Dielectric study of allyl chloride - alcohol mixtures using time domain reflectometry technique

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ABSTRACT

Dielectric study of Allyl chloride (AC), Alcohol and their binary mixtures have been carried out over the frequency range from 10 MHz to 10 GHz at temperature 288 K using Time Domain Reflectometry (TDR) for 11 different concentrations. Dielectric constant, Relaxation time, Kirkwood correlation factor, Excess parameters were estimated and discussed to yield information on the molecular structure and dynamics of the mixture. The values of dielectric constant and relaxation time decreases with increase in concentration of alcohol in Allyl chloride. The Bruggeman plot shows a non-linearity of the curve for all the concentration; indicates the hetrointeraction which may be due to hydrogen bonding of the OH group of alcohol with Allyl chloride molecule. The excess inverse relaxation time values are negative for all the concentrations indicate that the solute-solvent interaction hinders the rotation of the dipoles of the system.

Keywords: Time Domain Reflectometry, Dielectric relaxation, Kirkwood correlation factor, Bruggeman factor etc.

INTRODUCTION

The knowledge of frequency dependent dielectric properties of binary liquid mixture is important both in fundamental studies of solvent structure determination and its dynamics as well as in the practical applications of microwave heating processes. At a fundamental level, the frequency dependent dielectric behavior of liquid mixtures provides information on molecular interactions and mechanism of molecular process. The dielectric relaxation behavior of mixtures of polar molecules varying conditions of compositions is very important as it helps in obtaining information about relaxation process in mixtures. There have been several investigations on the dielectric behavior of solvent mixtures in which dielectric relaxation spectra were used to inspect molecular orientations, hydrogen bonding networks and micro dynamics of these systems. The aim of the present investigation is to use dielectric relaxation measurements to study the inter molecular interaction in Allyl chloride-alcohols mixtures in the microwave region (10 MHz to 20 GHz) with varying concentrations (0 % to 100 %) using TDR technique for temperature at 288 K. Alcohols are bounded by strong intermolecular Hydrogen bonding. Double bond and a highly reactive chlorine atom (CH₂=CH-CH₂-Cl) are present in the Allyl chloride molecules and these molecules are associated with each other through strong dipole-dipole interaction. Because of presence of different type of association in both molecules, it is interesting to study the nature of intermolecular interaction between Allyl chloride and Alcohol molecules. The permittivity, relaxation time, excess permittivity, excess inverse relaxation time is reported. The Kirkwood correlation factor is used to understand the molecular orientation in the mixtures.

EXPERIMENTAL

Chemicals

The chemicals used in the present study are Allyl chloride, Methanol, Ethanol and 2-Propanol of spectroscopic grade. The solutions were prepared
at eleven different volume percentage of Allyl chloride 0% to 100% in steps of 10%. Using these volume percents the mole fraction is calculated.

**Apparatus**

The complex permittivity spectra were studied using time domain reflectometry. The Hewlett-Packard HP 54750 sampling oscilloscope with HP 54754 A TDR plug-in module was used. A fast rising step voltage pulse of about 39 ps rise time generator was propagated through a coaxial line system of characteristic impedance of 50 generated by a pulse ohm. The transmission line system under test was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell, coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length.

All measurements were done under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this experiment, a time window of 5ns was used. The reflected pulse without sample R1 (t) and with sample Rx (t) were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through a 1.44 MB floppy diskette drive.

A temperature controller system with a water bath and thermostat has been used to maintain the constant temperature within the accuracy limit ± 1° C. The sample cell was surrounded by a heat-insulating container through which the water of constant temperature using a temperature controller system was circulated. The temperature at the cell is checked using the electronic thermometer.

**Data analysis**

The time dependent data were processed to obtain complex reflection coefficient spectra \( \rho^*(\omega) \) over a frequency range 10 MHz to 20 GHz by using Fourier transform\(^{15,16} \) as

\[
\rho^*(\omega) = \frac{c}{j\omega d} \left[ \rho(\omega) \right] \quad \text{...(1)}
\]

The complex permittivity spectra \( \varepsilon^*(\omega) \) were obtained from reflection coefficient spectra \( \rho^*(\omega) \) by applying bilinear calibration method\(^{17} \).

The static permittivity and relaxation time constant were obtained using the nonlinear least squares fit method\(^{18} \).

The general form of the relaxation model is given by the Havriliak-Negami equation \([19]\).

\[
\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{\left[ 1 + (j\omega\tau)^{1-\alpha} \right]^\beta} \quad \text{...(2)}
\]

**Excess properties**

**Excess permittivity**

For the detection of the cooperative domains in the mixture it is useful to compute the excess permittivity \( \varepsilon^E \) which may be further used to study dynamics of the mixture due to molecular interactions\(^{20} \). The excess permittivity \( \varepsilon^E \) is defined as

\[
\varepsilon^E = (\varepsilon_0)_m - [(\varepsilon_0)_A X_A + (\varepsilon_0)_B X_B] \quad \text{...(3)}
\]

Where \( X \)– mole fraction and suffices \( m \), A, B represents mixture, liquid A and liquid B respectively. The excess permittivity provides qualitative information about (formation of monomers and multimers in the mixture as follows) structural aspects of the mixture.

If \( \varepsilon^E = 0 \): indicates the liquid A and B do not interact at all.

If \( \varepsilon^E < 0 \): indicates the liquid A and B interaction in such a way that the total effective dipole gets reduced. This suggests that the liquid A and B may form multimers leading to less effective dipoles or in other words there is a tendency of dipole to align in antiparallel direction.

If \( \varepsilon^E > 0 \): indicates the liquid A and B interaction in such a way that the total effective dipole moment increases. There is a tendency of dipole aligned in parallel direction.

**Excess inverse relaxation time**

The information related to dynamics of the solute-solvent interaction might be obtained by excess properties related to the relaxation time in the mixture. The excess inverse relaxation time is defined as
\[
\frac{1}{\tau^E} = \frac{1}{\tau}_m - \left[ \frac{1}{\tau}_X x_X + \frac{1}{\tau}_Y x_Y \right] 
\]

(4)

Where \( \frac{1}{\tau^E} \) is the excess inverse relaxation time which represents the average broadening of dielectric spectra. The information regarding the dynamics of solute solvent interaction from this excess property is as follows:

- \( \frac{1}{\tau^E} = 0 \): Indicates there is no change in the dynamics of liquid A and B.
- \( \frac{1}{\tau^E} < 0 \): Indicates liquid A and B interaction produces a field such that the effective dipole rotates slowly.
- \( \frac{1}{\tau^E} > 0 \): Indicates liquid A and B interaction produces a field such that the effective dipoles rotate rapidly, i.e., the field will co-operate in the rotation of the dipoles.

**Kirkwood correlation**

The structural information about the liquids from the dielectric relaxation parameters may be obtained using the Kirkwood correlation factor \( g \),

\[
\frac{4\pi N \mu^2 \rho}{9 k T M} g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} 
\]

(5)

where \( \varepsilon_0 \) is static permittivity, \( \varepsilon_\infty \) is permittivity at high frequency, \( \mu \) is dipole moment in gas phase, \( r \) is density at temperature T, M is

**Table 1: Dielectric constant (\( \varepsilon \)) of AC-Alcohol at 288K**

<table>
<thead>
<tr>
<th>Mole fraction of Allyl Chloride</th>
<th>( \varepsilon ) Methanol</th>
<th>( \varepsilon ) Ethanol</th>
<th>( \varepsilon ) Propanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.26</td>
<td>8.26</td>
<td>8.26</td>
</tr>
<tr>
<td>0.9479</td>
<td>10.35</td>
<td>9.15</td>
<td>8.42</td>
</tr>
<tr>
<td>0.8898</td>
<td>12.51</td>
<td>9.87</td>
<td>9.55</td>
</tr>
<tr>
<td>0.8248</td>
<td>15.4</td>
<td>11.04</td>
<td>9.95</td>
</tr>
<tr>
<td>0.7517</td>
<td>18.54</td>
<td>12.59</td>
<td>11.66</td>
</tr>
<tr>
<td>0.6687</td>
<td>21.73</td>
<td>14.85</td>
<td>12</td>
</tr>
<tr>
<td>0.5736</td>
<td>25.67</td>
<td>17.06</td>
<td>12.16</td>
</tr>
<tr>
<td>0.4638</td>
<td>27.84</td>
<td>19.96</td>
<td>14.96</td>
</tr>
<tr>
<td>0.3353</td>
<td>31.48</td>
<td>22.61</td>
<td>16.88</td>
</tr>
<tr>
<td>0.1832</td>
<td>32.85</td>
<td>24.83</td>
<td>18.18</td>
</tr>
<tr>
<td>0</td>
<td>33.61</td>
<td>25.8</td>
<td>18.29</td>
</tr>
</tbody>
</table>

**Table 2: Relaxation time of AC-Alcohol at 288K**

<table>
<thead>
<tr>
<th>Mole fraction of AC</th>
<th>( \tau ) Methanol</th>
<th>( \tau ) Ethanol</th>
<th>( \tau ) Propanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>55.91</td>
<td>163.23</td>
<td>278.11</td>
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<tr>
<td>0.1832</td>
<td>60</td>
<td>158.58</td>
<td>265.37</td>
</tr>
<tr>
<td>0.3353</td>
<td>60.29</td>
<td>157.05</td>
<td>238.011</td>
</tr>
<tr>
<td>0.4638</td>
<td>59.67</td>
<td>154.46</td>
<td>209.28</td>
</tr>
<tr>
<td>0.5736</td>
<td>59.14</td>
<td>145.01</td>
<td>131.68</td>
</tr>
<tr>
<td>0.6687</td>
<td>56.87</td>
<td>134.07</td>
<td>79.21</td>
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<tr>
<td>0.7517</td>
<td>48.8</td>
<td>116.05</td>
<td>55.06</td>
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<tr>
<td>0.8248</td>
<td>42.07</td>
<td>99.55</td>
<td>35.48</td>
</tr>
<tr>
<td>0.8898</td>
<td>29.51</td>
<td>68.53</td>
<td>21.73</td>
</tr>
<tr>
<td>0.9479</td>
<td>16.09</td>
<td>34.04</td>
<td>17.11</td>
</tr>
<tr>
<td>1</td>
<td>10.65</td>
<td>10.65</td>
<td>10.65</td>
</tr>
</tbody>
</table>
molecular weight, \(K\) is Boltzman constant, \(N\) is Avogadro’s number. A modified form of this equation has been used to study the orientation of electric dipoles in binary mixtures. For the mixtures of two polar liquids, say A and B, equation (6) is modified by assuming that \(g_{\text{eff}}\) has become the effective correlation factor in the mixture. The Kirkwood equation for the mixture can be expressed as follows.

\[
\frac{4\pi N}{9\kappa T} \left( \frac{e_1^0 d_1}{M_1} - \frac{e_2^0 d_2}{M_2} \right) g_{\text{eff}} = \frac{(c_{\text{am}} - c_{\text{am}})(2c_{\text{am}} + c_{\text{am}})}{c_{\text{am}}(c_{\text{am}} + 2)}^2
\]

...(6)

where \(g_{\text{eff}}\) is the effective Kirkwood correlation factor for a binary mixture with \(X_A\) and \(X_B\) as volume fractions of liquids A and B, respectively, \(\varepsilon_0\) is permittivity, \(\varepsilon_{\infty}\) is permittivity at high frequency, \(\mu\) is dipole moment in gas phase, \(\rho\) is density at temperature \(T\), \(M\) is molecular weight, \(K\) is Boltzman constant, \(N\) is Avogadro’s number.

**Bruggeman factor**

The modified Bruggeman equation [25] is another parameter, which is used to study intermolecular interactions between two (components of) liquids A and B respectively. The Bruggeman factor \(f_B\) is given by

\[
f_B = \left( \frac{\varepsilon_{0A} - \varepsilon_{0B}}{\varepsilon_{0A} - \varepsilon_{0B}} \right)^{1/3} = 1 - V \quad ...(7)
\]

According to equation (7) a linear relationship is expected between Bruggeman factor and volume fraction of Allyl chloride. Any deviation from this linear relation indicates existence of intermolecular interactions.

**RESULTS AND DISCUSSION**

The value of static dielectric constant for the mixtures increases as the concentration of AC decreases. Increase in the dielectric constant is due to the transition of spherical molecular aggregates into elongated aggregates. Similar conclusions are drawn by P. Sivagurunathan et al.,\(^4\) for Butyl methacrylate-alcohol system and by Shirke et al.,\(^10,11\) for ethyl acetate-alcohol systems. This tends to indicate that heterointeraction, which may arise due to the formation of hydrogen bonding between the OH Group of Alcohol molecules with Allyl Chloride molecule. The dielectric relaxation time decreases with increasing concentration of AC molecules and offers hindrance to the rotation of the molecule. The \(\varepsilon\) for AC-Propanol is less as compared to AC-Methanol & AC-Ethanol this is due to centre of symmetry of 2-Propanol molecule. The presence of OH group with the central carbon decreases the dielectric constant.

This trend could be attributed to the decrease in the number of dipoles in the complex, which may lead to a decrease in the molar volume of the rotated molecule\(^27\). It is also noticed that, though the \(\tau\) values of mixtures lie between the

<table>
<thead>
<tr>
<th>Mole fraction of AC</th>
<th>(g_{\text{eff}}) Methanol</th>
<th>(g_{\text{eff}}) Ethanol</th>
<th>(g_{\text{eff}}) Propanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.75</td>
<td>2.92</td>
<td>1.26</td>
</tr>
<tr>
<td>0.1832</td>
<td>2.87</td>
<td>3</td>
<td>1.39</td>
</tr>
<tr>
<td>0.3353</td>
<td>2.95</td>
<td>3.05</td>
<td>1.43</td>
</tr>
<tr>
<td>0.4638</td>
<td>2.81</td>
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<td>1.4</td>
</tr>
<tr>
<td>0.5736</td>
<td>2.82</td>
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<td>1.41</td>
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<td>0.6687</td>
<td>2.62</td>
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<td>1.41</td>
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<tr>
<td>0.7517</td>
<td>2.49</td>
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<td>2.2</td>
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</tr>
<tr>
<td>0.9479</td>
<td>2.18</td>
<td>2.54</td>
<td>1.79</td>
</tr>
<tr>
<td>1</td>
<td>2.19</td>
<td>2.19</td>
<td>2.19</td>
</tr>
</tbody>
</table>

Table 3: \((g_{\text{eff}})\) Kirkwood correlation factor of AC-Alcohol at 288K
with change in volume fraction of ally chloride with alcohols. This suggests intermolecular interactions are taking place within these systems. Earlier reporter\textsuperscript{3-13} was evaluated excess permittivity (\(\varepsilon^E\)) to conform the formation of multimers the excess permittivity is found negative for all concentrations of Ethanol & Propanol. Excess permittivity is found to be positive as well as negative for methanol this is due to as the concentration of alcohol decreases monomers will oxidizes to form multimers. Negative excess permittivity indicates decrease of dipole moment & the total number of dipoles in the system decreases, which is due to the antiparallel alignment of the dipoles Allyl chloride and Alcohol molecules.

The value of excess inverse relaxation time are negative for all concentrations and, indicates slower rotation of the dipoles, due to the interaction of liquid A and B through the hydrogen bonded structures which produces a field in such a way that the effective dipole rotation is hindered.

In equation (7) the values of \(g^\text{eff}\) will change from \(g_A\) to \(g_B\) as the concentration of the liquid B is increased from 0 % to 100 %. The values of \(g^\text{eff}\) are as shown in Table 3. The calculated values of the Kirkwood correlation factor \(g^\text{eff}\), which provides valuable information about ordering of the molecules in the state; that is, it quantifies the extent of polarization of the medium for all the mixtures, at all temperatures, the \(g^\text{eff}\) values are greater than unity, indicating parallel alignment of the electric dipoles. Higher value of \(g^\text{eff}\) confirms strong intermolecular bonding within the system and charge distribution is exposed so that neighbors can assume very strong interaction. According to equation (7) a linear relationship is expected between Bruggeman factor \((f_B)\) and volume fraction of Allyl chloride. Fig 3 shows non-linear behavior of \(f_B\) against Allyl chloride indicates that there is intermolecular interaction takes place in the mixtures. The investigated values of dielectric parameters show systematic change in dielectric values with increase in concentration of Allyl chloride in Alcohol.

CONCLUSIONS

The dielectric constants, relaxation times, the Kirkwood correlation factor and excess inverse relaxation time, excess permittivity, for AC-Alcohol...
mixtures for various concentrations have been reported. These data provide information regarding solute–solvent interaction in liquids. The dielectric parameters show systematic change with concentration and alkyl chain length in Alcohol. The excess inverse relaxation time values are negative for all the systems indicating the solute solvent interaction hinders the rotation of the dipoles of the system. Non ideal behavior in Bruggeman plot confirms intermolecular interactions in AC-Alcohols. In this system the solution properties varies smoothly with solute composition reflecting hetero cooperative interactions.

REFERENCES