$^{13}$C NMR and dielectric relaxation studies of methanol+nitrile systems

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$^{13}$C NMR studies for both spin-lattice relaxation time ($T_1$) and chemical shifts were obtained for two systems namely methanol+acetonitrile and methanol+acrylonitrile. The dielectric dispersion data was also obtained for these systems. The $^{13}$C NMR and dielectric dispersion data with a view to understand the conformation of these systems and also to understand the basic mechanisms of relaxation in the same have been presented. A correlation between the rotational correlation time from NMR and the dielectric relaxation time for the two systems have been reported. The confirmation of the ring-like conformer for methanol+acetonitrile system using $^{13}$C NMR chemical shift data.

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1 Introduction

Studies of binary liquid mixtures has been an active field of interest for long. It is seen that most of these studies are limited to the use of a single experimental tool such as dielectric measurements. Even in studies attempting to compare the results from two different experimental techniques (such as NMR and dielectric measurements), often the actual experimental data is limited to one technique only, with the other data drawn from literature.

Bloembergen Purcell and Pound (BPP) first suggested the possible correlation [Eq. (1)] between the dielectric relaxation time ($\tau$) and NMR rotational correlation time ($\tau_c$) based on the fact that both the times have their origin in brownian motion of the system under study. It was suggested by BPP that the $\tau_c = \tau/3$. This correspondence between the dielectric relaxation time and the NMR rotational correlation time has been studied previously both theoretically and experimentally.

The study of this correspondence between $\tau_c$ and $\tau$ for two systems namely methanol+acetonitrile and methanol+acrylonitrile has been reported. $^{13}$C NMR chemical shift and $T_1$ measurements are made in addition to the determination of dielectric relaxation time. The NMR results of one of the systems namely methanol+acetonitrile are used to confirm the ring like conformation of previously predicted for the same.

The possible structures of methanol+acetonitrile binary system were calculated using ab initio methods up to 6-31G basis set by Sathyan et al. They have reported the existence of two conformations based on energy considerations. One is a linear conformer and the other is a circular conformer, as shown in Fig. 1.(a and b) respectively. On the basis of energy minimisation considerations, the linear conformer was found to be the most probable one.

An earlier study by us on the dielectric studies on this system and hence the calculations of the dipole moment lead us to conclude that the circular conformer is the most probable. This conclusion was reached by comparing the dipole moment as obtained from the experiment with that of the two conformers obtained theoretically from ab initio computations. Since the study of the dynamics of liquids and the determination of the structure of hydrogen bonded systems in the liquid state is a complex phenomenon, we followed this by a $^{13}$C NMR study of the binary system. The chemical shift and the spin-lattice relaxation time ($T_1$) were determined.

Spin-lattice relaxation time ($T_1$) and dielectric relaxation—Spin-lattice relaxation mechanism in the
$^{13}$C nuclei is predominantly a C-H dipole-dipole interaction. Taking into account this dipole-dipole interaction the expression for $T_1$ as given by BPP is:

$$\frac{1}{T_1} = \hbar^2 \gamma_H^2 \gamma_C^2 \sum \tau_i^6$$

... (1)

$\gamma_H$ — gyromagnetic ratio of hydrogen; $\gamma_C$ — gyromagnetic ratio of carbon; $\tau_C$ — NMR rotational correlation time; $r_{ij}$ — intermolecular distance.

It is seen that BPP equations give a correlation time that is $\frac{1}{2}$ to $\frac{1}{10}$ that of experimental values as determined from the dielectric measurements.$^{13,14}$ According to Moniz et al.$^{12}$ the discrepancy in the results is due to the time dependence of the rotational angular correlation functions of the molecules; and this time dependence is governed by dynamic coherence rather than frictional forces as given by BPP.

BPP took into account both intermolecular and intramolecular relaxation mechanisms and gave the expression for $T_1$ as:

$$\frac{1}{T_1} = \frac{1}{T_{1p}} + \frac{1}{T_{1n}}$$

... (2)

where

$$\frac{1}{T_{1p}} = \frac{9\gamma^4 \hbar^2 \tau_c}{10 b^6}$$

... (3)

is due to the intra-molecular relaxation and

$$\frac{1}{T_{1n}} = \frac{9\pi^2 \gamma^4 \hbar^2 N_o}{5kT}$$

... (4)

is due to the intermolecular (neighbour) relaxation.

Use of Eqs (2-4) gives the values of $T_1$ much smaller than the experimental values, for proton NMR. Since these equations predict relaxation mechanisms that are much faster than those observed from dielectric experiments, alternate models to explain the relaxation mechanism are looked for. Of the various alternates suggested, Allerhand et al.$^9$ took into account the group rotation in the molecules.

This concept was further refined by Ap Simon$^{10}$ with the expressions for $T_1$ as:

$$\frac{1}{T_1} = \frac{\hbar^3}{b} \gamma_H^2 \gamma_C^2 N_o \tau_g \left[ A + B \left( \frac{\tau_g}{\tau_g + \tau_c} \right) + C \left( \frac{\tau_g}{3\tau_g + 2\tau_c} \right) \right]$$

... (5)

where

$$A = \left( \cos^2 \theta - 1 \right)$$

$$B = \left( 3 \sin^2 \theta \cos^2 \theta \right)$$

$$C = \left( 3 \sin^4 \theta / 4 \right)$$

$\tau_g$ is the correlation time of rotation of group and $\tau_c$ rotational correlation time.

For tetrahedral carbon (methyl group) $A = 1/9$, $B = 8/27$ and $C = 16/2$. These expressions have been used in the present study to estimate $T_1$ and are determined for two cases namely $\tau_g = \tau_c$ and $\tau_g << \tau_c$.

In order to account for the discrepancy between the theory and experimentally observed results Mehrotra$^6$ has used the expression for the relaxation time as given by Murthy$^{19}$. Replacing $\tau$ by $\tau_a$ was seen to give better results and $\tau_a$ is determined from Eq. (7):

$$\tau_a = \left[ \frac{6\pi \eta \alpha}{(\varepsilon + 2) kT} \right]$$

... (7)

where $\alpha$ is the polarizability of the solute molecule as determined from refractivity studies, $\varepsilon$ and $\eta$ are the dielectric constant and the viscosity of the solvent namely benzene. The dielectric constant here is the value measured using a sodium vapour lamp as source and is hence $= \varepsilon_\alpha$. This was the relaxation time used in the present studies to correlate the NMR correlation time and the dielectric relaxation time from $\tau_c$ values taken to be $\tau_a/3$.

Since the chemical shift ($\delta$) is a function of the electron density around the nucleus under study, the chemical shifts were used to determine the most probable conformer of methanol+acetonitrile binary system. The shift in the chemical shift ($\Delta \delta$) is defined as:

$$\Delta \delta = \delta_{\text{carbon in the pure system}} - \delta_{\text{same carbon in the binary system}}$$

... (8)

The experimental accuracy of $\delta$ is 0.002 ppm. $\Delta \delta$ is useful to determine the sites of bonding in the binary systems.

2 Experimental Details

Two systems were considered for the present study namely (a) methanol (CH$_3$OH)+acetonitrile (CH$_3$CN) and (b) methanol+acrylonitrile (CH$_2$CHCN). All samples were of spectroscopic grade for NMR studies and of Analar grade with purity greater than 99% for dielectric studies and were distilled before use and
stored over 4Å molecular sieves to avoid the capture of atmospheric water and other contaminants by the prepared samples. The non-polar solvent used for dielectric studies was benzene. The details of the dielectric measurements are reported in our previous paper. The relaxation times according to the Debye model and from polarisation measurements are reported here. The high frequency dielectric constant was determined from the refractive index studies using the relationship \( \varepsilon_\infty = \frac{n^2_D}{2} \), where \( n^2_D \) is the refractive index for light from a sodium vapour source. The refractive index was measured using a Carl-Zeiss Abbe refractometer. All experiments were performed at room temperature (27°C). The molecular radii were determined using the software package PCMODEL and used to calculate the relaxation time according to Debye’s model. The dielectric relaxation times were obtained by three methods namely (a) from the Cole-Cole dielectric dispersion plots \( \tau_o \), (b) from Debye’s equation

\[
\tau_D = \left( \frac{6\pi}{kT} \right) \eta b^3
\]

(e) from refractivity measurements \( \tau_n \).

\(^13\)C NMR chemical shifts and spin-lattice relaxation time data were acquired using a JEOL GSX 400 model FT NMR instrument working at 23°C. The \((180°-\tau-90°-\tau)\) inversion recovery technique was used to determine \( T_1 \). A rough estimate of \( T_1 \) was made by making a few trial runs and a recovery time of about 5\( T_1 \) was given.

3 Results and Discussion

The relaxation times as determined from the previously described methods are reported in Table 1. The non-zero value of the distribution parameter \( \zeta \) of the Cole-Cole plot indicates the presence of more than one relaxation times in these systems. Acrylonitrile, with a double bond present is seen to have larger value for \( \zeta \). The experimentally determined spin-lattice relaxation time \( (T_1) \) and the chemical shifts (\( \delta \)) are reported in Table 2. For the methanol +acetonitrile system, a significant shift in the chemical shift values of the methyl group of methanol and acetonitrile is seen with respect to the chemical shift values in the pure systems. From the predicted conformers for the binary system it is clear that the linearly bonded system will not have the methyl group participating in the bonding. On the other hand the circular conformer will call for the participation of the methyl group and hence account for the shift in chemical shift noted experimentally. Hence the present study of the \(^13\)C NMR chemical shifts of the methanol+acetonitrile binary systems indicate that the circularly bonded conformer is more likely than the linear structure.

It is seen from Table 2 that the value of \( T_1 \) when \( \tau_g = \tau_c \) is much smaller than the observed value and the value when \( \tau_g << \tau_c \) is much larger. Hence the real process can be inferred to be an intermediary one. This is to say that the rotation of the methyl group about the symmetry axis plays a significant role in the relaxation mechanism, although the exact contribution to the relaxation process cannot be evaluated in the present case.

4 Conclusions

It is found from \(^13\)C NMR chemical shift studies that the circular conformer of methanol+acetonitrile is

<table>
<thead>
<tr>
<th>System</th>
<th>( \tau_o ) (ps)</th>
<th>( \tau_D ) (ps)</th>
<th>( \tau_{\alpha} ) (ps)</th>
<th>( \zeta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol +</td>
<td>(Cole-Cole plots)</td>
<td>(Debye equation)</td>
<td>(Murthy’s Equation)</td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>27.69</td>
<td>3.68</td>
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<td>0.15</td>
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<tr>
<td>Acrylonitrile</td>
<td>45.58</td>
<td>4.51</td>
<td>11.08</td>
<td>0.35</td>
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</table>

<table>
<thead>
<tr>
<th>System</th>
<th>Group</th>
<th>( \delta )</th>
<th>( \Delta \delta )</th>
<th>( T_1 ) (Experimental) (s)</th>
<th>( T_1 ) (( \tau_g = \tau_c )) (s)</th>
<th>( T_1 ) (( \tau_g &lt;&lt; \tau_c )) (s)</th>
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</thead>
<tbody>
<tr>
<td>Methanol (M) +</td>
<td>CN</td>
<td>118.391</td>
<td>-0.091</td>
<td>35.9424</td>
<td>8.38</td>
<td>38.51</td>
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<td></td>
<td>CH₃(M)</td>
<td>49.964</td>
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<td>17.3957</td>
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<td>CH₃</td>
<td>1.300</td>
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<tr>
<td>Acrylonitrile</td>
<td>CH₂</td>
<td>138.807</td>
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<td>10.3932</td>
<td>6.84</td>
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<tr>
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<tr>
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<td>CH₃(M)</td>
<td>50.313</td>
<td>0.653</td>
<td>17.1456</td>
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</table>
more probable than the linear structure previously proposed. This is in agreement with our previous results from dielectric studies. Group relaxation of the \( \text{CH}_3 \) group is found to contribute significantly to the \( T_1 \) relaxation mechanism in methanol+acetonitrile/acrylonitrile systems. A better correlation is found from the refractive index measurements and NMR than the data from dielectric dispersion studies. Both systems namely methanol+acetonitrile/acrylonitrile are seen to have multiple dielectric relaxation mechanisms as seen from the non-zero value of the distribution parameter of the Cole-Cole plots, with the methanol-acrylonitrile system having a greater distribution parameter, indicating the presence of more relaxation mechanisms compared to the methanol-acetonitrile system.

References