Studies of Hydrogen Bonding Between N, N-Dimethylacetamide and Primary Alcohols

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Abstract: Hydrogen bonding between N, N-dimethylacetamide (DMA) and alcohols has been studied in carbon tetrachloride solution by an X-band Microwave bench at 936GHz. The dielectric relaxation time ($\tau$) of the binary system are obtained by both Higasi’s method and Gopalakrishna method. The most likely association complex between alcohol and DMA is 1:1 stoichiometric complex through the hydroxyl group of the alcohol and the carbonyl group of amide. The results show that the interaction between alcohols and amides is 1:1 complex through the free hydroxyl group of the alcohol and the carbonyl group of amide and the alkyl chain-length of both the alcohols and amide plays an important role in the determination of the strength of hydrogen bond (O-H: C=O) formed and suggests that the proton donating ability of alcohols is in the order: 1-propanol < 1-butanol < 1-pentanol and the accepting ability of DMA.

Keywords: Hydrogen Bonding, Higasi’s method, N,N-dimethylacetamide, Dielectric relaxation time.

Introduction

Alcohols are industrially and scientifically important organic compounds and the hydroxyl group of alcohol are largely determines their physical and chemical properties. Amides are the simplest molecules containing peptide linkage and a study of their hydrogen bonding ability yields insight into the nature of protein structure. The role of non-covalent interactions in stabilizing polypeptide structure was studied by Lcao-Mo-SCF method. X-ray diffraction and NMR method Amides are associated through inter-molecular hydrogen bonding and also show strong dependence on solvent environment, temperature and concentration. To understand the molecular behavior of associating molecules it is necessary to determine the various dielectric parameters, which are related to inter- and intra-molecular association and internal rotation with temperature variation. The Kirkwood theory of dipolar liquids defines the short-range dipolar interactions through a dimensionless parameter (g). In the present work, the hydrogen bonding between hydroxyl group of alcohol and carbonyl group of DMA in carbon tetrachloride has been studied.
Experimental

The N, N-dimethylacetamide (>99% pure) used in this investigation were purchased from Aldrich and used without further purification. AnalaR grade alcohols and carbon tetrachloride (>99.5% pure) were purified by standard methods. The physical parameters of all the chemicals used here have been checked against their literature values.

The measurement of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) were carried out in the X-band microwave frequency of 9.84 GHz. The experimental set-up and the procedure employed were the same as reported by Aggarwal et al. The values of $\varepsilon'$ and $\varepsilon''$ so obtained are accurate within ±1% and ±5%, respectively. The static dielectric constants ($\varepsilon_0$) were measured by heterodyne beat method at 303 K using a commercial instrument, Dipole meter DM 01 supplied by wissenschaftliche Technische Werkstatte, Germany operated at 220 volts. Error in the measurement of $\varepsilon_0$ is less than ±0.5%. The refractive indices were measured by an Abbe's refractometer with an accuracy of ±0.0005. The percentage of deviation in the measurement of refractive index is about ±0.02%. The temperature of all the measurements were maintained at 30±0.1 °C using water circulating thermostat.

The proton donors (alcohols) and the acceptors (N, N-dimethylacetamide) under study were separately dissolved at the same molar concentration in the solvent carbon tetrachloride. Their dielectric constants were measured separately. Then the two solutions were mixed in different proportions but with the total concentration kept at a fixed value and were subjected to the dielectric constant measurements. As the maximum deviation of dielectric constant for all the systems studied occurs at equi-molar ratio of the solutes, it is presumed that the deviation is due to the formation of 1:1 complexes alone. The dielectric relaxation time $\tau$ have been calculated by Higasi’s method, the overall dielectric relaxation time $\tau_{(1)}$ is best described by

$$\tau_{(1)} = \frac{a'}{\omega(a'-a_\infty)}$$

(1)

While the average dielectric relaxation time $\tau_{(2)}$ is given by,

$$\tau_{(2)} = \frac{(a_\infty - a')}{\omega a'}$$

(2)

The most probable mean relaxation time $\tau_{(0)}$ is obtained by,

$$\tau_{(0)} = \sqrt{\tau_{(1)}\tau_{(2)}}$$

(3)

Where $\omega$ is the angular frequency selected for the measurements and assuming $\varepsilon', \varepsilon_0, \varepsilon_\infty$ and $\varepsilon''$ vary linear with weight fraction $w_2$ of the solute. The Debye equation in terms of $a_\infty, a', a''$ and $a_\infty$ yields two independent equations (1) and (2).

$$\varepsilon_0 = \varepsilon_1 + a_\infty w_2$$

(4)

$$\varepsilon' = \varepsilon_1 + a' w_2$$

(5)

$$\varepsilon'' = a'' w_2$$

(6)

$$\varepsilon_\infty = \varepsilon_1 + a_\infty w_2$$

(7)

In which subscript 1 refers to the pure solvent and 2 refers to the solute, 0 refers to the static frequency and $\infty$ refers to the infinite or optical frequency measurements and $w_2$ is the weight fraction of the solute. The values of relaxation time are given in Table 1.
Results and Discussion
In the present study, we are concerned with interaction of the OH group and C=O groups with surrounding molecules in carbon tetrachloride solution. The possibility of solute–solute hydrogen bonding in particular will be investigated.

The systems selected were \( N, N \)-dimethylacetamide with proton donors (1-propanol, 1-butanol, 1-pentanol) using carbon tetrachloride as solvent. The static dielectric constant \( (\varepsilon_0) \), dielectric constant at infinite dilution \( (\varepsilon_\infty) \), dielectric constant at an angular frequency \( (\varepsilon_1^1) \), dielectric loss factor \( (\varepsilon_1^{11}) \) and dielectric relaxation time \( (\tau_0) \) for \( N, N \)-dimethylacetamide with proton donors (1-propanol, 1-butanol,1-pentanol) in carbon tetrachloride at 303 K are provided in Table 1. A perusal of Table 1 shows that, the value of relaxation time increases with increasing chain length of alcohols and \( N, N \)-dimethylacetamide and offers hindrance to the rotation of the molecule. The increase in relaxation time may be due to the increase in effective radius of the rotating unit.

Table 1. Values of dielectric constants and relaxation time at 303 K.

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>System</th>
<th>( \varepsilon_0 )</th>
<th>( \varepsilon_\infty )</th>
<th>( \varepsilon_1^1 )</th>
<th>( \varepsilon_1^{11} )</th>
<th>Relaxation time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>DMA+ 1-Propanol with carbon tetrachloride</td>
<td>2.8096</td>
<td>2.2156</td>
<td>2.6499</td>
<td>0.2681</td>
<td>11.3</td>
</tr>
<tr>
<td>2:1</td>
<td>DMA+ 1-Propanol with carbon tetrachloride</td>
<td>2.8603</td>
<td>2.2164</td>
<td>2.5784</td>
<td>0.2692</td>
<td>13.9</td>
</tr>
<tr>
<td>1:1</td>
<td>DMA+ 1-Propanol with carbon tetrachloride</td>
<td>2.9546</td>
<td>2.2258</td>
<td>2.5898</td>
<td>0.2765</td>
<td>14.2</td>
</tr>
<tr>
<td>1:2</td>
<td>DMA+ 1-Propanol with carbon tetrachloride</td>
<td>2.8546</td>
<td>2.2158</td>
<td>2.5765</td>
<td>0.2665</td>
<td>13.8</td>
</tr>
<tr>
<td>1:3</td>
<td>DMA+ 1-Propanol with carbon tetrachloride</td>
<td>2.8226</td>
<td>2.2153</td>
<td>2.574</td>
<td>0.2465</td>
<td>12.8</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th>Mole fraction</th>
<th>System</th>
<th>( \varepsilon_0 )</th>
<th>( \varepsilon_\infty )</th>
<th>( \varepsilon_1^1 )</th>
<th>( \varepsilon_1^{11} )</th>
<th>Relaxation time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>DMA+ 1-Propanol with carbon tetrachloride</td>
<td>2.7096</td>
<td>2.1156</td>
<td>2.4876</td>
<td>0.2481</td>
<td>12.4</td>
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<tr>
<td>1:1</td>
<td>DMA+ 1-Propanol with carbon tetrachloride</td>
<td>2.8603</td>
<td>2.1946</td>
<td>2.497</td>
<td>0.2662</td>
<td>16.7</td>
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<tr>
<td>1:2</td>
<td>DMA+ 1-Propanol with carbon tetrachloride</td>
<td>2.9546</td>
<td>2.2258</td>
<td>2.4998</td>
<td>0.2765</td>
<td>19.4</td>
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<tr>
<td>1:3</td>
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<td>2.8546</td>
<td>2.1798</td>
<td>2.4938</td>
<td>0.2695</td>
<td>16.2</td>
</tr>
</tbody>
</table>

This result indicates the hydrogen bond, that is formation of molecular structure between the hydrogen atom in O-H group of alcohol and the oxygen atom in C=O group of amide and is shown in Figure 1 below.

Figure 1. Hydrogen bond between alcohols and DMA.

Where, \( R = C_3H_7 \) (1-propanol), \( C_4H_9 \) (1-butanol), \( C_5H_{11} \) (1-pentanol).

From Figure 2 it is observed that the values of dielectric relaxation time are highest for the system 1:1 molar ratio when compared to 3:1, 1:2, 2:1 and 3:1 molar ratio. This result confirms that molecular association are maximum in 1:1 molar ratio of DMA with Primary alcohol.
Conclusion

Hydrogen bonded complexes of DMA with primary alcohols (1-propanol, 1-butanol and 1-pentanol) in carbon tetrachloride were determined. From this study, one may conclude that the proton donating ability of alcohols and the proton accepting ability of amide linearly vary with the alkyl chain length of both alcohols and amides and plays a significant role in the determination of dielectric properties of the above systems studied. It may concluded that form present study the proton donating power of the primary alcohol are in the order of 1-propanol < 1-butanol < 1-pentanol. The relaxation time of proton acceptor increases, as donating ability of solute environment increases. The increasing in relaxation time provides information regarding the orientation of dipoles between the interacting compounds.

References
