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EXCESS DIELECTRIC PROPERTIES OF 2, 3-DICHLORANILINE AND 2-PROPOXYETHANOL USING MICROWAVE FREQUENCY AT 20^{0}C

B.G. Nemmaniwar
Department of Physics, Digambarrao Bindu Arts, Commerce and Science College, Bhokar.
Dist. Nanded – 431605 (MS) India.
E-mail –bhupesh.nemmaniwar@rediffmail.com

ABSTRACT :

Dielectric constant (ε') and dielectric loss (ε'') have been experimentally determined for binary liquid mixtures of 2, 3-Dichloroaniline+2-Propoxyethanol at 10.985 GHz microwave frequencies at 20^{0}C and over the complete mole fraction range. The calculated excess permittivity (Δε') and the excess dielectric loss (Δε'') suggest that the structural behavior and dipolar rotation of the binary liquid mixtures. From the studied system indicates that the solute-solvent type of interaction taking place. These parameters have been used to explain the formation of hydrogen bonding and formation of complex in the binary liquid mixtures. These parameters have been used to explain the formation of 1:1 complex in the system.

KEYWORDS : *2,3-Dichloroaniline, 2-Propoxyethanol, Dielectric constant and dielectric loss*

INTRODUCTION

Dielectric studies are of interest to scientists in various branches of physics, chemistry, electrical engineering and biology. The dielectric constant is an important property of the mixed solvents, and plays an important role in the characterization of material electrical properties. When a binary mixture is formed, the expected thermodynamic parameters, such as volume, dielectric parameters and refractive index do not vary linearly Rowlinson, J.S.(1956). The excess dielectric permittivity plays an important role in the domain of binary dielectrics. Knowledge of frequency-dependent dielectric properties of binary liquid mixtures is important both in fundamental studies of solvent structure determination and its dynamics as well as in the practical applications. At a fundamental level, the frequency-dependent dielectric behavior of liquid mixtures provides information on molecular interactions and mechanism of molecular process. In pharmaceutical and analytical sciences the dielectric constant of mixed solvents is required to predict the solubility and chemical stability of the drug Sengwa, R.J. Sankhla, S. Khatri,V.(2009). This work is a continuation of our previous studies Nemmaniwar,B.G. and Kadam, P.(2014) & Nemmaniwar, B.G. Panchal,V and Kadam, P.L.(2014) of dielectric and excess dielectric properties of various binary liquid systems, which are of special interest in chemical and electrochemical processes. Alcohols are the center of interest, because of its outstanding role in chemistry and biology and the study of hydrogen bonding (H-bonding) in liquid systems are important Prajapati, A.N. Rana, V.A. Vyas, A.D. Bhatnagar, S.P. (2011) & Sengwa, R.J. Sankhla, S.(2007). The OH groups form associative liquid due to hydrogen bonding, the effect of molecules with other functional groups on these molecules is very important to understand the behavior of hydrogen bonding in the presence of other groups. Alcohols present a complex and interesting problem in liquid structure, which has been extensively, studied by researchers Chaudhari, A. Shirke, R.M. More, N.M. Patil, P.B. (2002), Sengwa, R.J.(2003) & Sato, T. Chiba, A. Nozaki, R.(2000).The non-associated liquids are also important because of their importance to organic chemistry and biochemistry. It is an intermediate for pharmaceuticals, pesticides and other organic compounds. The solution chemistry for these compounds can be strongly influenced by solute–solute and solvent–solute H-bonding interactions, which consequently plays an important role in determining the physical properties of these molecules Prajapati, A.N. Rana, V.A. Vyas, A.D. Bhatnagar, S.P. (2011).

EXPERIMENTAL:

2.1 Materials:

2,3-Dichloroaniline GC Grade from Sigma-Aldrich, Germany and 2-propoxyethanol AR Grade 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-PE as solvent.

2.2 Measurements:

These liquids used as solute and solvent. Microwave power measured by PM-437 (Attest) power meter, Chennai, India using source of Reflex klystron 2 K 25 (USSR). The densities and viscosities of the pure components and their binary mixtures were measured by using DMA 35 portable vibrating density meter. Anton paar Autria (Europe) having accuracy of density 0.001 gm/cm^3, repeatability 0.0005 gm/cm^3 and resolution 0.0001 gm/cm^3 Nemmaniwar, B.G. Panchal, V. Kadam,P. (2014) and viscosity by LVDL, V-pro II Brook field viscometer (USA) Nemmaniwar, B.G. Kalyankar, N.V. and Kadam, P.L. (2013). Rectangular wave guide working TE$_{10}$ 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 X-band microwave bench was used to measure wavelengths in the dielectric and the voltage standing wave ratio (VSWR). The dielectric constant (ε′) and the dielectric loss (ε′′) of dilute solutions of binary mixture of 2,3-DCA and 2-PE were calculated using microwave absorption techniques of Nemmaniwar, B.G. Kalyankar, N.V. and Kadam, P.L. (2013). All the measurements were carried out at temperatures 20^{0}C and the temperature was thermostatically controlled within $\pm$0.5^{0}C.

RESULTS AND DISCUSSION:

The excess dielectric properties such as excess permittivity $(\Delta \in ')$ can be obtained by using the equation Nemmaniwar, B. G. Mokle, S. S. and Kadam, P. L. (2013).

$$\Delta Y = Y_m - \left(X_1 Y_1 + X_2 Y_2\right) \qquad \text{………….. (1)}$$

When ΔY any excess parameter and Y is refers to the above mentioned quantities, that is, permittivity $(\in ')$, loss factor $(\in '')$, activation energy (E_a) etc. The subscripts m, 1 and 2 used in the above equation are respectively for the mixture, liquid (1) and liquid (2). X_1 And X_2 are the mole fractions of the two components in the liquid mixtures. Qualitative information regarding the solute-solvent interaction may be obtained by the excess permittivity as follows.

The equation (1) for the excess permittivity $(\Delta \in ')$ can be written as

$$\Delta \in ' = \in_m' - \left(X_1 \in_1' + X_2 \in_2'\right) \qquad \text{……..……. (2)}$$

We have three cases, if

1. $\Delta \in ' = 0$: This indicates the solute and solvent do not interact at all.
2. $\Delta \in ' < 0$: This means that solute and solvent interact in such a way that the total effective dipoles get reduced. The solutes and solvents may form multimers leading to the less effective dipoles. In general, the negative excess permittivity indicates the formation of multimers in the binary mixtures. The excess permittivity $(\Delta \in ')$ is associated with the polarization.
3. $\Delta \in ' > 0$: In this case the solute and solvent interact in such a way that the effective dipoles tend to be more. This means the reduction of multimers either in solute or solvent due to the interactions between solute and solvent.

The excess dielectric permittivity's (Δε') and the excess dielectric loss (Δε'') of 2, 3-DCA+2-PE are listed in Table 1.

The excess parameters $\Delta\varepsilon'$ and $\Delta\varepsilon''$ with mole fraction (X) of 2,3-DCA for the binary mixture liquid system of 2,3-DCA+2-PE at 20^0 C

X	$\Delta\varepsilon'$	$\Delta\varepsilon''$
0.0000	0.0000	0.0000
0.1209	-0.5456	-0.1062
0.2430	-1.4704	-0.7150
0.3662	-1.9023	-0.7298
0.4906	-1.7244	-0.6489
0.6161	-1.9968	-0.5694
0.7429	-1.8980	-0.0909
0.8708	-0.8549	-0.1039
1.0000	0.0000	0.0000

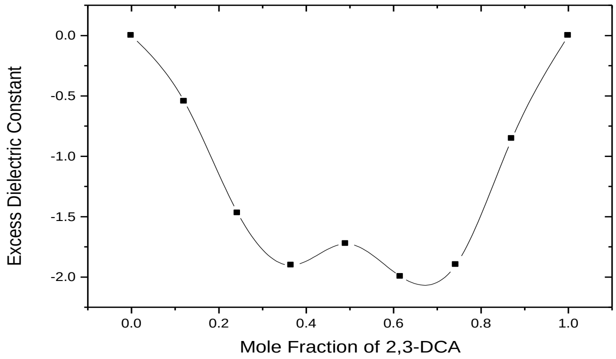

Fig 1: Variation of Excess Dielectric Constant vs. Mole fraction of 2, 3-DCA at 30^0C.

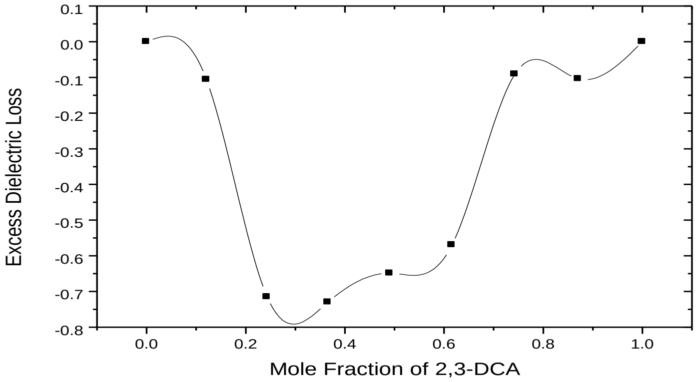

Fig 2: Variation of Excess Dielectric Loss vs. Mole fraction of 2, 3-DCA at 30^0C.

The variation of excess dielectric permittivity ($\Delta\varepsilon'$) versus mole fraction (X) of 2,3-DCA as shown in Fig. 1. From Fig. 1. excess dielectric permittivity ($\Delta\varepsilon'$) is negative entire range of concentration of mole fraction 2,3-DCA,which indicates that the solute-solvent interactions takes place in such a manner that it reduces the dipole moment and waveform multimers leading to less effective dipoles. The excess dielectric permittivity ($\Delta\varepsilon'$) values of the binary mixture of polar solvents is commonly used to obtained insight into the strength of hetero molecular structure and hydrogen bonded structure and dipolar ordering and also the stoichiometric composition corresponding the formation of stable complex adduct. The intersection of two minima at the concentration of X=0.5 mole fraction of 2,3-DCA correspond to the maximum magnitude of

Δε', suggesting the formation of stable complex with1:1 molar ratio which governs their molecular dielectric polarization. The similar results are reported Vyas,A.D. Rana, V.A. and Gadani, D.H. (2011).

The variation of excess dielectric loss (Δε") versus mole fraction (X) of 2,3-DCA as shown in Fig 2, it is observed that it is negative for entire concentration range of mole fraction of 2,3-DCA in binary mixture of 2,3-DCA+2-PE. It appears to be that the Δε" is nonzero for the microwave frequency X-band for all the binary mixture combination. It may be explained from the fact that the Δε" is observed as minimum at X=0.3662 mole fraction of 2, 3-DCA which are closed to the value of mole fraction of 2-PE at which we accept the formation of complex on the basis of tanδ curve. The Δε" regarded due to the molecular motion which are govern by the complex forces of molecular interactions. Thus the Δε" may be regarded as a parameter which reflects the entropy change in binary system. The similar results are found to be Kalamse *et. al* Narwade, B.S. Gawali, P.G. Pande, R. Kalmse, G.M. (2005).

CONCLUSION:

It is observed that the excess dielectric constant (Δε') for 2, 3-DCA in binary mixture of 2, 3-DCA+2-PE are negative over entire concentration range of mole fraction of 2, 3-DCA. The negative values of Δε' indicates that molecules of the mixtures form multimer structure via hydrogen bonding in such a way that the effective dipole moments get reduced. Also negative values of Δε' indicates that one of the mixture constituents acts self-associcated structure with orientation of some of the neighboring dipoles in an anti-parallel direction. The excess dielectric loss (Δε") of the binary mixture are negative for 2, 3-DCA+2-PE. The excess dielectric loss (Δε") regarded due to the molecular motion which are govern by the complex forces of molecular interactions. Thus Δε" may be regarded as a parameter which reflects the entropy change in binary system.

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