Studies on fluid structure and molecular interactions of amides

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Fluid structure in amides could be readily studied by dielectric measurements by virtue of the influence of local order and the overall dipole moment. The short-range interactions between permanent dipoles could be described by the Kirkwood-Frohlich correlation factor. In dilute solutions of amides with inert solvents, the interaction between the solute species among themselves may be given by the modified form of the correlation factor \(g'(r)\) by taking care of solvent-solvent interaction. The dielectric constants of the binary mixtures of acrylamide, acetamide, benzamide and phthalimide in 1,4-dioxan were measured at 298, 308 and 318 K. The results were interpreted in the light of the theory. The nature of interaction was identified in all systems.

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**Keywords:** Dielectric constant, Kirkwood correlation factor, H-bond, Multimers

1 Introduction

Dielectric studies are of great help in the assignment of the molecular structures or configurations, particularly those of organic compounds. Although infrared (IR), ultrasonic and nuclear magnetic resonance (NMR) studies are the powerful tools for studying intermolecular H-bonds, dielectric studies provide very useful information about molecular association and intermolecular rotation. Determination of the modified Kirkwood correlation factor \(g'(r)\) provides the information about intermolecular association in the associating molecules. The solute-solvent interactions in associated systems are better understood by the significant structure model proposed by Eyring and John. It is possible to reconcile the data obtained from static dielectric measurements by measuring the dielectric relaxation\(^1\). The survey of literature shows that very little work on amides has been reported. Ultrasonic studies on alcohol-amide (formamide, acetamide, NN-dimethyl acetamide and benzamide) binary mixtures have been reported by many researchers. Mehrotra and Pawar\(^9\) had studied interaction of chlorobenzene with dimethyl formamide using dielectric studies. Mesrieh\(^11\) reported the dielectric absorption of \(p\)-hydroxy N-phenyl maleimide. The \textit{ab-initio} calculations have been carried out on formamide and N-methyl acetamide\(^12\). A number of researchers have reported dielectric relaxation studies on amides\(^13\). Some work on ultrasonic studies of amine-alcohol mixture was reported\(^18\). In this context, the variation of linear correlation factor was studied with composition and temperature for the binary systems. The following binary systems acrylamide in 1,4-dioxan (I), acetamide in 1,4-dioxan (II), benzamide in 1,4-dioxan (III) and phthalimide in 1,4-dioxan (IV) were studied, based on Kirkwood-Frohlich model.

2 Materials and Methods

The dielectric constant was measured at 1 kHz using a digital VLCR-7 meter supplied by M/s Vasav Electronics, Secunderabad. The scale of the instrument was calibrated using standard liquids like carbon tetrachloride, benzene, toluene and chlorobenzene. The temperature was maintained at 298±3,08±3,318±1 K using a water bath supplied by M/s Raaga Industries, Chennai. The refractive indices were measured using Abbe’s refractometer. Densities were determined using a 10 ml specific gravity bottle and a K-Ray microbalance. Amides were obtained from M/s S.D. Fine-chemicals Ltd., Mumbai and they were used as solutes. Extrapure AR grade 1, 4-dioxan was obtained from SRL Pvt. Ltd., Mumbai and it was purified by standard methods. The uncertainties in the measurement
of dielectric constants, refractive indices and densities were ± 0.0001, ± 0.0002 and ± 0.0001 gm/cc respectively.

3 Theory

Attractive forces, dipole-dipole interactions and other slowly varying interactions play a role in the structure of the liquids. The modern theories of liquids show that the repulsive intermolecular forces dominate the structure of the denser fluids.

In the case of associated liquids it is almost impossible to account for their dielectric behaviour in the continuum approach and one has to recourse to the theories based on the statistical mechanical approach of the dielectric constants. Theoretical interpretations of the measured dielectric constants of associated liquids were enhanced by the Kirkwood’s theory of dielectric polarization which was later modified by Frohlich. The Kirkwood-Frohlich treatment takes care of short range correlations like hydrogen bonding through the introduction of the dimensionless correlation parameter \( g' \).

The interactions between the polar solute and the non-polar solvent may be considered by a modification of the Kirkwood correlation factor, which takes into account the interactions between the solvent molecules among themselves. If \( g' \) is the linear correlation factor of dielectric polarization between the solute and the solvent species, one can write:

\[
g' = [B(T) - w_1 B_1(T)] \frac{27kM_2}{(n^2 + 2)^2 4 \pi N_A w_2} \times \ldots (1)
\]

where \( \langle \mu_2^2 \rangle \)

\[
B_1(T) = \frac{(\varepsilon - n^2)(2\varepsilon_n + n^2)T}{3\varepsilon \rho}
\]

and

\[
B(T) = \frac{(\varepsilon - n^2)(2\varepsilon + n^2)T}{3\varepsilon \rho}
\]

where \( \varepsilon, n \) and \( \rho \) represent the static dielectric constant, refractive index and the density of the solution respectively and the suffix 1 indicates the solvent, \( k \) is the Boltzmann constant, \( \langle \mu_2^2 \rangle \) is the squared dipole moment of the polar species, \( w_1 \) and \( w_2 \) are the weight fractions of the solvent and solute, \( M_2 \) is the molecular weight of the polar solute and \( N_A \) is the Avagadro number. The value of \( g' \) can be determined for different concentrations by measuring the dielectric constant, refractive index and density of the solutions.

4 Discussion

The variations of density, refractive index, dielectric constant and Kirkwood-Frohlich correlation factor \( g' \) with concentration of the liquids for the systems I, II, III and IV at 298 K are given in Table 1. The variation of \( g' \) with concentration of amides at temperatures 298, 308 and 318 K is given in Fig 1. It is found that the value \( g' \) increases with increase of dilution in all the systems studied. Except for the system I, \( g' \) increases with the increase of temperature. For the systems II, III and IV, \( g' \) is the maximum at higher dilution.

Many researchers have interpreted the fluid structure using the Kirkwood correlation parameter. The deviation of \( g' \) from unity is a measure of the molecular interaction. If the interactions in the system result in an average orientation of the neighbours parallel to the orientation of the representative dipole, the average correlation is positive and \( g' > 1 \). On the other hand, if the interactions result in an average orientation of the neighbours anti-parallel to the orientation of the representative dipole, the average correlation is negative and \( g' < 1 \). If \( g' \) is unity, it means that fixing the position of one dipole does not influence the position of the others except through the long-range electrostatic forces. It is found that \( g' > 1 \) for all amides studied here. This indicates the presence of \( \alpha \) multimers. High values of \( g' \) at higher dilution may be due to the interactions between the solute molecules. At high dilution, solute molecules may be considered to be in a cage of solvent molecules. Hence solute-solute interaction may exist. The very high values of \( g' \) are explained as follows: The amide molecules are planar and cannot form closed dimers. The formation of linear multimers is favoured as proposed by Cole and Dannhauser. The rotation about the hydrogen bond is more restricted, the correlation between the dipoles in chain increases, leading for this type of molecules to higher values of \( g' \). As dilution decreases, \( g' \) decreases. This may be explained as follows: With the decrease of dilution, more solute molecules may be available for the interaction with solvent molecules. This may lead to the rupture of the H-bonds between the solute molecules and the solute molecules may tend to interact with the
Table 1 – Variation of density, refractive index, dielectric constant and $g'$ with concentration at 298 K.

<table>
<thead>
<tr>
<th>System</th>
<th>$x_i$</th>
<th>$d$ gm/cc</th>
<th>$n$</th>
<th>$\varepsilon_1$</th>
<th>$g'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylamide</td>
<td>0.0277</td>
<td>1.0308</td>
<td>1.4245</td>
<td>3.2160</td>
<td>1.79</td>
</tr>
<tr>
<td>+</td>
<td>0.0361</td>
<td>1.0369</td>
<td>1.4250</td>
<td>3.4464</td>
<td>1.64</td>
</tr>
<tr>
<td>1,4-dioxan</td>
<td>0.0361</td>
<td>1.0351</td>
<td>1.4248</td>
<td>3.7024</td>
<td>1.73</td>
</tr>
<tr>
<td>Acetamide</td>
<td>0.0277</td>
<td>1.0335</td>
<td>1.4245</td>
<td>3.9328</td>
<td>1.66</td>
</tr>
<tr>
<td>+</td>
<td>0.0481</td>
<td>1.0357</td>
<td>1.4248</td>
<td>3.9328</td>
<td>1.66</td>
</tr>
<tr>
<td>1,4-dioxan</td>
<td>0.0395</td>
<td>1.0341</td>
<td>1.4250</td>
<td>4.2144</td>
<td>1.54</td>
</tr>
<tr>
<td>Benzaamide</td>
<td>0.0179</td>
<td>1.0335</td>
<td>1.4245</td>
<td>2.5248</td>
<td>3.94</td>
</tr>
<tr>
<td>+</td>
<td>0.0293</td>
<td>1.0332</td>
<td>1.4245</td>
<td>2.8832</td>
<td>1.83</td>
</tr>
<tr>
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<td>1.0340</td>
<td>1.4250</td>
<td>3.4720</td>
<td>1.47</td>
</tr>
<tr>
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<td>0.0180</td>
<td>1.0341</td>
<td>1.4255</td>
<td>2.5504</td>
<td>4.19</td>
</tr>
<tr>
<td>+</td>
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<td>1.0355</td>
<td>1.4305</td>
<td>2.7296</td>
<td>3.01</td>
</tr>
<tr>
<td>1,4-dioxan</td>
<td>0.0383</td>
<td>1.0381</td>
<td>1.4316</td>
<td>3.6000</td>
<td>1.74</td>
</tr>
</tbody>
</table>

solvent molecules through a weak H-bond. As dilution decreases, the interaction between the solute and solvent molecules may dominate, decreasing the value of $g'$. It may also be due to the hindrance of the solute molecules. With the decrease of dilution, number of solute molecules in the mixture increases whereas the number of solvent molecules decreases. The solute molecules may offer hindrance. As a result the hydrogen bonds in the linear chain of the solute molecules get ruptured. This results in the smaller size of the solute clusters leading to smaller value of $g'$, but with $g'>1$, giving rise to parallel orientation between the dipoles. Even at very little dilution studied, the solute molecules exist with parallel orientation. Increase of $g'$ with increase of temperature is found to exist in all the amides except in acrylamide. Increase of $g'$ with increase of temperature is due to the increase of average multimer size. At high dilution, as temperature increases, solute-solvent interaction may be less favoured due to hindrance of the solvent molecules. This results in favour of more solute-solute interactions. Increase of temperature at very high dilutions may increase the size of the molecules (linear multimers) favouring parallel orientation of the solute molecules, which may be the reason for the increase of $g'$ values with the temperature.

In pthalimide, solute-solvent interaction may be through the H-bonding between H-atom of the pthalimide and O-atom of the 1,4-dioxan. The solute-solute interaction may be due to the H-bonding between H-atom of the NH group of pthalimide and the carbonyl oxygen atom of the other pthalimide molecule. In case of pthalimide, even $\beta$-multimer is found to exist ($g'<1$). This may be due to the anti-parallel orientation of the solute molecules. In pthalimide, the solute-solvent interaction seems to be more prominent than in the other systems taken for the investigation. At very high dilution, $g'$ is large, (except for acrylamide mixture II)
which indicates the dominance of solute-solute interactions. The strength of the solute-solute interactions is in the order of the systems IV < II < I < III.

References


