Dielectric Relaxation Studies of Ethyl Formate with Primary Alcohols using Time Domain Reflectometry

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ABSTRACT

Dielectric relaxation studies of ethylformate with 1-propanol, 1-butanol and 1-pentanol binary mixtures have been carried out at micro frequency range 9.36 GHZ at temperature of 303K. Different dielectric parameters like dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), static dielectric constant ($\varepsilon_0$) and dielectric constant at optical frequency ($\varepsilon_\infty$) have been determined. The Relaxation time ($\tau$) has been obtained by Higasi and Cole-Cole method. The dielectric constant ($\varepsilon_0$) and relaxation time ($\tau$) decreased with increasing the concentration of ethylformate in alcohol system. The relaxation time ($\tau$) increased with increase in chain length of the alcohols. The result shows that the strength of this molecular interaction depends upon the carbon chain length of the alcohols. Hence the proton donating ability of alcohols is in the order of 1-propanol<1-butanol<1-pentanol

Key words: Ethyl formate, Dielectric relaxation, Alcohols.

INTRODUCTION

The dielectric relaxation studies are one of the useful techniques to elucidate the nature of interactions that exist in solute-solvent component of a system. Jianhuattu et al have studied the excess enthalpies, excess isobaric heat capacities, densities and speeds of sound of the mixtures ethyl formate + benzene, + ethanol, and + 2,2,2-trifluoroethan-1-ol, at 298.15 K. Ethylformate is an ester. P.k.Choi et al have observed rotational isomeric relaxations in methyl and ethyl formates using the Plano-concave ultrasonic resonator method. It is used in the lacquer industry as a solvent for cellulose nitrate. It is also used as fumigant and larvacide or tobacco. It is a highly attractive option for bulk disinfestations of unprocessed dried fruit during ware housing. The molecular interaction studies of liquid mixtures with alcohols as one of the components is of particular interest, since alcohols are highly polar and self associated through hydrogen bonding. The carbonyl group (C=O) present in the ethyl formate tends to participate in hydrogen bonding interactions with hydroxyl (OH) group of alcohols. The present work is an attempt to study the molecular interactions between of ethyl formate with 1-Propanol, 1-Butanol and 1-pentanol using time domain reflectometry technique at 303K.

MATERIALS AND METHODS

Ethylformate and alcohols of AR grade were obtained from E-Merck India and used with out further purification. The purity of liquids analysed with the standard physical quality values. The dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) have been measured using X-band microwave frequency oscillator of frequency 9.36 GHZ at 303K. The refractive index ($\mu$) of all the solutions has been measured by Abbe’s refractometer. The viscosities were measured with the help of Ostwald’s viscometer. The densities were measured by using 5cc specific gravity bottle.

Higasi’s Method

The dielectric relaxation time ($\tilde{\tau}$) was calculated using Higasi’s method. Assuming
\( \varepsilon_0, \varepsilon', \varepsilon'' \) and \( \varepsilon_\infty \) vary linearly with weight fraction \( w_2 \) of the solute. The slopes \( a_0, a', a'' \) and \( a_\infty \) determined from the determined values. We have

\[
\begin{align*}
\varepsilon_0 &= \varepsilon_1 + a_0 w_2 \\
\varepsilon' &= \varepsilon_1 + a' w_2 \\
\varepsilon'' &= a'' w_2 \\
\varepsilon_\infty &= \varepsilon_1 + a_\infty w_2 \\
\tau_1 &= \frac{a'}{\omega (a' - a_\infty)} \\
\tau_2 &= \frac{(a_\infty - a')}{\omega a'} \\
\tau_0 &= \sqrt{\frac{\tau_1 \tau_2}{\tau_1 + \tau_2}}
\end{align*}
\]

Here \( \tau_0 \) is the mean relaxation time. The free of activation of dielectric relaxation \( \Delta F \) and viscous flow have been calculated using Eyring’s equation

\[
\tau = \left( \frac{h}{kT} \right) \exp \left( \frac{\Delta F}{RT} \right)
\]

\( \eta = \left( \frac{Nh}{R\gamma} \right) \exp \left( \frac{\Delta F_\eta}{RT} \right)
\]

Where \( h \) is Planck’s constant, \( k \) is Boltzmann constant, \( N \) is Avogadro number and \( V \) is the molar volume.

**Cole-Cole Method**

The measured values of \( \varepsilon_0, \varepsilon', \varepsilon'' \) and \( \varepsilon_\infty \) are fitted in a complex plane plot with a depressed circular arc. The angle made by the diameter drawn through the centre from the \( \varepsilon_\infty \) point and the abscissa axis is equal to \( \pi \alpha/2 \). From the Cole-Cole arc, the relaxation time \( \tau \) can be found using the equation

**Table 1: Values of dielectric constant(\( \varepsilon_0 \)), relaxation time(\( \tau \)) of ethylformate with alcohols at 303K**

<table>
<thead>
<tr>
<th>Volume % of alcohols</th>
<th>( \varepsilon_0 )</th>
<th>( \varepsilon' )</th>
<th>( \varepsilon'' )</th>
<th>( \varepsilon_\infty )</th>
<th>Relaxation Time ( \tau ) (ps)</th>
<th>Activation energy ( \Delta F )</th>
<th>( \Delta F_\eta )</th>
<th>kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System : Ethylformate with 1-Propanol</strong></td>
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</tr>
<tr>
<td>0</td>
<td>3.243 2.642 0.248</td>
<td>2.219 15.78 19.89 17.67</td>
<td>8.057 11.86 13.55</td>
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<tr>
<td>25</td>
<td>3.121 2.677 0.269 2.215 16.37 20.43 18.29</td>
<td>8.568 12.29 13.98</td>
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<tr>
<td>75</td>
<td>2.874 2.661 0.284 2.225 16.03 21.25 18.46</td>
<td>12.521 12.38 14.01</td>
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<tr>
<td>100</td>
<td>2.785 2.636 0.273 2.209 15.62 19.71 17.55</td>
<td>13.126 11.76 13.52</td>
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<tr>
<td><strong>System : Ethylformate : 1-Butanol</strong></td>
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<tr>
<td>0</td>
<td>3.069 2.541 1.209 3.068 18.52 26.0 21.98</td>
<td>24.583 12.22 13.92</td>
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<tr>
<td>25</td>
<td>2.930 2.539 0.191 2.929 16.69 21.47 18.93</td>
<td>17.846 11.98 12.92</td>
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<tr>
<td>50</td>
<td>2.928 2.538 0.192 2.929 16.28 23.35 19.50</td>
<td>25.631 10.09 12.81</td>
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<td>2.821 2.518 0.179 2.821 15.67 18.38 16.97</td>
<td>17.125 11.32 13.04</td>
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<tr>
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<td>2.819 2.527 0.181 2.818 15.65 19.44 17.44</td>
<td>26.783 11.62 12.25</td>
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<tr>
<td><strong>System : Ethylformate : 1-Pentanol</strong></td>
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<td>0</td>
<td>3.047 2.572 0.219 2.241 20.03 30.28 24.63</td>
<td>28.615 12.07 13.97</td>
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<td>25</td>
<td>2.892 2.547 0.191 2.232 18.49 25.65 21.77</td>
<td>22.928 11.76 13.25</td>
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<td>29.742 11.99 12.32</td>
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<tr>
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<td>22.437 11.08 12.94</td>
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<tr>
<td>100</td>
<td>2.748 2.479 0.176 2.223 17.29 20.47 18.81</td>
<td>30.875 11.43 12.20</td>
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</tbody>
</table>
\((\omega t)^{1-\alpha} = V/U\) \ldots(5)

Where \(\omega\) is the angular frequency of the micro wave and \(\alpha\) can be obtained from the Cole-Cole plot.

RESULTS AND DISCUSSION

The dielectric parameters of the selected system have been reported as shown in the table 1. The relaxation time depends up on the size and shape of the rotating molecular entities in the liquid mixture. Here the relaxation time \((\tau)\) values increase while increase in the concentration of alcohols. This trend may show that the hydrogen bond formation between the C=O group of ethyl formate and the O-H group of the alcohol. Similar conclusions have been reported by Dharmalingam \(8\). Table-1 signified that the \(\varepsilon_0\) value gradually decreased with increasing the carbon atom present in the alkyl chain of the alcohols. This trend may show that the decrease in the number of dipoles in the complex, which lead to a decrease in the molar volume of the rotated molecules. It is evident from this study that the molar free energy of activation for viscous flow \((\Delta F_\eta)\) is greater than the free energy activation over dielectric relaxation \((\Delta F_\tau)\). It may revealed that the viscous flow involved both the rotational and translation form of motion. Similar results were reported as earlier \(9,12\). The result shows that the strength of this molecular interaction depends upon the carbon chain length of the alcohols. Hence the proton donating ability of alcohols is in the order of 1-propanol<1-butanol<1-pentanol.

CONCLUSION

Dielectric relaxation parameters have been reported in the paper for primary alcohols with ethylformate in various concentrations at 303K, the relaxation time increases with increasing acidity of proton donor complex systems. The systematic change of dielectric parameters with alcohols show that the proton donating ability of alcohols is in the order of 1-propanol<1-butanol<1-pentanol.

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REFERENCES