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Molecular Association of 2, 3-Dichloroaniline and 2-Ethoxyethanol Using Microwave Frequency in GHz

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ABSTRACT
Densities, viscosities, refractive index, dielectric constant (ε') and dielectric loss (ε") of 2,3-dichloroaniline (2,3-DCA)+2-ethoxyethanol (2-EE) for different mole fractions of 2,3-dichloroaniline in binary mixture have been measured at single microwave frequency 10.985 GHz by Surbers technique at microwave X-band. The values of dielectric parameters (ε') have been used to evaluate the molar polarization (P_{12}), loss tangent (tan δ) explain the formation of complexes in the system. It is found that dielectric constant (ε'), dielectric loss (ε"), loss tangent (tan δ), molar polarization (P_{12}) varies non-linearly but activation energy (Ea),viscosity (η), density (ρ) and refractive index (n) varies linearly with increasing mole fraction in binary mixture of 2,3-dichloroaniline+2-ethoxyethanol. Hence, solute-solvent molecular associations have been reported.

Keywords: Molecular interaction of polar liquids, 2,3-Dichloroaniline, 2-Ethoxyethanol, Binary mixtures

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I. INTRODUCTION

Recently several workers [1-3] have reported the utility of dielectric measurement while studying the molecular interaction in a binary mixture of liquids. [4] Have studied the relaxation time and distributed parameters for binary mixture of 3-bromoanlineand 1-proponal and suggested the interaction between the constitute molecules. [5] Have studied the density, viscosity and excess parameters of binary mixture of 2-ethoxyethanol (2-EE) with N,N-dimethylacetamide (DMA)and explained the deviation of excess parameters in terms of interaction between unlike molecules in the binary mixture. [6] Have studied the molar polarization and free energy activation of cyclohexylamide (CHA) and throw a light on the dynamic characteristics of molecular association in the binary mixture. In this paper our aim is to provide the information regarding the possibilities of complex formation due to molecular association between two polar liquids namely 2,3-DCA and 2-EE. In this paper the dielectric properties and molecular behavior of 2,3-DCA with 2-EE and their binary mixture are discussed. We report here the values of dielectric constant (ε') and dielectric loss (ε") obtained experimentally by employing Surber's technique of measuring reflection coefficient from air dielectric boundary of the liquid.

II. EXPERIMENTAL

2,3-Dichloroaniline (GC Grade) from Sigma-Aldrich, Germany and 2-ethoxyethanol (ARGrade) were obtained from SD Fine-Chem Limited, Mumbai (India). Without further purification the two liquids according to their proportions by volume were mixed well and kept 6 hours in well stoppered bottles to ensure good thermal equilibrium. 2,3-DCA was used as solute and 2-EE as solvent.

MESURMENTS

The dielectric constant (ε') and dielectric loss (ε") have been measured using microwave X-band bench oscillating frequency of 10.985 GHz using source of Reflex klystron 2 K 25 (USSR) by [7]. The densities and viscosities of the pure components and their mixtures were measured by using DMA 35 portable vibrating density meter. Anton paar Autria (Europe) having accuracy of density 0.001 g/cm^3, repeatability 0.0005 g/cm^3 and resolution 0.0001 g/cm^3 [8] and viscosity by LVDL, V-pro II Brook field viscometer (USA) [9]. A plunger waveguide is converted into a cavity by introducing a coupling hole in the entrance and shorting the other end with the calibrated plunger. The sample occupies the entire volume of the cavity. The Frequency was kept constant and the length of the plunger Cavity was changed. Hence several nodes appear as one increase the length of the cavity plunger. Whenever the length of the cavity equals the half integral multiples of the waveguide wavelength inside the medium, the plunger waveguide resonates. The distance through which the plunger is move between two successive cavity nodes gives half of the wavelength (λ) of the

microwave inside the medium. The measurement of reflected power at resonance gives the attenuation coefficient of the sample [10]. Refractive indices for sodium D-line were measured by using Abbe's refractometer, having accuracy up to the third place of decimal microwave power measured by PM-437 (Attest) power meter, Chennai, India. Rectangular wave guide working TE10 mode, 10 dB, Vidyut Yantra Udyog, India. To hold the liquid sample in the liquid cell, thin mica window whose VSWR and attenuation were neglected is introduced between the cell and rest of microwave bench. The values of (ε') and (ε") for low loss liquids are calculated according to [10] formula.

$$\in' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \quad \text{.....1}$$

$$\in'' = \frac{2}{\pi}\left(\frac{\lambda_0}{\lambda d}\right)^2 \frac{\lambda g}{\lambda d}\left(\frac{d\rho_{mean}}{dn}\right) \quad \text{.....2}$$

$$P_{12} = \left(\frac{\varepsilon'-1}{\varepsilon'+2}\right)\left[\frac{M_1X_1 + M_2X_2}{\rho}\right] \quad \text{.....3}$$

Where λ_c is the cut-off wavelength, λ_0 is the free space wavelength, λ_d is the wavelength in dielectric medium, λ_g is the wavelength in empty wave guide parameters and is the inverse voltage standing wave ratio. The values of molar polarization (P_{12}) of the binary mixture were obtained by using the formula [11]. Where M_1 and M_2 molecular weights of solute and solvent X_1 and X_2 are the mole fraction of solute and solvent and ρ is the density of binary mixture.

III. RESULTAND DISCUSSION

The density (ρ), viscosity (η), square of refractive index (n^2D) dielectric permittivity (ε'), dielectric loss (ε"), loss tangent (tanδ), activation energy (E_a) and molar polarization (P_{12}) for viscous flow with increasing mole fraction (X) of 2,3-DCA for the binary mixtures of 2,3-DCA+2-EE are reported in Table 1.

Table 1

X	ρ gm/cm³	η CP	n^2D	ε'	ε''	tanδ	E_a (Kcal/mol)	P_{12}
0.0000	0.9236	2.400	1.9460	3.2563	0.1294	0.0397	6.7281	41.8846
0.1048	0.9818	2.850	2.0192	4.5620	0.0650	0.0142	6.8316	53.9956
0.2147	1.0382	3.310	2.0851	5.9963	0.5291	0.0882	6.9217	63.5288
0.3298	1.0945	3.520	2.1580	7.7122	0.3801	0.0492	6.9587	71.8797
0.4506	1.1521	4.260	2.2320	8.9245	0.4276	0.0479	7.0736	77.1415
0.5775	1.2043	4.730	2.2922	10.8564	0.1184	0.0109	7.1367	83.8052
0.7110	1.2603	5.010	2.3716	12.0206	0.5564	0.0462	7.1713	88.0919
0.8516	1.3106	5.360	2.4221	13.6520	0.0228	0.0016	7.2120	93.3504
1.0000	1.3784	5.580	2.5281	14.8625	0.5651	0.0380	7.2469	96.6302

The density of binary mixture of 2,3-DCA 2-EE are increasing as mole fraction of 2,3-DCA in the binary mixture is increasing. This is expected because density of pure 2,3-DCA is more than that of pure 2-EE. This variation of density is shown in Table1. From Table1 it can also be seen that square of refractive index (n^2D) is increasing with increase in mole fraction of 2,3-DCA in the mixture. This increase in n^2D is further supported by the increase in density of the binary mixture with increase in mole fraction of 2,3-DCA.

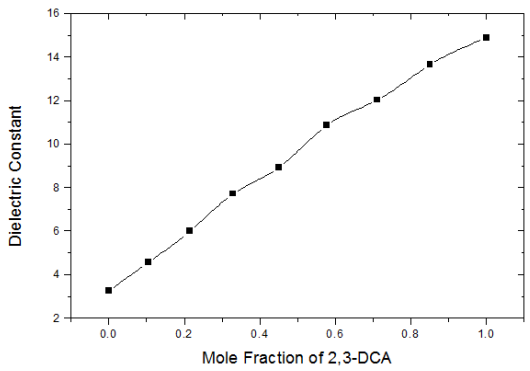

Fig.1. (a) Variation of dielectric constant vs. Mole fraction of 2, 3-DCA

The variation of dielectric constant (ε') versus mole fraction (X) of 2,3-DCA as shown in Fig.1(a). From graph the dielectric constant (ε') are nonlinearly increasing with increasing in mole fraction of 2,3-DCA, which suggest the formation of hydrogen bonded complex in this binary mixture over the entire concentration range. The same results have been reported [12]. The deviation is maximum at about X=0.6 of 2,3-DCA hence formation of 1:1 complex in the binary mixture [13].

The variation of loss tangent (tanδ) and mole fraction (X) of 2,3-DCA is reported in Table 1, which shows the two maxima and a three minima where observed for the binary system, same type of behavior was represented [14] in aniline+2-BE. They suggest that the formation of adduct complex at the minima. Such type of behavior may be due to the presence of -O and -OH group in 2-EE which is responsible for multiple

complexations in the binary mixtures which shows the wobbling nature of the curve.

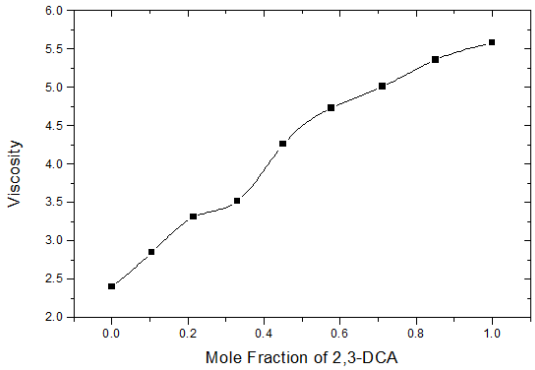

Fig.1. (b) Variation of Viscosity vs. Mole fraction of 2, 3-DCA

The viscosity curve indicates that the solute-solvent interactions between 2,3-DCA and 2-EE as shown in Fig. 1(b). Viscosity increases with increase in mole fraction of 2,3-DCA. 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 assume that dipole-dipole association arising from the fractional negative charge on nitrogen of amino group of 2,3-DCA molecules and fractional positive charge on hydrogen of alcohol 2-EE molecules. Also the increases in viscosity (η) may be attributed to mutual viscosity of alcohol amines molecules as provided [15] and [16].

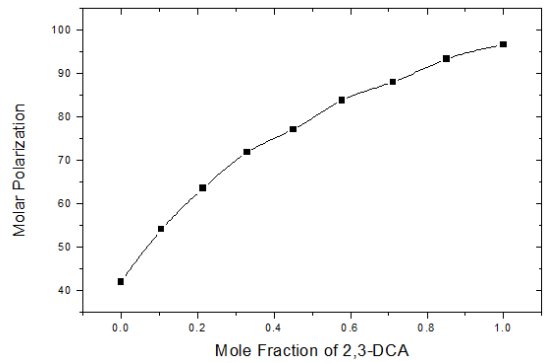

Fig.1. (c) Variation of Molar Polarization vs. Mole fraction of 2, 3-DCA

The variation of molar polarization (P_{12}) versus mole fraction (X) of 2,3-DCA in the binary mixture is represented in the Fig. 1(c). The intersection of straight lines at X=0.4 representing separate region of high and low concentration of 2,3-DCA can be interpreted as a point of maximum concentration which corresponds to 1:1 complex for the system. The amount of complex present is responsible for the shape of polarization curve. Thus this result regarding the formation of complex is supported by our earlier conclusion made for the tanδ vs. mole fraction of 2, 3-DCA curve for the system. Strong positive deviation from additivity in molar polarization (P_{12}) is an indication of tendency towards formation of a miscibility gap. The same results have been reported [17]

IV. CONCLUSION

The density of binary mixture of 2,3-DCA+2-EE are increasing as mole fraction of 2,3-DCA in the binary mixture is increasing. It can also be seen that viscosity (η), square of refractive index (n^2D) and activation energy (Ea) is increasing with increase in mole fraction of 2, 3-DCA in the binary mixture. This increase in η, n^2D and Ea is further supported by the increase in density of the binary mixture with increase in mole fraction of 2, 3-DCA. Viscosity (η) increases as mole fraction of 2, 3-DCA in the binary mixture increases. Increase in viscosity of binary mixture can be attributed to increase in effect of hydrogen bonding with decrease in mole fraction of 2-EE. This is because pure 2,3-DCA is more viscous than pure 2-EE. It is due to presence of strong hydrogen bonding in 2,3-DCA, more number of carbon atoms and long straight chain compound. It is assume that dipole-dipole association arising from the fractional negative charge on nitrogen of amino group of 2,3-DCA molecules and fractional positive charge on hydrogen of alcohol 2-EE molecules. Also the increases in viscosity (η) may be attributed to mutual viscosity of alcohol and amines molecules. The dielectric constant (ε') increase with increase in mole fraction of 2,3-DCA in the binary mixture. This can be attributed to the increase in hydrogen bonding in the binary mixture. This is because there is dipole-dipole interaction in pure 2,3-DCA and weak hydrogen bonding as in pure 2-EE. It is observed that the formation of adduct complex at the minima. Such type of behavior may be due to the presence of -O and -OH group in 2-EE which is responsible for multiple complexes in the binary mixtures which shows the wobbling nature of the curve. Molar polarization (P_{12}) curve suggests 1:1 type complex formation in the binary mixture

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