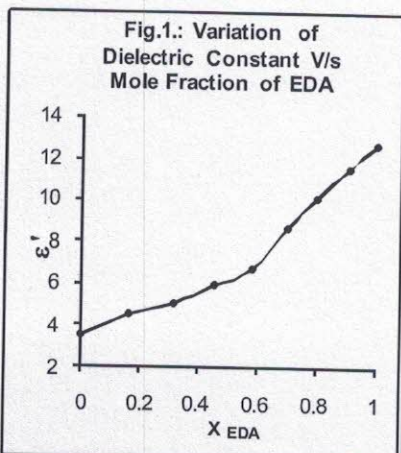


Table:1

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 ($\tan \delta$), activation energy (E_a) and molar polarization (P_{12}) for binary liquid system of (EDA + IBA) at 29°C.

X	ρ	η (cp)	n_D^2	ϵ'	ϵ''	$\tan \delta$	E_a Kcal/mol e	P_{12}
0.0000	0.7844	1.8830	1.9628	3.5682	0.3488	0.0977	3.4600	43.037
0.1647	0.8116	1.9743	1.9940	4.5505	0.7667	0.1685	3.4886	46.712
0.3152	0.8274	2.0589	2.0221	5.0879	1.4140	0.2779	3.5138	48.586



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0.4531	0.8401	1.9587	2.0477	5.9932	2.0014	0.3339	3.4838	50.390
0.5784	0.8503	1.5340	2.0678	6.7582	4.4231	0.6545	3.3371	51.040
0.6958	0.8608	1.3476	2.0851	8.7145	2.4586	0.2821	3.2682	53.837
0.8045	0.8702	1.2806	2.1025	10.0959	2.4386	0.2411	3.2287	54.304
0.9057	0.8764	1.1736	2.1170	11.5559	1.9391	0.1678	3.1763	54.510
1.0000	0.8894	1.0796	2.1316	12.6020	1.0070	0.0799	3.1263	53.690

Table – 2

Values of excess parameters $\Delta\epsilon'$, $\Delta\epsilon''$, $\Delta\eta$, Δn_D^2 and ΔE_a along with mole fraction (X) of EDA for the binary liquid system of IBA+EDA at 29°C.

X	$\Delta\epsilon'$	$\Delta\epsilon''$	$\Delta\eta$	Δn_D^2	ΔE_a
0.1647	-0.4968	0.1665	0.2238	0.00314	0.0832
0.3152	-1.3109	0.5877	0.4293	0.00607	0.1587
0.4531	-1.6441	0.9609	0.4398	0.00847	0.1748
0.5784	-2.0043	3.1913	0.1158	0.00741	0.0699
0.6958	-1.1024	1.0476	0.0444	0.00488	0.0403
0.8045	-0.6972	0.8568	0.0439	0.00390	0.03716
0.9057	-0.1459	0.2077	0.0183	0.00134	0.01860


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