Study of Structural Properties of Polar Liquids in Binary Mixture Using Microwave Techniques

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ABSTRACT: The study of dielectric relaxation properties in the binary mixture of polar molecules has been carried out at 25°C temperature for 11 different concentrations using time domain reflectometry technique. The dielectric properties of solute-solvent mixture in the microwave frequency range of 10MHz to 30GHz gives information about the formation of monomers and multimers as well as interaction between the molecules of the mixture. The dielectric parameters viz static dielectric constant and relaxation time have been obtained from the least square fit method using Debye equation. In liquids, the molecule has rotational freedom and its dispersion occurs at microwave frequency. Hence studying the dielectric properties at microwave frequency will reveal the dielectric relaxation of polar molecules and its variation with respect to the interaction with the neighboring polar as well as non polar molecules.

KEYWORDS: Time domain reflectometry, Static dielectric constant, Relaxation time, excess properties.

I. INTRODUCTION

The study of dielectric properties not only gives the information regarding solute-solvent interaction in the binary mixture but also monomers and multimers [1-3]. In this work we report the dielectric properties at different concentrations of 1, 2-dichloroethane (DCE) and n,n-dimethylformamide (DMF). DCE is a non polar associative liquid and DMF is highly polar liquid. One with chloro group and the other with C=O respectively. It is very interesting to notice the interaction of DCE with DMF for 11 different concentrations. The main objective of this paper is to give brief information of dielectric properties in DCE- DMF system at 20°C using time domain reflectometry. The study of mixtures is most interesting. It is possible to approach the description of such mixtures in terms of the properties of the components with respect to the molecular interaction. The phenomena of dielectric relaxation of binary mixture of like and unlike molecules at microwave frequency has been carried out by many workers [4-8]. DCE and DMF have high polarity and strong solvating power, which makes them very effective in the industrial and technological applications.

II. LITERATURE WORK

The dielectric relaxation study provides useful information regarding solute-solvent interactions in liquid mixtures. The extensive studies have been done to understand these interactions on different types of binary mixtures having different molecular groups. In Microwave research laboratory, Department of Physics, Dr. B. A. M. University, Aurangabad and S. R. T. M. University, Nanded has done the work on the binary mixtures of various polar liquids such as tert. butyl alcohol-water [9], ethylene glycol-water [10], amide-water [11], 2-nitroacetophenon-ethanol [12], 2-propanol-water [13], N, N-dimethylformamide-water [14], aniline-methanol [15], p-flurophenylacetinitrile-methanol [16], methanol-algae [17], pyridine-amide [18], 2-ethoxyethanol, ethanol and 1-propanol in dimethyl formamide [19], aniline-alcohol [20], 2-ethoxethanol, ethanol and propane-1-ol in dimethyl sulfoxide [21], tetraphropheron in methanol and ethanol.
The solutions were prepared at 11 different volume percentage of DCE from 0% to 100%. Using volume percent mole fraction is calculated as

$$x_i = \frac{(v_i\rho_i/m_i)}{[\ (v_1\rho_1/m_1)+ (v_2\rho_2/m_2)\ ]}$$

where $m_i$, $v_i$ and $\rho_i$ represents the molecular weight, volume percent and density of the $i^{th}$ ($i=1,2$) liquids respectively.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Molecular weight (g/mol)</th>
<th>Density (g/cm$^3$)</th>
<th>This Work</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCE(C$_2$H$_4$CL$_2$)</td>
<td>98.959$^a$</td>
<td>1.25$^a$</td>
<td>10.2</td>
<td>10.42$^a$</td>
</tr>
<tr>
<td>DMF(C$_3$H$_7$NO)</td>
<td>87.122$^a$</td>
<td>3.8$^a$</td>
<td>38.37</td>
<td>38.25$^a$</td>
</tr>
</tbody>
</table>

where $a$ and $b$ are taken from the references [45-47].

II.2 APPARATUS

The dielectric spectra were obtained by the time domain reflectometry (TDR) technique [48-52]. Tektronix model number DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 has been used for the TDR. A repetitive fast rising voltage pulse with 18ps incident rise time was fed through coaxial line system of impedance 50 ohm. All measurements are carried out in open load condition. Sampling oscilloscope monitors changes in step pulse after reflection from the end of line. Reflected pulse without sample $R_X(t)$ and with sample $R_S(t)$ were recorded in time window of 5ns and digitized in 2000 points. The nature of reflected pulse with and without sample for DCE and DMF are observed.

III. DATA ANALYSIS

The time dependent data were carried out to obtain complex reflection coefficient spectra $\rho^{*}(\omega)$ over the frequency range of 10 MHz to 30 GHz using Fourier transformation [53-54]

$$\rho^{*}(\omega) = (c/j\omega d) [\rho(\omega)/q(\omega)]$$

where $\rho(\omega)$ and $q(\omega)$ are Fourier transforms of [$R_X(t)$-$R_S(t)$] and [$R_S(t)+R_X(t)$] respectively, $c$ is the velocity of light, $\omega$ is the angular frequency, $d$ is the effective pin length and $\lambda=\sqrt{1-j}$. The effective permittivity spectra $\varepsilon^{*}(\omega)$ were obtained from reflection coefficient spectra $\rho^{*}(\omega)$ by applying bilinear calibration method [55].

The experimental values of $\varepsilon^{*}$are obtained by Debye equation [56]

$$\varepsilon^{*}(\omega) = \varepsilon_\infty + \varepsilon_0 - \varepsilon_\infty/(1+j\omega\tau)$$

where $\varepsilon_0$, $\varepsilon_\infty$ and $\tau$ are fitting parameters. A nonlinear least square fit method [57] was used to determine the values of dielectric parameters.
The table 1 shows the comparison values of static permittivity practical with literature, molecular weights and density of pure liquids (DCE & DMF). The static dielectric constant value of DMF is greater than DCE it is due to presence of C=O. It may also depend upon molecular weight; lesser molecular weight liquids have more static dielectric constant.

IV. RESULTS AND DISCUSSIONS

By fitting experimental data in the Debye equation static dielectric constant ($\varepsilon_0$), dielectric constant at high frequency ($\varepsilon_\infty$) and relaxation time ($\tau$) obtained are listed in table2. The values of static dielectric constant decreases with increase in temperature as expected. However the relaxation time doesn’t follow a linear pattern.

The variation of static dielectric constant ($\varepsilon_0$) and relaxation time ($\tau$) with volume fraction is shown in fig. 1. As the concentration of DMF in DCE-DMF system increases the static dielectric constant values also increases.

The information related to liquid 1 and 2 may be obtained by excess properties [58] $\varepsilon^E$ is defined as

$$
\varepsilon^E = \left( \varepsilon_0 - \varepsilon_\infty \right) m - \left( \left( \varepsilon_0 - \varepsilon_\infty \right) x_1 + \left( \varepsilon_0 - \varepsilon_\infty \right) x_2 \right)
$$

(4)

where $x$ represents mole fraction and suffices m,1,2 represents mixture, liquid 1(DCE) and liquid 2 (DMF) respectively. The excess permittivity may provide qualitative information of multimers formation in the mixture as shown below:

1. $\varepsilon^E = 0$ indicates the liquid 1 (DCE) and 2 (DMF) doesn't interact at all.
2. $\varepsilon^E < 0$ indicates the liquid 1 and 2 interaction in such a way that the total effective dipoles get reduced. The liquid 1 and 2 may form multimers leading to the less effective dipoles.
3. $\varepsilon^E > 0$ indicates the liquid 1 and 2 interaction in such a way that the total effective dipoles moment increases. There is a tendency to form multimers, dipole aligned in parallel direction.

Similarly, the excess inverse relaxation time defined as

$$
(1/\tau)^E = (1/\tau)_m = \left( (1/\tau)_1 x_1 + (1/\tau)_2 x_2 \right)
$$

(5)

where $(1/\tau)_1$ is excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectra line broadening in the resonant spectroscopy [59].

<table>
<thead>
<tr>
<th>$x_2$</th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon_\infty$</th>
<th>$\tau$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (DCE)</td>
<td>9.89(0)</td>
<td>2.51</td>
<td>8.8(1)</td>
</tr>
<tr>
<td>10</td>
<td>13.56(0)</td>
<td>2.78</td>
<td>12.10(2)</td>
</tr>
<tr>
<td>20</td>
<td>16.58(0)</td>
<td>2.89</td>
<td>13.05(1)</td>
</tr>
<tr>
<td>30</td>
<td>19.43(1)</td>
<td>3.32</td>
<td>13.64(1)</td>
</tr>
<tr>
<td>40</td>
<td>23.05(0)</td>
<td>3.15</td>
<td>14.96(0)</td>
</tr>
<tr>
<td>50</td>
<td>23.57(0)</td>
<td>2.99</td>
<td>14.27(1)</td>
</tr>
<tr>
<td>60</td>
<td>28.32(0)</td>
<td>3.82</td>
<td>13.81(0)</td>
</tr>
<tr>
<td>70</td>
<td>31.15(0)</td>
<td>3.57</td>
<td>12.93(0)</td>
</tr>
<tr>
<td>80</td>
<td>32.86(0)</td>
<td>4.69</td>
<td>12.93(0)</td>
</tr>
<tr>
<td>90</td>
<td>36.08(1)</td>
<td>6.13</td>
<td>12.68(1)</td>
</tr>
<tr>
<td>100 (DMF)</td>
<td>37.26(1)</td>
<td>5.09</td>
<td>11.64(1)</td>
</tr>
</tbody>
</table>

where $x_2$ represents the volume fraction of DMF in DCE

4. $(1/\tau)^E = 0$ indicates there is no change in the dynamics of liquid 1 and 2 interaction.
5. $(1/\tau)^E < 0$ indicates the liquid 1 and 2 interaction produces a field such that the effective dipole rotates slowly.
6. $(1/\tau)^E > 0$ indicates the liquid 1 and 2 interaction produces a field such that the effective dipoles rotates fastly that is the field will cooperate in rotation of dipoles.
Fig. 1. (a) Static dielectric constant ($\varepsilon_0$), (b) relaxation time ($\tau$), versus volume fraction ($x_2$) of DMF in DCE for 11 different concentrations at 25ºC.

The variation of $\varepsilon^E$ and $1/\tau^E$ with mole fraction DMF 25ºC are shown in fig 2. The experimental values of both the excess parameters were fitted to the Redlich Kister equation [60-61].

$$A^E = (x_1x_2) \sum B_n (x_1-x_2)^n$$

(5)

where $A$ is either $\varepsilon^E$ or $1/\tau^E$. By using these $B_n$ values, $A^E$ value were calculated and with these values smooth curve is drawn as shown in fig 2.

Fig. 2. (a) Excess permittivity ($\varepsilon^E$), (b) Excess inverse relaxation time ($1/\tau^E$), versus mole fraction ($x_2$) of DMF in DCE for 11 different concentrations at 25ºC.

III. CONCLUSION

Dielectric properties have been for DCE-DMF system for 11 different concentrations at 25ºC temperature. This work provides the information about molecular interaction as well as structural changes. The static dielectric constant increase, due to increase in the concentration of DMF in DCE. The relaxation time of DMF is found to be much higher to that of DCE. The value of relaxation time in the solution increases exponentially with an increase in concentration of NMF. The excess properties indicate the structural changes in the system. It is due to intermolecular interaction of the chloro group with C=O bonded liquids. The dielectric parameter shows systematic change with concentration. The excess dielectric constant values evaluated from mole fraction mixture conclude that these mixtures have intermolecular interactions.

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REFERENCES


