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Dielectric Study of Binary Liquid Mixtures of 1,2 di-amino-propane (1,2-Dap) With Methanol At 9.85 Ghz Microwave Frequency

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ABSTRACT

Using Surber's technique of measuring reflection coefficient from the air-dielectric boundary of liquid the dielectric constant (ε′), dielectric loss(ε″) of 1,2-Diaminopropane (1,2-DAP) with methanol and their binary mixtures for different mole fractions of 1,2-Diaminopropane (1,2-DAP) have been measured at 9.85 GHz microwave frequency at 30 ^{0}C.The values of density (ρ), viscosity (η), Square refractive index (n_D^2) of pure liquids as well as those of binary mixtures are reported. The observed data have been utilized to calculate various parameters such as the molar polarization (P_{12}), loss tangent (tanδ), activation energy (E_a). The excess Square of refractive index (Δn_D^2), viscosity ($\Delta\eta$), and activation energy (ΔE_a) of the viscous flow have been estimated.These parameters have been used to explain the formation of complexes in the system. The results were discussed in terms of the existence of intermolecular interactions between the components in the liquid mixtures.

Keywords: 1,2-Diaminopropane (1,2-DAP), methanol, binary mixture, excess parameters.

INTRODUCTION

Dielectric studies of the binary mixtures of both polar and polar-non polar are important for understanding the intermolecular and intra molecular interactions due to the dipole interactions and hydrogen bonding. The dielectric investigations of binary polar liquid mixtures provide valuable information regarding intermolecular interactions and the consequent structural rearrangement of molecules in solution. The heterogeneous and homogeneous interactions in binary mixtures using dielectric measurements have been studied and reported by several investigators. The refractive index measurements in combination with density and other analytical data have wide application in chemical analysis and industry. Measurement of relative permittivity has been shown to be a useful technique in characterizing the molecular structure, solute – solute and solute - solvent interactions in solutions. [1,5]. 1,2-Diaminopropane (1,2-propanediamine) is organic compound with the formula $CH_3CH(NH_2)CH_2NH_2$. It is the simplest chiral diamine commonly used as a bidentate ligand in coordination chemistry. 1,2-Diaminopropane can be converted to *N,N'*-disalicylidene-1,2-propanediamine, a useful salen-type ligand that is abbreviated salpn. Salpn is used as a fuel additive as a metal deactivator in motor oils. Trace metals degrade the fuels by catalyzing oxidation processes that lead to gums and solids. Metal deactivators like salpn form stable complexes with the metals, suppressing their catalytic activity [2]. Methanol is a polar liquid at room temperature. It is used as antifreeze, solvent, fuel, and as a denaturant for ethanol Methanol is essential in our lives every day. It is also used in automotive antifreezes, in rocket fuels, and as a general solvent. Methanol is also a high-octane, clean-burning fuel that is a potentially important substitute for gasoline in automotive vehicles. The methanol derived from wood is used chiefly for rendering ethyl alcohol unfit to drink. Literature survey shows that intermolecular interaction among the components of binary mixtures lead to dipole – dipole or polarization interaction between molecules confirm the interaction.[6]

METHODOLOGY

The chemicals used were of AR grades and purified.The densities were measured using Picnometer.The viscosities were measured with the help of Ostwalds viscometer.The refractive indices were measured by an Abbes refractometer.The mesurement of dielecric constant and dielecric loss at an angular frequency were carried out in the X-band microwave frequency of 9.85 GHz

Dielectric Parameters:

The dielectric constant (ε') and dielectric loss (ε″) have been calculated from the following equations. [12], [10], [11].

$$\varepsilon' = \left(\frac{\lambda_o}{\lambda_c}\right)^2 + \left(\frac{\lambda_o}{\lambda_d}\right)^2 \qquad (1)$$

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_o}{\lambda_c}\right)^2 \left(\frac{\lambda_g}{\lambda_d}\right)\frac{d\rho}{dn} \qquad (2)$$

Where, λ_o is free space wavelength, λ_c is cut off wavelength for the wave guide and λ_d is the wavelength in the wave guide filled with the solution. ρ is the inverse of the voltage standing wave ratio (VSWR) and $\frac{d\rho}{dn}$ is the slope of ρ versus n where, n = (1, 2, 3 ……) such that $\frac{n\lambda_d}{2}$ represents the length of the dielectric filled with waveguide.

The free energy of activation E_a of the viscous flow for the pure liquids and their binary mixtures is obtained by using the following equation

$$\eta = \left(\frac{hN}{V}\right)\exp\left[\frac{E_a}{RT}\right] \qquad (3)$$

Where, η is the viscosity and V is molar volume of the liquid.

The values of molar polarization of the mixtures were obtained by using the formula

$$P_{12} = \left(\frac{\varepsilon'-1}{\varepsilon'+2}\right)\left[\frac{M1X1+M2X2}{\rho}\right] \qquad (4)$$

Where, M_1 and M_2 are the molecular weight, $X_1$and X_2 are the mole fraction of the constituents of the mixture. The excess dielectric properties such as excess permittivity(Δε̇), excess loss factor (Δε''),excess

activation energy a (ΔE_a) and excess viscosity ($\Delta\eta$) etc. can be obtained by using the relations of the form.

$$\Delta Y = Y_m - [X_1Y_1 + X_2Y_2] \quad (5)$$

Where, ΔY any excess parameter and Y is refers to the above mentioned quantities, that is, permittivity ($\acute{\varepsilon}$), loss factor (ε'') activation energy(E_a)etc. The subscripts, 1 and 2 used in the above equation are respectively for the mixture, liquid (1) and liquid (2). X_1andX_2 are the mole fractions of the two components in the liquid mixtures.

RESULT AND DISCUSSION

The variation of dielectric constant (ε') with the mole fraction (X) of 1,2-DAP in the mixture is shown in Figure-1 According to Narwade et al [7], if relationship observed between dielectric constant (ε') and mole fraction for the binary mixture is non linear then thereis complex formation and curve show the maximum deviation from linearity at mole fraction X= 0.22 of DAP.

The variation of viscosity (η) with the mole fraction (X) 1,2 DAP in the mixture is shown in Figure-2 The graph indicates that the solute- solute interactions between metanol and 1,2 DAP the value of viscosity (η) increases around 0.3204 mole fraction of. 1,2 DAP. Therefore it is seems reasonable to assume that the formation of associates composed of metanol and 1,2 DAP in this composition range is held together by comparatively stronger intermolecular dipole-dipole interactions. The increase in viscosity (η) may also be attributed to the mutual viscosity of alcohol-amine molecules as per Andrade's theory [4]. The variation of molar polarization (P_{12}) with mole fraction of DAP shown in Figure-3 shows the nonlinear and maximum slope occurs at X = 0.22 mole fraction of DAP which supports to our earlier conclusion that complexion is at X = 0.22 mole fraction of DAP.

The values of excess viscosity ($\Delta\eta$) shown in Figure-4 are positive for the entire range of mole fraction of DAP. It indicates that there is a strong interaction between unlike molecules of the system[3]. The values of excess dielectric loss ($\Delta\varepsilon''$) with the molar concentration (X) of ethylene diamine DAP in the

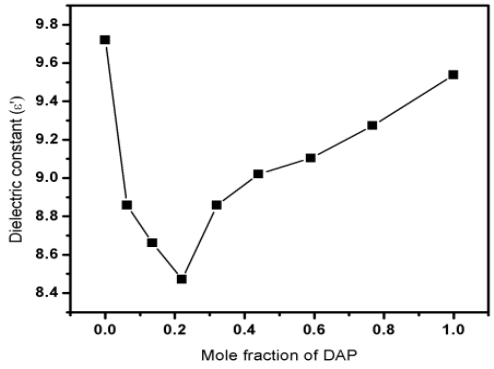

Figure-1

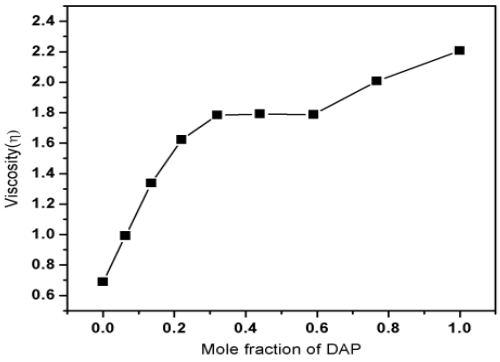

Figure-2

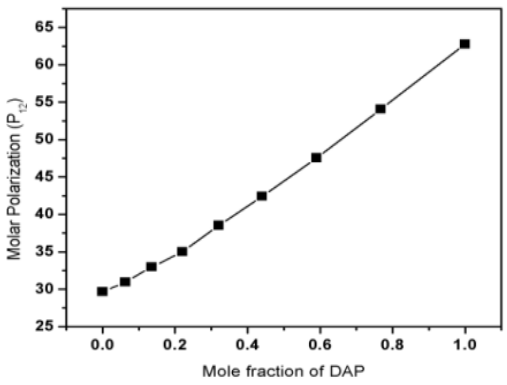

Figure-3

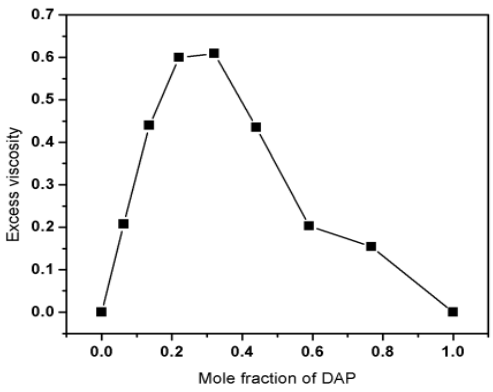

Figure-4

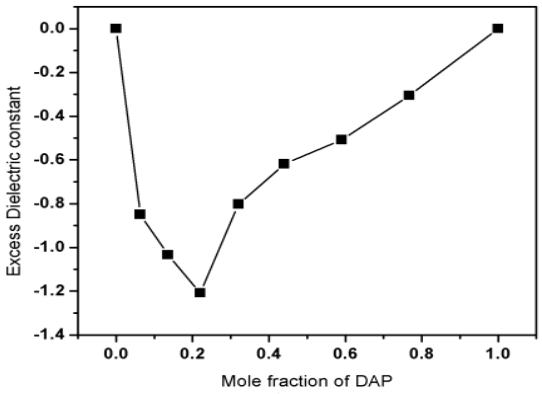

Figure-5

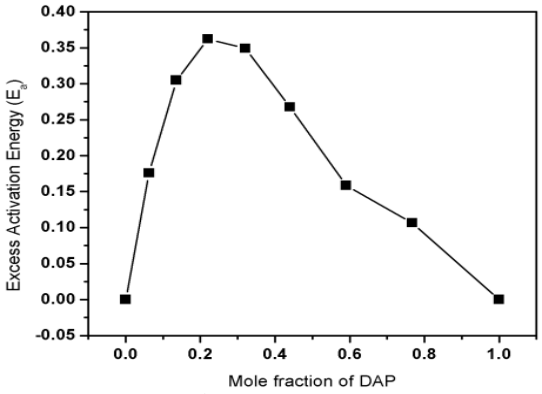

Figure-6

Table-1 The values of viscosity (η), square of refractive index (n_D^2), dielectric constant (ε'), loss factor (ε″), loss tangent (tanδ), activation energy (E_a), and the molar polarization (P_{12}) with increasing mole fraction (*X*) of DAP with Methanol.

Mole fraction (X) of 1,2-DAP	Density gm/cm^3 ρ	Viscosity (η) cp	Refractive index n^2_D	Dielectrc constant ε′	Dielectrc loss ε″	Loss tangent tanδ	Activation energy *Ea* (Kcal/mol)	Molar polarization P12
0.0000	0.8039	0.6883	1.7828	9.7199	2.4035	0.2472	3.0093	29.6537
0.0631	0.8111	0.9916	1.8832	8.8575	2.1474	0.2424	3.2292	30.9541
0.1358	0.8228	1.3370	2.0868	8.6607	2.1675	0.2502	3.4091	32.9713
0.2205	0.8421	1.6227	2.0695	8.4707	2.7351	0.3228	3.5258	35.0072
0.3204	0.8551	1.7838	2.0378	8.8575	2.2431	0.2532	3.5828	38.5268
0.4400	0.8675	1.7913	2.0349	9.0201	2.4224	0.2685	3.5853	42.4132
0.5903	0.8728	1.7870	2.0637	9.1032	2.4403	0.2680	3.5815	47.5633
0.7674	0.8733	2.0074	2.0906	9.2729	2.7300	0.2944	3.6539	54.0652
1.0000	0.8740	2.206	2.0927	9.5371	2.5455	0.2669	3.7107	62.7621

Table-2 The values of excess viscosity (η), excess dielectric constant (ε'), excess loss factor (ε″), excess activation energy (E_a), and the excess molar polarization (P_{12}) with increasing mole fraction (*X*) of DAP with Methanol

Mole fraction of DAP(X)	(Δη)	Δε′	Δε″	Δ*Ea*	ΔP12
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0631	0.2076	-0.8498	-0.2648	0.1759	-0.7858
0.1358	0.4397	-1.0334	-0.2550	0.3048	-1.1755
0.2205	0.5998	-1.2079	0.3005	0.3621	-1.9439
0.3204	0.6092	-0.8028	-0.2056	0.3491	-1.7318
0.4400	0.4352	-0.6183	-0.0433	0.2677	-1.8052
0.5903	0.2028	-0.5078	-0.0467	0.1585	-1.6313
0.7674	0.1544	-0.3057	0.2177	0.1067	-0.9929
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000

mixture are occurs negative up to mole fraction X= 0.1358 and it becomes positive at X=0.2205. As the molar concentration DAP increases, excess dielectric loss becomes negative up to mole fraction X= 0.5903.

The excess dielectric permittivity is associated with the polarization and excess loss is regarded due to molecular motions which are governed by the complex forces of the molecular interaction. [9] The

variation of excess dielectric constant (Δε′) shown in Figure-5 with the mole fraction (*X*) of 1,2 DAP in the mixture is shown in fig.3. The excess dielectric constant (Δε′) is negative over entire range of mole fraction of DAP indicating the solute-solute interactions such that the total effective dipoles gets reduced [13][14][8].

The values of excess activation energy (ΔE_a) shown in Figure-6 are positive for the entire range of mole fraction of DAP .It indicates that there is a strong interaction between the solute-solvent[7], which supports to our earlier conclusion. The values of viscosity (η), square of refractive index (n_D^2), dielectric constant (ε'), loss factor (ε″), loss tangent (tanδ), activation energy (E_a), and the molar polarization (P_{12}) with increasing mole fraction (*X*) of DAP with Methanol are listed in table (1).

The values of excess viscosity (η), excess dielectric constant (ε'), excess loss factor (ε″), excess activation energy (E_a), and the excess molar polarization (P_{12}) with increasing mole fraction (*X*) of DAP with Methanol are listed in table (2).

CONCLUSION

This study suggests the strong interaction between 1,2- Diaminopropaneand Methanol molecules. Also from the dielectric constant viscosity curve suggest formation of 1:1 complex in the binary mixture.

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