Studies on dielectric properties of cyclohexylamine in non-polar solvents—Kirkwood correlation factor, molar polarization and excess free energy

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The study of the dielectric properties of binary mixture of cyclohexylamine (CHA) in non-polar solvents such as benzene, n-heptane and 1,4-dioxane has been investigated. The low frequency molecular dynamics of CHA molecule have been studied by evaluating the Kirkwood correlation factor \((g)\), molar polarization \((p_2)\), excess correlation factor \((\delta\xi)\) and excess free energy \((\Delta G_\text{ex})\). The observed values of \(g\) significantly deviated from unity, which confirm the inter-molecular association in CHA molecule in dilute solutions. The presence of \(\alpha\)- and \(\beta\)-multimers in the above system was identified. CHA establishes H-bonding with oxygen of 1,4-dioxane resulting in reinforcement of inter-molecular association and causes higher values of \(g\) as compared to benzene and n-heptane. The high frequency molecular dynamics were examined using \(8.93\) GHz, which reveals that a single relaxation process exists in CHA. These parameters have been used to throw light on the dynamic characteristics of molecular association in these binary mixtures of polar-non-polar liquids.

[Keywords: Dielectric properties, Non-polar solvents, Kirkwood correlation factor, Molar polarization, Excess free energy]

1 Introduction

Investigations on dielectric properties of a polar liquid in its mixture with non-polar solvent are regarded as useful tools for interpreting liquid structure in mixture. These investigations include evaluation of relaxation times, dipole moment, distribution parameter, Kirkwood correlation factor, molar polarization and excess free energy of activation. The experimentally determined values of dielectric constant of binary mixture of an associated liquid with non-polar solvent can be used for the evaluation of \(g\) and, as such, for the interpretation of liquid structure. In this context, the significant structure model proposed by Eyring & John is helpful in understanding the solute-solute interaction in associated system.

The correlation factor \((g)\) is a shape-dependent correlation factor and is a measure of short-range inter-molecular force leading to dipole-dipole interaction. \(g\) is also an useful index to the degree of hindered rotation in a liquid. \(g > 1\) indicates predominance of \(\alpha\)-multimers with parallel dipolar orientation, whereas \(g < 1\) indicates the predominance of \(\beta\)-multimers with anti-parallel orientation. On dilution of an associated liquid with a non-polar solvent, the value of \(g\) undergoes a change, signifying change in the nature of multimerization.

Several attempts have been made to study the associating behaviour of alcohols, mono-alkyl ethers, ortho and para substituted benzaldehydes, amines, di-isobutyl ketone by evaluating molar polarization, Kirkwood correlation factor, dipole moment and dielectric relaxation in dilute solutions of non-polar solvents and also in pure liquid state.

In the present paper, an attempt has been made to study the molecular association in cyclohexylamine in the dilute solutions of benzene, 1,4-dioxane and n-heptane by determining above parameters.

2 Theory

The Kirkwood correlation factor \((g)\) has been calculated by the modified Kirkwood-Forhlich
equation for dilute solutions in non-polar solvent.

$$g = \frac{K T (2 \varepsilon_m + \varepsilon_\infty)}{4 \pi N f_2 (\varepsilon_\infty + 2)^2 (2 \varepsilon_m + 1)}$$

$$\left[ \frac{V (\varepsilon_m - 1)}{2 \varepsilon_m + \varepsilon_\infty} \right] - \frac{3 V f_1 (\varepsilon_1 - 1)}{2 \varepsilon_m + \varepsilon_\infty} - \frac{3 V f_3 (\varepsilon_\infty - 1)}{2 \varepsilon_m + \varepsilon_\infty}$$

$$(1)$$

where $\varepsilon_m$ is the static dielectric constant of the solution, $\varepsilon_\infty$ the square of refractive index at the frequency of D-lines of sodium for pure solute, $\varepsilon_1$ the static dielectric constant of pure solvent, $f_1$ the mole fraction of the solvent, $f_3$ the mole fraction of the solute, $V$ the molar volume of the solution and $V_1$ and $V_2$ are the molar volume of pure solvent and pure solute, respectively. $K, T$ and $N$ are Boltzmann's constant, absolute temperature and Avogadro's number, respectively. Molar polarization of solutions is:

$$P = f_1 P_1 + f_3 P_3$$

$$(2)$$

from which the molar polarization of the solute is:

$$P_3 = P_1 + \left[ \frac{(P - P_1)}{f_2} \right]$$

$$(3)$$

where $P_1$ is the molar polarization of the solvent, which is given by:

$$P_1 = \left[ \left( \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \right) V_1 \right]$$

$$(4)$$

and $P$ is the molar polarization of the solution which is given by:

$$P = \left[ \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) V \right]$$

$$(5)$$

The calculated values of $g$ are plotted against percentage (%) mole fraction of the solute.

The excess Gibb's free energy of mixing $\Delta G_i$ in the binary mixture of an associated liquid and a non-polar solvent is given by the expression as used by Ray & Roy:

$$\Delta G_i = \frac{N}{2} \left( R_2 - R_2^0 \right) f_3 \mu^2 \left\{ f_2 (g - 1) + 1 \right\}$$

$$(6)$$

where

$$R_2^0 = \frac{8 \pi N (\varepsilon_m - 1) (\varepsilon_\infty + 2)}{9 V_2 (2 \varepsilon_m + \varepsilon_\infty)}$$

and

$$R_2 = \frac{8 \pi N (\varepsilon_m - 1) (\varepsilon_\infty + 2)}{9 V_2 (2 \varepsilon_m + \varepsilon_\infty)}$$

$\varepsilon_i$ is the dielectric constant for pure solute (CHA).

The excess correlation function $\delta g$ in the binary mixture is given by:

$$\delta g = g - (g_1 f_1 + g_2 f_2)$$

$$(7)$$

The expression for excess free energy of mixing in Eq. (6) mainly depends on $\varepsilon_1 - \varepsilon_\infty$. Hence, $\Delta G_i$ values have similar type of variation for all the mixtures. Therefore, the result does not reflect any specific structural correlation between the solute and solvent molecules. So, the authors have substituted the excess correlation factor $\delta g$ in place of $g$ in Eq. (6). Hence, the excess free energy of mixing for the binary mixture of polar and non-polar liquids can be expressed as:

$$\Delta G_n = -\frac{N}{2} \left( R_2 - R_2^0 \right) f_3 \mu^2 \left\{ f_2 (\delta g - 1) + 1 \right\}$$

$$(8)$$

It has been observed that, static permittivity ($\varepsilon_\infty$), dielectric constant ($\varepsilon'$), loss factor ($\varepsilon''$) and high frequency limiting permittivity ($\varepsilon_\infty$) are linear functions of the concentration of solute for these molecules in dilute solutions of benzene, 1,4-dioxane and n-heptane. The linear slopes $\alpha_0, \alpha', \alpha''$ and $\alpha_n$ corresponding to $\varepsilon_\infty, \varepsilon', \varepsilon''$ and $\varepsilon_n$ versus weight fraction of solute at different concentrations have been used for the determination of the relaxation times and molecular dipole moment. The average relaxation time ($\tau_\infty$) and distribution parameter ($\alpha$) were calculated by Higasi's method. The relaxation times $\tau(1)$ and $\tau(2)$ have been determined by Higasi et al.'s method. Molecular dipole moments of these molecules have been calculated using Higasi's method.

3 Experimental Details

Compounds used in the present study of AR grade were all procured from BDH, India. 1,4-dioxane, benzene and n-heptane were distilled twice before use.

The dielectric constant $\varepsilon'$ and the dielectric loss $\varepsilon''$ at 8.93 GHz microwave frequency, were computed by the method of Heston & Smyth. The accuracy of measurement in the values of $\varepsilon'$ and $\varepsilon''$ are of the order of ±1% and ±5%, respectively. The
dielectric constant $\varepsilon_a$ at 100 kHz was measured using a dipole meter by directly measuring the capacitance and calibrating it for standard liquids. The dielectric constant ($\varepsilon_a$) at optical frequency was obtained by squaring the refractive index for sodium D-lines, measured with the help of an Abbe's refractometer.

The density measurements were made with a pyknometer. All measurements were made at constant temperature 313K.

![Graph showing variation of Kirkwood correlation factor with mole fraction of cyclohexylamine](image)

**4 Results and Discussion**

Fig. 1 shows the Kirkwood correlation factor ($g$) value for cyclohexylamine plotted against percentage mole fraction of solute ($f_2$) in the dilute solutions of benzene, $n$-heptane and 1,4-dioxane. For benzene and $n$-heptane, observed $g$ values are greater than and less than unity, which shows that, these molecules associate to form multimers with parallel dipole moment and also with anti-parallel dipole moment. This indicates that, $\alpha$-multimers are converted into $\beta$-multimers with increasing the concentration of CHA in the mixture. As far as the trend of 1,4-dioxane is concerned, it was found that, $g$ values were greater than 1 indicating the presence of $\alpha$-multimers. As the dilution decreases, $g$ values decrease. This trend shows that, if we further decrease the dilution, there may be presence of $\beta$-multimers also. The deviation of $g$ value from unity is the measure of molecular interaction. Among the systems studied above, the deviation of $g$ value from unity is such that, molecular interaction is in the order of the system 1,4-dioxane>$n$-heptane>benezene. This is in accordance with the obtained values of $g$, as shown in Table 1, at same mole fraction (0.07) for all the three systems. It is also found that, $g$ values for 1,4-dioxane are comparatively towards higher side than those of $n$-heptane and benzene. This may be attributed to the fact that, CHA established H-bonding with oxygen of 1,4-dioxane and results in reinforcement of inter-molecular association of CHA molecule and hence increases the value of $g$. But, there is no such possibility of H-bonding for other two systems. Similar results were obtained by Acharya et al.7 in the case of dioxane for di-isobutyl ketone (DBK). Table 1 shows that, $P_2$ values in all the mixtures are positive and these are found to be in the order 1,4-dioxane>$n$-heptane>benezene, when the results are compared at about the same concentration. In all the three solvents, molar polarization ($P_2$) follows the Kirkwood correlation factor ($g$) i.e., at higher values of $g$, molar polarization is large while for lower $g$ values, it is small.

The excess correlation function $\delta g$ and excess free energy $\Delta G_0$ values for the binary mixtures of CHA in benzene, $n$-heptane and 1,4-dioxane are presented in Table 1. The excess correlation factor $\delta g$ is similar to that of Winkelmann & Quitzsch9 ($g_{eqv}$-1). The excess free energy $\Delta G_0$ is positive in all the cases. $\Delta G_0$ values were observed to be lowest in 1,4-dioxane as compared to the other two solvents. This supports our earlier finding that, interaction 1,4-dioxane is stronger than that of benzene and $n$-heptane. For solvent-rich region, there is reinforcement of correlation, resulting in more $\alpha$-multimers and, hence, there is a fall in the value of $\Delta G_0$.

The values of most probable relaxation time ($\tau_m$), the relaxation times $\tau(1)$ and $\tau(2)$, the molecular dipole moment ($\mu$) and distribution parameter ($\alpha$) are given in Table 2. It is evident from Table 2 that, average relaxation time ($\tau_m$) of CHA in non-polar solvent is in the order of 1,4-dioxane >benezene >n-
Table 1 — Values of $\epsilon_0$, $g$, $P_2$, $\delta g$, $\Delta G_1$ and $\Delta G_{11}$ with concentration in different solvents at 313K

<table>
<thead>
<tr>
<th>$f_2$</th>
<th>$\epsilon_0$</th>
<th>$g$</th>
<th>$P_2$ (CC)</th>
<th>$\delta g$</th>
<th>$\Delta G_1$ (J/mole)</th>
<th>$\Delta G_{11}$ (J/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01141</td>
<td>2.316</td>
<td>1.37</td>
<td>101.64</td>
<td>0.88</td>
<td>7.19</td>
<td>7.20</td>
</tr>
<tr>
<td>0.01887</td>
<td>2.344</td>
<td>1.27</td>
<td>96.69</td>
<td>0.58</td>
<td>11.66</td>
<td>11.60</td>
</tr>
<tr>
<td>0.02622</td>
<td>2.356</td>
<td>1.06</td>
<td>85.96</td>
<td>0.29</td>
<td>16.06</td>
<td>15.81</td>
</tr>
<tr>
<td>0.05075</td>
<td>2.444</td>
<td>1.07</td>
<td>85.86</td>
<td>0.19</td>
<td>29.14</td>
<td>28.13</td>
</tr>
<tr>
<td>0.06256</td>
<td>2.456</td>
<td>0.94</td>
<td>78.99</td>
<td>0.03</td>
<td>35.57</td>
<td>33.69</td>
</tr>
<tr>
<td>0.07407</td>
<td>2.496</td>
<td>0.95</td>
<td>79.66</td>
<td>0.04</td>
<td>40.88</td>
<td>38.34</td>
</tr>
<tr>
<td>0.09627</td>
<td>2.544</td>
<td>0.89</td>
<td>76.27</td>
<td>0.04</td>
<td>51.22</td>
<td>46.67</td>
</tr>
</tbody>
</table>

| $n$-Heptane |
| 0.02510 | 2.00 | 2.81 | 191.62 | 1.76 | 21.77 | 21.02 |
| 0.03318 | 2.012 | 2.43 | 169.88 | 1.36 | 27.16 | 25.71 |
| 0.037718 | 2.028 | 2.23 | 158.39 | 1.15 | 32.44 | 30.15 |
| 0.07752 | 2.064 | 1.13 | 101.47 | 0.06 | 71.42 | 56.57 |
| 0.11368 | 2.164 | 1.21 | 99.89 | -0.04 | 104.52 | 73.73 |
| 0.15033 | 2.192 | 0.96 | 86.04 | -0.36 | 144.34 | 86.22 |
| 0.18110 | 2.216 | 0.84 | 78.72 | -0.56 | 179.77 | 92.20 |

| 1,4-dioxane |
| 0.06231 | 2.608 | 3.20 | 127.53 | 2.17 | 19.77 | 20.64 |
| 0.07463 | 2.619 | 2.76 | 114.20 | 1.73 | 23.61 | 24.08 |
| 0.08931 | 2.620 | 2.32 | 101.25 | 1.28 | 28.43 | 28.02 |
| 0.09162 | 2.621 | 2.27 | 99.72 | 1.23 | 29.17 | 28.61 |
| 0.11365 | 2.622 | 1.85 | 87.25 | 0.89 | 36.51 | 33.96 |
| 0.13201 | 2.623 | 1.61 | 80.05 | 0.55 | 42.73 | 37.95 |
| 0.15642 | 2.630 | 1.40 | 73.64 | 0.33 | 50.88 | 42.53 |
| 0.19629 | 2.642 | 1.16 | 66.60 | 0.07 | 64.36 | 48.38 |

Table 2 — Values of slopes $a_0$, $a'$, $a''$, $a_\infty$ relaxation times $\tau_0$, $\tau(1)$, $\tau(2)$, dipole moment $\mu$ and distribution parameter $\alpha$.

<table>
<thead>
<tr>
<th>Solute cyclohexylamine</th>
<th>Temperature 313 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>$a_0$</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.54</td>
</tr>
<tr>
<td>$n$-Heptane</td>
<td>2.00</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>2.25</td>
</tr>
</tbody>
</table>

heptane. Similar results were obtained by Purohit & Sengwa$^{15}$. Density of solvent plays an important role in deciding the average relaxation time ($\tau_0$).

Higher density of the solvent produces large hindrance and results in the higher values of relaxation time. Densities of the solvents are in the order 1,4-dioxane (density= 1.032) $>$ benzene (density=0.867) $>$ $n$-heptane (density= 0.666) at 40$^\circ$C, respectively. The same is the order of average relaxation time. Similar effects of bulky solvent on average relaxation time have been observed earlier in monoalkyl ethers of ethylene glycol, monoalkyl ethers of diethylene glycol$^{15}$, polyethylene glycols$^{16}$. The appreciable increase of relaxation times ($\tau_0$), $\tau(1)$ and $\tau(2)$ in 1,4-dioxane may be considered anomalous, because of inter-molecular H-bonding other than the density effect which contributes to the large value of relaxation times of CHA in it. Table 2 shows that, the values of $\tau_0$, $\tau(1)$ and $\tau(2)$ for CHA molecule are almost the same in the dilute solutions of all three non-polar solvents. This shows that, a single relaxation process exist in CHA molecule i.e. no intra-molecular relaxation process exist in CHA.
molecule, because the presence of this relaxation process might have caused significant difference between \( \tau(1) \) and \( \tau(2) \). Table 2 also shows that, the values of distribution parameter (\( \alpha \)) for CHA in the dilute solutions of all three non-polar solvents under investigation is very small. A very small value of \( \alpha \) was reported by Vyas \textit{et al.}\(^{27} \) for pyridine, suggesting a simple Debye type relaxation behaviour of the system. This is a usual behaviour of rigid polar molecules, which generally exhibit a simple Debye relaxation pattern.

The dipole moment values (\( \mu \)) are also shown in Table 2. The dipole moment (\( \mu \)) of CHA in 1,4-dioxane are comparable well with the values reported by Chelliah \& Sabesan\(^{18} \). The values of \( \mu \) do not show any direct relationship with relaxation times, although \( \mu \) is one of the various factors involved in influencing the relaxation mechanism. This suggests that, other factors like size and shape of the molecule, the intra-molecular forces and solute-solute interaction play an important role in the relaxation mechanism.

5 Conclusions

The presence of \( \alpha \)- and \( \beta \)-multimers is noticed in binary mixtures of cyclohexylamine in different non-polar solvents such as, benzene, \( n \)-heptane and 1,4-dioxane. Higher \( g \) values in 1,4-dioxane as compared to benzene and \( n \)-heptane is attributed to the fact that, CHA established H-bonding with oxygen of 1,4-dioxane and results in reinforcement of inter-molecular association of CHA molecule and hence increases the value of \( g \). The high frequency molecular dynamics reveal that, a single relaxation process exists in CHA.

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References