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

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ASTRACT: values of dielectric constant (ϵ'), dielectric loss (ϵ'') of n-butyl alcohol (nBA), 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

INTRODUCTION:

The study of dielectric behavior of binary mixtures of polar molecules under varying conditions of composition has evoked considerable interest. Because when the binary mixture is formed, the viscosity, density, refractive index and dielectric parameters do not vary linearly. The deviation of these parameters from linearity is called excess parameters. The excess parameters are more sensitive towards inter molecular interactions in the liquid mixtures and gives valuable information about dipole – dipole interaction in the liquid mixture and molecular motions. Das and Hazra[1] have studied the excess properties of binary mixtures of $N-N$ dimethylacetamide with 2-ethoxyethenol and explained in terms of the interaction between unlike molecules in the mixture. Anwar Ali et al.,[2] has studied the excess molar volume, excess viscosity and excess activation energy of $N-N$ dimethylacetamide with 1-hexanol and 1-heptanol and explained the nature of extent of interactions between the component molecules in the binary mixtures. Though the information in this field is steadily being enlarged by a number of workers[1–5] the nature of complex formation in binary mixtures is still far from clear. With this in view, the present investigation is aimed at studying the dielectric behavior of binary mixtures of *n* butyl alcohol (nBA) and ethylenediamine (EDA) which may provide useful information about the formation of complex in the mixtures

EXPERIMENTAL DETAILS:

Pure samples of *n*-butyl alcohol (nBA) 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 Pycknometer 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 technique[6] at 9.85 GHz microwave frequency and temperature 29°C.

The liquids for which dielectric properties were to be determined were taken in dielectric cells. A thin mica window, whose VSWR and attenuation were assumed to be negligible, was introduced between the cell and the rest of the microwave bench. The movable short plunger of the liquid cell was moved in and out, and the corresponding reflection coefficient $|\Gamma|$ was 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.

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 Sharma[4]

Surber[6] 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 (Ea) of the viscous flow for pure liquids and their mixtures is obtained by using the relation.7,8

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

The values of polarization of the mixtures were obtained using the formula7,9

$$P_{12} = \left[\frac{(\epsilon'-1)}{(\epsilon'+2)}\right]\left[\frac{X_1M_1 + X_2M_2}{d}\right]$$

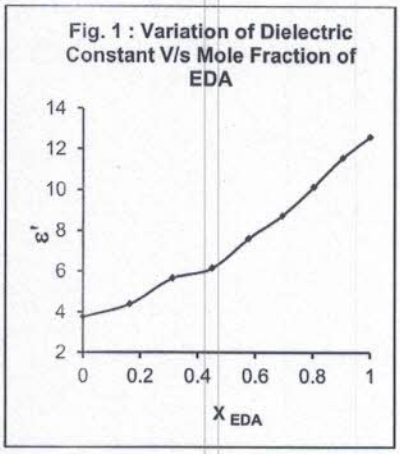
where M_1 and M_2 are the molecular weights, X_1 and X_2 the molar concentrations of the constituents of the mixture and d the density of the mixture.

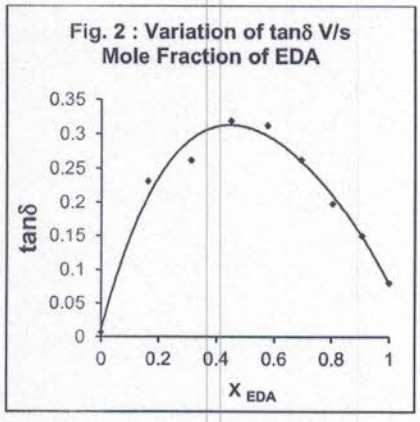
RESULT AND DISCUSSION:

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 *nBA+EDA* are listed in table.1

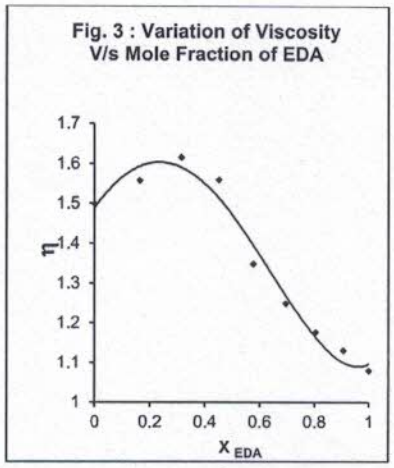
The graph of dielectric constant (ϵ') versus mole fraction (X) of *EDA* in the mixture shows deviation from linearity, indicating the complex formation in the mixture as suggested by P. Job[7]. The deviation is maximum at about 0.52 mole fraction of *EDA* , hence formation of 1:1 complex in the mixture.

The graph of $\tan\delta$ versus mole fraction (X) of *EDA* indicates that the microwave energy absorption is maximum in the mixture than in the pure liquids. The existence of prominent maximum in the $\tan\delta$ curve is nearly at the equimolar ratio of the interacting solutes. An interaction causing association between two types of molecules may be responsible for non linear behaviour[8].





The viscosity curve indicates that the solute-solute interaction between *nBA* and *EDA* increases to maximum value around 0.50 mole fraction of *EDA*. Therefore, it seems reasonable to assume that the formation of associates composed in this composition range is held together by comparatively stronger intermolecular dipole-dipole interactions. It is assumed that dipole – dipole association arising from the fractional negative charge on nitrogen of amine molecules and fractional positive charge on hydrogen of alcohol molecule. Also the increase in the viscosity (η) may be attributed to mutual viscosity of alcohol amine molecules as provided by Andrade's theory.[9,10] Beyond the mole fraction 0.50 of *EDA*, the viscosity follow reverse trend. Here we may expect the disruption of nBA+EDA association with further increase in EDA component in the mixture.



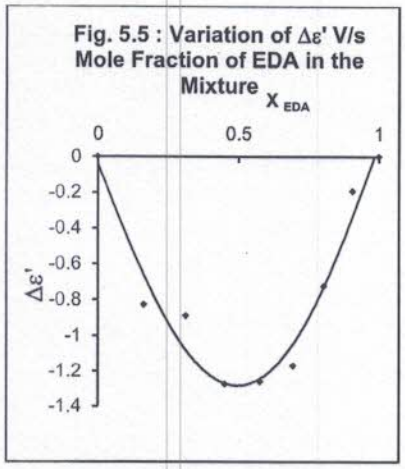
The excess parameters of a binary liquid system is a measure of the deviation from ideal behaviour of the mixture and are found to be highly sensitive towards the molecular interactions in the liquid mixture.

The values of excess permittivities ($\Delta\in'$, $\Delta\in''$), excess viscosity ($\Delta\eta$), excess square of refractive index (Δn_D^2)and excess activation energy (ΔE_a) are shown in table 2 and have been calculated using relation [1,4].

$$\Delta Y = Y_m - (X_1 Y_1) + (X_2 Y_2) \qquad (4)$$

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 mixtures.

It is found that the graph of excess permittivity ($\Delta\in'$) versus mole fraction (X) of *EDA* shows negative deviation over entire range of mole fraction of *EDA* indicating solute-solute interaction such that total effective dipoles get reduced. In general, the negative excess permittivity indicates the formation of multimers in the binary mixture [11,12].



The excess activation energy ΔEa and excess square refractive index Δn_D^2 are positive, indicating the strong interactions between alcohol and amine molecules. For all these excess parameters, the maxima for the nBA + EDA mixture occur at about 0.5 mole fraction of EDA.

CONCLUSION:

Values of dielectric parameters, viscosity, activation energy and excess activation energy, and squares of refractive indices have been reported for different mole fractions of EDA in the binary mixture of nPA + EDA. These studies suggest the strong interactions between *n*-butyl alcohol and ethylenediamine molecules. Dielectric constant and viscosity curves suggest formation of a 1 : 1 complex in the binary mixture.

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

X	ρ	η (cp)	n_D^2	$\in'$	$\in''$	$\tan\delta$	E_a Kcal/mole	P_{12}
0.0000	0.8016	1.4982	1.9712	3.769	0.0229	0.0061	3.3226	44.30
0.1635	0.8187	1.5578	1.9994	4.384	1.0189	0.2306	3.3466	46.507
0.3132	0.8320	1.6151	2.0249	5.645	1.4782	0.2618	3.3680	48.610
0.4508	0.8427	1.5588	2.0477	6.476	2.0606	0.3183	3.3468	51.978
0.5777	0.8521	1.3484	2.0678	7.610	2.3738	0.3119	3.2597	53.292
0.6952	0.8613	1.2488	2.0851	8.739	2.2914	0.2621	3.2136	53.860
0.8041	0.8718	1.1759	2.1025	10.146	2.0080	0.1978	3.1775	54.280
0.9055	0.8806	1.1305	2.1170	11.573	1.7305	0.1495	3.1539	54.330
1.0000	0.8894	1.0796	2.1316	12.602	1.0070	0.0799	3.1263	53.690

Table :2

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

X	$\Delta\in'$	$\Delta\in''$	$\Delta\eta$	Δn_D^2	ΔE_a
0.1635	-0.8290	0.8270	0.1280	0.00196	0.0559
0.3132	-0.8898	1.1470	0.2480	0.00348	0.1069
0.4508	-1.2750	1.5990	0.2493	0.00424	0.1127
0.5777	-1.2619	1.7823	0.0920	0.00397	0.0505
0.6952	-1.1705	1.5843	0.0416	0.00242	0.0275
0.8041	-0.7254	1.1941	0.0143	0.00232	0.0127
0.9055	-0.1936	0.8165	0.0113	0.00581	0.0090