Dielectric Behaviour of Binary Mixture of 2-Chloroaniline with 2-Methoxyethanol and 2-Ethoxyethanol

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Abstract: Densities, viscosities, refractive indices, dielectric constant (ε') and dielectric loss (ε'') of 2-chloroaniline (2CA) + 2-methoxyethanol (2ME) and 2-chloroaniline (2CA) + 2-ethoxyethanol (2EE) for different mole fractions of 2-chloroaniline in binary mixture have been measured at single microwave frequency 10.985 GHz at 30°C by Surber method using microwave X-band. The values of dielectric parameters (ε' and ε'') have been used to evaluate the molar polarization (P_{12}), loss tangent (tanδ), viscosity (η), activation energy (E_a), excess permittivity (Δε'), excess dielectric loss (Δε''), excess viscosities (Δη), excess polarization (ΔP_{12}) and excess activation energy (ΔE_a) have also been estimated. These parameters have been used to explain the formation of complexes in the system. It is found that dielectric constant (ε'), dielectric loss (ε''), loss tangent (tanδ), molar polarization (P_{12}) varies non-linearly but activation energy (E_a), viscosity (η), density (ρ), and refractive index (n) varies linearly with increasing mole fraction in binary mixture of 2-chloroaniline (2-CA) + 2-methoxyethanol (2-ME) and 2-chloroaniline (2-CA) + 2-ethoxyethanol (2-EE). Hence, solute-solvent molecular associations have been reported.

Keywords: molecular interaction; polar liquids; binary mixture; excess parameters.

1. INTRODUCTION

Effects of molecular orientations are very sensitive to all kinds of interactions. Experimental investigation of dielectric properties of polar liquids from microwave absorption is of great value in understanding the nature of complex formation. When a binary mixture is formed the viscosity, density, refractive index, thermodynamic parameters and dielectric parameters do not vary linearly. The deviation from linearity of these parameters is termed as excess parameters which are useful to understand the nature of bonding between the two liquid mixtures.

The nature of complex formation between the molecules may be ascertained by studying apparent molar polarization and is useful in determine the nature of molecular interactions in the liquid systems. In past, several workers have made dielectric studies of liquid mixtures by taking amines as one of the constituent components in the binary mixture [1-7]. Vural et al. [8] have studied the excess molar volumes to refractive index of binary mixture glycerol + methanol and glycerol + water at 298.15 K and 303.15 K, respectively and Kamble et al. [9] have studied the excess parameters of binary systems of cyclohexane and methyl acetate.

Dielectric study of 2-CA + 2-ME and 2-CA + 2-EE mixture have not been carried out in the past. As such it was felt that the present study provides most useful information regarding the molecular interaction and the formation of complexes in the mixture of 2-CA + 2-ME and 2-CA + 2-EE.

2-Methoxyethanol (2-ME) is also called as methyl cellosolve and used as a solvent for mainly different purpose, such as varnishes, dyes, resins and an additive in airplane deicing solutions while 2-ethoxyethanol (2-EE) commercially known as “Cello solves” and widely used as complexes of solvents, coemulsifiers so stabilizers of emulsions, dyes and lacquers.

2. MATERIAL AND METHODS

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2.1. Materials

2-Chloroaniline (GC Grade) from Merck Schuchardt, Germany. 2-Methoxyethanol and 2-ethoxyethanol (AR Grade) were obtained from M/S Sd. Fine chemical, Mumbai, India without further purification. The two liquids according to their proportions by volume were mixed well and kept 6h in well stoppered bottles to ensure good thermal equilibrium. These liquids used as solute and solvent.

2.2. Measurements

The dielectric constant (ε’) and dielectric loss (ε'”) have been measured using microwave X-band bench oscillating frequency of 10.985 GHz [10] at 30°C using source of Reflex kystron 2 K 25 (USSR). 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 gm/cm³ and viscosity by Oswald viscometer. 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 Vantra 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 present investigation, for low loss liquids according to Heston et al. [11].

\[ \varepsilon' = \left( \frac{\lambda_0}{\lambda_d} \right)^2 + \left( \frac{\lambda_0}{\lambda_c} \right)^2 \]  \[ \text{.............. (1)} \]

\[ \varepsilon'' = \frac{2}{\pi} \left( \frac{\lambda_g}{\lambda_d} \right) \left( \frac{\lambda_0}{\lambda_c} \right)^2 \left( \frac{dp}{dn} \right) \]  \[ \text{.............. (2)} \]

Where \( \lambda_c \) is the cut-off wavelength, \( \lambda_d \) is the free space wavelength, \( \lambda_d \) is the wavelength in dielectric medium and \( \lambda_g \) is the wavelength in empty wave guide parameters \( \rho \) is inverse voltage standing wave ratio, \( n \) is the number of minima.

The precision of measurements for the wavelength with the available X-band microwave test bench is ±0.001 cm corresponding to this accuracy value, the error in the measurements of ε’ is estimated. For simplification, involved errors due to non zero impedance of the short circuit plunger are ignored.

The errors of measurements are calculated by using the conventional method of error analysis [12]. Over all estimated accuracy of measurements for ε’ and ε’” by this method is about ±1% and ±5%, respectively.

The ε’ and ε’” were measured by reflectometric technique by measuring reflection coefficient from the air dielectric boundary of the liquid [13-18]. The ε’ and ε’” for different mole fractions of 2CA in the binary mixture of 2-CA+2-ME and 2-CA+2-EE are measured at 30°C.

In order to determine the dielectric wavelength (\( \lambda_d \)), dielectric constant (ε’),dielectric loss (ε'”), loss tangent (tanδ) and molar polarization (Pₙ), the movable short of the liquid cell was moved in and out and corresponding reflection coefficient was measured using crystal detector in the directional coupler [19].

The relationship between the reflected power and depth of liquid columns is given by a damped sinusoidal curve. The distance between two adjacent minima of this curve gives \( \lambda_d/2 \). Thus the knowing the values of wavelength in dielectric medium \( \lambda_d \), free space wavelength (\( \lambda_0 \)) cut off wavelength (\( \lambda_c \)), waveguide wavelength (\( \lambda_g \)) and molar polarization (Pₙ), were determined by Surber relations [10, 19-21].

3. RESULTS AND DISCUSSION

The values of viscosity (η), Refractive index (n), density (ρ), dielectric constant (ε’), dielectric loss (ε'”), loss tangent (tanδ) and activation energy (Eₐ) for viscous flow with increasing mole fraction (X) of 2 CA for the binary mixtures of 2-CA + 2-ME and 2-CA+2-EE are reported in (Tables 1 and 2).

3.1. Microwave absorption

It is seen from Fig.1b that the absorption in the mixture is greater than that in pure liquids, a maxima in the tan δ curve occurring at X=0.0964 and X=0.4277 (2-ME and 2-EE) mole fraction of 2-CA in to our case the formation of complex will increases
the dielectric absorption due to the following consideration. In the complex, the dipole moment can
be taken as, \((\mu_{D1} + \mu_{D2})_1\), \(\mu_{D1}\) and \(\mu_{D2}\) being the dipole
moments of the constituent molecules. For \(n\) molecules of each liquid forming the complex the
absorption would be proportional to \(n (\mu_{D1}^2 + \mu_{D2}^2)\) for
pure liquids, assuming no interaction. On the other
hand, in the mixture absorption would be proportional
to the greater term \(n (\mu_{D1}^2 + \mu_{D2}^2)\).

Table 1. Values of mole fraction (X) of 2-CA density (\(\rho\)), viscosity (\(\eta\)), refractive index (n), dielectric constant
\((\varepsilon')\), dielectric loss \((\varepsilon'')\), loss tangent (tan\(\delta\)) and activation energy (\(E_a\)) for binary liquid system at 30\(^0\)C.

<table>
<thead>
<tr>
<th>X</th>
<th>(\rho) gm/cm(^3)</th>
<th>(\eta) CP</th>
<th>n</th>
<th>(\varepsilon')</th>
<th>(\varepsilon'')</th>
<th>tan(\delta)</th>
<th>(E_a) (Kcal/mol)</th>
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<tr>
<td>0</td>
<td>0.9569</td>
<td>1.3577</td>
<td>1.391</td>
<td>6.6882</td>
<td>0.5752</td>
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<tr>
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<td>1.5502</td>
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<tr>
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<td>0.0908</td>
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<tr>
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<td>0.0974</td>
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<td>1.547</td>
<td>4.4318</td>
<td>0.2975</td>
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<tr>
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<td>1.575</td>
<td>4.1455</td>
<td>0.2585</td>
<td>0.0624</td>
<td>3.8931</td>
</tr>
</tbody>
</table>

Table 2. Values of mole fraction (X) of 2-CA density (\(\rho\)), viscosity (\(\eta\)), refractive index (n), dielectric constant
\((\varepsilon')\), dielectric loss \((\varepsilon'')\), loss tangent (tan\(\delta\)) and activation energy (\(E_a\)) for binary liquid system at 30\(^0\)C.

<table>
<thead>
<tr>
<th>X</th>
<th>(\rho) gm/cm(^3)</th>
<th>(\eta) CP</th>
<th>n</th>
<th>(\varepsilon')</th>
<th>(\varepsilon'')</th>
<th>tan(\delta)</th>
<th>(E_a) (Kcal/mol)</th>
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<tr>
<td>0</td>
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<tr>
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<td>1.554</td>
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<td>2.6800</td>
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<td>4.1456</td>
<td>0.2780</td>
<td>0.0671</td>
<td>3.8931</td>
</tr>
</tbody>
</table>
3.2. Maxima in the viscosity curve

When the viscosity (\(\eta\)) is plotted against mole fraction, the curve shows sharp maxima in Fig.1c. The maxima for the 2-CA+2-ME mixture accuracy at X=0.691 mole fraction of (2-CA) and for 2-CA+2-EE mixture it occur curve at X=0.839 mole fraction of (2-CA) the maxima for the 2-EE is much pronounced than that for 2-ME. Huyskens et al. [8] have explained the increases in viscosity for the acid amine and 2-ME or 2-EE mixture due to the formation of dissociated ions in the mixture. Which is exothermic and depends upon the acidic strength of 2-ME and 2-EE. Since in the present case 2-EE react with (2-CA) by an exothermic reaction, the pronounced maxima for the 2-ME may be associated with the formation of dissociated ions in the mixture and due to the more acidic character of 2-ME than 2-EE. The spectacular increases in viscosity (\(\eta\)) may also be attributed to the mutual that viscosity of the alcohols and amine molecules, as provided by the Andrade’s theory [20].

3.3. Excess parameters

The excess values of dielectric permittivity \(\Delta\varepsilon\)', excess viscosity \(\Delta\eta\), excess square of refractive index \(\Delta\n^2\)D, excess activation energy \(\Delta E_a\) for 2-CA+2-ME and 2-CA+2-EE system are presented in Fig. 2.

The excess value calculated by using the relation:

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

Where \(\Delta Y\) any excess parameters and Y is refers to the above mentioned quantities the subscripts m, 1 and 2 used in the above equation are respectively for the mixture, component 1 and component 2. X1 and X2 are the mole fraction of two components in the liquids mixture.

The excess viscosities, excess square of refractive index and excess activation energy are all positive indicating strong interaction between the alcohols and amines molecules. For all there excess parameters the maxima for the 2-CA+2-ME mixture occur at X=0.55469 mole fraction of 2-CA and for 2-CA+2-EE mixture maxima occur at about X= 0.35551 mole fraction of 2CA (Fig. 2a, 2b, 2c).

The dipole moment of 2-ME and 2-EE calculated by formula [21]:

\[
\mu_D = 0.0127 \times 10^{-18} \sqrt{(P_{12} - P_0)T} 
\]

The values of dipole moment \(\mu_D\) obtained for 2-ME and 2-EE are \(\mu_D =0.8994\) esu and \(\mu_D =0.5580\) esu, respectively. The higher \(\mu_D\) value of 2-ME indicates that dipole-dipole interaction in 2-ME is stronger than 2-EE. This behavior of 2-ME is supported by the higher values of activation energy and excess activation energy of 2-ME as compared to 2-EE. The deviation of excess activation energy of viscous flow in these systems indicates the increases the internal energy of viscous flow thus, supporting the presence of strong interaction in the system of alcohols and amines (Fig. 2c).

The variation of the square of refractive indices on mixing with the mole fraction of 2-CA it can be seen that in (Fig. 2b) That the changes in refractive index of 2-CA+2-ME and 2-CA + 2-EE are positive throughout the entire composition range, and that as the hydrogen bonding of the interactions increases the change in refractive index becomes more negative.

The excess dielectric constant of the mixture was plotted against the mole fraction of 2-CA in the mixture at 30°C and is shown in Fig. 2d from the figure it can be seen that negative (2-ME ) 0 ≤ X ≤ 0.27,0.38 ≤ X ≤ 0.53 and at 0.78 ≤ X ≤ 1. Positive at X=0.27 ≤ X ≤ 0.38 and 0.58 ≤ X ≤ 0.72. (2-EE) positive at 0 ≤ X ≤ 0.28, 0.40 ≤ X ≤ 0.58 and again at 0.72 ≤ X ≤ 1. Negative at 0.28 ≤ X ≤ 0.40 and 0.58 ≤ X ≤ 0.72, respectively and again showing a positive value of 50% of 2-EE and 55% of 2-ME concentration of 2-CA, for both the systems. At the concentration for which \(\Delta \varepsilon\) is negative indicates that molecules of the mixtures form multimer structure via hydrogen bonding in such a way that the effective dipole movement is reduced where as the concentrations for which \(\Delta \varepsilon\) is positive indicates that the molecules of the mixture form multimer structure via hydrogen bonding in such a way that the effective dipole moments are increased.

4. CONCLUSION

The dielectric constant, dielectric loss, loss tangent, viscosity, density, refractive index and excess parameters have been reported for 2-CA+2-ME and 2-CA+2-EE binary mixture at the various concentrations. These suggest the strong interaction between the alcohols and amine molecules. The excess parameter curves suggest the more acidic
character of 2-ME than 2-EE.

5. ACKNOWLEDGMENTS

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6. REFERENCES AND NOTES


