CHAPTER-4

RESULTS AND DISCUSSION

(PART-2)

SOLVATION BEHAVIOUR THROUGH

NMR STUDIES
4.1 BACKGROUND OF COPPER NMR STUDIES

Stabilization of copper (I) salts in solution leads to application in the hydrometallurgical purification of copper and silver. Therefore, stabilization of concentrated copper (I) solutions is industrially a useful subject. The uncomplexed copper (I) ion is unstable in water and immediately disproportionates into copper (II) and metallic copper:

\[
2\text{Cu}^+ \xleftrightarrow{} \text{Cu}^{2+} + \text{Cu}^0
\]

In the presence of strongly coordinating anions such as halides or cyanide and in some dipolar aprotic solvents, however, the stability of copper (I) increases largely. Thus the disproportionation constant of Cu (I) decreases from ca. 10\(^6\) dm\(^3\) mol\(^{-1}\) in water\(^5\) to nearly unity in dimethylsulphoxide\(^7,8\) and becomes ca. 10\(^{-14}\) dm\(^3\) mol\(^{-1}\) in pyridine\(^9\) and ca. 10\(^{-21}\) dm\(^3\) mol\(^{-1}\) in acetonitrile\(^10\). The stabilization of Cu (I) in two latter solvents is due to the formation of a strong solvation complex [CuS\(_4\)]\(^+\), of nearly tetrahedral symmetry\(^11\). In binary mixtures of acetonitrile with several co-solvents including water, copper (I) is remarkably stable up to very high concentrations of the co-solvent\(^12,13\). The solvation behaviour of copper (I) in mixed solvents containing AN as a component have been studied\(^14-19\) by using conductance, viscosity, transference number and EMF measurements. Some such studies have also been reported in this dissertation. All these studies indicated a strong preferential solvation of copper (I) cation by acetonitrile or by the co-solvent. A technique allowing a detailed examination of the solvation site itself is NMR spectroscopy of the central metal ion, which provided that a magnetically active isotope of the metal exists and that the complex is diamagnetic. Both conditions are fulfilled in the case of copper (I).

Information on solvation may be obtained from the measurements of linewidth (\(\Delta\)), intensity (I), chemical shift (\(\delta\)) and relaxation time (\(\tau\)) as well as from quadrupole coupling constant (\(e^2Qq/h\)). In some favourable cases the number of solvent molecules in the first coordination sphere can also be directly deduced from coupling patterns of the NMR signals\(^20\).

Copper has two stable isotopes, \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\), with a very wide chemical shift range and have large quadrupole moments but very favourable sensitivities. Because of its large natural abundance (69.1\%) \(^{63}\text{Cu}\) has been preferred over \(^{65}\text{Cu}\) for NMR studies. Although, \(^{63}\text{Cu}\) NMR studies are very interesting but such studies are very rare due to
several difficulties. Firstly, Cu NMR studies can be carried out using only diamagnetic copper salts. For this purpose copper (I) salts have to be prepared and in the pure state. Secondly, copper (I) solutions are stable only in a limited number of solvents, therefore, the choice of an appropriate solvent or solvent mixture is generally very laborious and difficult. Thirdly, $^{63}$Cu and $^{65}$Cu nuclei have large quadrupole moment ($-0.211 \times 10^{-28} \text{ m}^2$ and $-0.195 \times 10^{-28} \text{ m}^2$ respectively) due to which copper NMR signal is usually very broad in pure solvents and becomes even broader in mixed solvents because of the strong field gradient. Fourthly, copper NMR signal can be observed only in those cases where Cu$^+$ is coordinated (solvated) by four ligand molecules and the cubic or tetrahedral symmetry is maintained at the copper nucleus. Tetrahedrally coordinated cuprous complexes such as $[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$ or $[\text{Cu(CH}_3\text{CN)}_4]\text{BF}_4$ which produce tetrahedrally coordinated copper (I) complex ions in solution are shown to be the most suitable salts for copper NMR studies. For bi-coordinated and tri-coordinated copper (I) complexes in solution, copper NMR signal, however, cannot be observed. The symmetry at the copper site is thus very important for copper NMR measurements.

4.2 COPPER (I) NMR MEASUREMENTS

In the present work, we have studied the solvation behaviour of $[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$ in AN and AN + ADN mixtures containing 100, 95, 90, 85, 80 and 75 mol % AN using copper NMR studies. The chemical shift ($\delta$) and linewidth ($\Delta$) have been measured for $^{63}$Cu and $^{65}$Cu NMR signals using 0.064 M $[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$ solutions in binary mixtures of AN with ADN. In all measurements 0.064 M $[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$ solution in pure AN was taken as reference solution for which the chemical shift ($\delta$) value was set as 0 ppm. The line width ($\Delta$) values thus obtained are reported in Table 2 and 3. The variation of line width ($\Delta$), chemical shift ($\delta$) for $^{63}$Cu and $^{65}$Cu NMR signals from 0.064 M $[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$ solution with mol % of ADN in AN and ADN binary mixtures at 298 K is shown in Figure 2 and 3 respectively. The magnitude of line width ($\Delta$) values increases with increase in ADN composition in the mixture. The line widths ($\Delta$) of the $^{63}$Cu and $^{65}$Cu NMR signal in the present measurement for 0.064 M $[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$ solution in pure AN are 482 Hz and 422 Hz respectively and are in good agreement with the the literature values. Comparison of $^{63}$Cu and $^{65}$Cu NMR signals for 0.064 M $[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$ solutions...
Figure 1 – Comparison of $^{63}\text{Cu}$ and $^{65}\text{Cu}$ NMR signals from 0.064M $[\text{Cu(CH}_3\text{CN})_4]\text{ClO}_4$ in pure acetonitrile.
Figure 2 – Line width (\(\Delta\)) for \(^{65}\)Cu and \(^{63}\)Cu NMR signals from 0.064 M \([\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4\) solution vs mol % of ADN in AN and ADN binary mixtures at 298 K.

Figure 3 – Chemical shift (\(\delta\)) for \(^{65}\)Cu and \(^{63}\)Cu NMR signals from 0.064 M \([\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4\) solution vs mol % of ADN in AN and ADN binary mixtures at 298 K.
in pure acetonitrile is shown in Figure 1. $^{63}\text{Cu}$ is the more sensitive nucleus while $^{65}\text{Cu}$ yields slightly narrower signals. The linewidth found increased significantly with the water content of the AN. Trace amounts of copper (II) as impurity in $[\text{Cu(\text{CH}_3\text{CN})}_4]\text{ClO}_4$ also increased the linewidth of the copper signal considerably. It was, therefore ensured that AN used was completely free from water as well as the trace amounts of copper (II) salt. The linewidths of the $^{63}\text{Cu}$ and $^{65}\text{Cu}$ NMR signals in pure AN from various samples were reproducible within the experimental error.

So these studies were expected to throw light on following two aspects:

1. Which of the two isotopes Cu$^{63}$ and Cu$^{65}$ gives more symmetrical copper (I) complexes and hence better NMR signals?

2. Whether or not nitriles with two -C≡N groups in the same molecule are better solvent for stabilization of copper (I) salts as compared to nitriles with single -C≡N groups?

### 4.3 EVALUATION OF QUADRUPOLE RELAXATION RATES ($1/T_2)_Q$, REORIENTATIONAL CORRELATION TIMES ($\tau_R$) AND QUADRUPOLE COUPLING CONSTANTS ($\epsilon^2Qq/h$)

Evaluation of quadrupole relaxation rate leads to estimation of quadrupole coupling constants which directly provide information on the geometry of the solvation sphere of ions. We have used the linewidth data to evaluate the quadrupole coupling constants of copper (I) complexes in AN and AN + ADN mixtures. The spin lattice relaxation of copper nucleus is essentially governed by the quadrupole relaxation rate ($1/T_2)_Q$, which is obtained from the linewidth ($\Delta$) and depends on the asymmetry factor of the solvation sphere ($\eta$) and the reorientational correlation time ($\tau_R$) according to the relations:

$$\left(\frac{1}{T_2}\right)_Q = \pi \Delta$$  \hspace{1cm} (1)

$$\left(\frac{1}{T_2}\right)_Q = \frac{3\pi^2(2I+3)}{10I^2(2I-1)}\left[1 + \frac{\eta^2}{3}\right]$$ \frac{e^2Qq}{h} \tau_R \hspace{1cm} (2)

where $\Delta$ represents the linewidth at half the height of the signal, $I$ is the nuclear spin for the copper nucleus and ($e^2Qq/h$) is the quadrupole coupling constant. Equation (1)
is applicable when NMR line shapes are Lorentzian and equation (2) is applicable for the limits of extreme narrowing when $\omega^2 \tau_R^2 << 1$. The $\eta$ values for all these systems were not available, therefore, it was not possible to evaluate the factor $(1+\eta^2/3)$ in equation (2). For the symmetrical complex $[\text{Cu(AN)}_4]^+$ formed in pure AN, where copper had tetrahedral symmetry at the copper nucleus, the value of $\eta$ is zero. In mixed solvents, the replacement of AN by ADN forming tetrahedral complexes of the type $[\text{Cu(AN)}_4-x(\text{ADN})_x]^+(x = 1 \text{--} 4)$, $\eta$ can have a value which may not be zero but is too small to be significant. Setting $I = 3/2$ for the $^{63}\text{Cu}$ nucleus and $(1+\eta^2/3) = 1$ as before$^{22,28}$, equation (2) simplifies to equation (3)

$$
\left( \frac{1}{T_2} \right) = 3.9478 \left[ \frac{e^2 Q q}{h} \right]^2 \tau_R
$$

(3)

from which $(e^2 Q q / h)$ can be calculated. When the size of the solute molecule is much larger than that of the solvent molecule, the reorientational correlation time $\tau_R$ in equation (3) can be calculated by using the relation$^{27}$

$$
\tau_R = \frac{4 \pi^2 \eta_s}{3 kT}
$$

(4)

where $r_s$ is the radius of the spherical solvated ion or solute molecule and $\eta_s$ is the viscosity of the solution. When the size of the solute and solvent molecules, however, becomes comparable, equation (4) is no longer valid. Gierer and Wirtz$^{29}$ proposed a method of calculating $\tau_R$ values of the solute molecules when the solute molecules are of comparable size to the solvent molecules. This model takes into account the microviscosity factor, $f_{GW}$, given by

$$
f_{GW} = \left[ 6 \frac{r_s}{r_i} + \left( \frac{2r_s}{r_i} \right)^3 \right]^{-1}
$$

(5)

where $r_s$ is the radius of the solute or solvated ion and $r_i$ is the radius of the solvent molecule. In the macroscopic limit when $r_i >> r_s$, this microviscosity factor becomes equal to unity but in case of neat liquids where $r_i \sim r_s$, its value lies between 0.06 and 0.17$^{30}$ For the ions and molecules of comparable size, the actual reorientational
correlation time $\tau_R$ can be calculated by applying micro-viscosity correction to $\tau_R$ in equation (4). The following relation then becomes valid for the calculation of actual $\tau_R$ values.

$$\tau_R = \frac{4 \pi \eta s}{3kT} \left[ \frac{6r_f}{r_s} + \left( 1 + \frac{2r_s}{r_f} \right)^{-1} \right]^{-1}$$

(6)

Using equation (1), (3) and (6) and the solution viscosity ($\eta_s$) for 0.064 M $[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$, the copper quadrupole coupling constants ($e^2Qq/h$) in AN + ADN binary mixtures have been calculated by taking solvated radii ($r_i$) for copper (I) from conductance data in AN and ADN and the average $r_i$ values at various compositions in different solvent mixtures. Using these $r_i$ values, the $\tau_R$ values have been calculated using equation (6). The solvent radii ($r_s$) were estimated by calculating the average molar volumes of the mixed solvents by using densities $\rho_0$ of the solvent mixtures from Table-1 given in chapter 2. The evaluated solvated radii ($r_i$) for copper (I) and

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**Figure 4** – Quadrupole coupling constant ($e^2Qq/h$) for $^{63}\text{Cu}$ and $^{65}\text{Cu}$ NMR signals from 0.064M $[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$ solution vs mol % of ADN in AN and ADN binary mixtures at 298 K.
average solvent radii \((r_s)\) are reported in Table 1. The micro-viscosity factor \(f_{\text{vis}}\) of equation (5) was found to lie between 0.24 and 0.29 in the present systems. The copper quadrupole coupling constants for \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\) complexes evaluated by this method are reported in Table 2 and 3. The variation of quadrupole coupling constant values for \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\) complexes with mol % of ADN is shown in Figure 4.

The quadrupole coupling constants for \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\) have the values of 5.06 and 4.7 respectively in pure AN which increases to 7.51 and 5.85 respectively in AN + ADN mixtures. The quadrupole coupling constant values increase largely by the increase of co-solvent composition. The increase in the quadrupole coupling constant values is large for \(^{65}\text{Cu}\) than the \(^{63}\text{Cu}\) nuclei.

Dinitriles are chelating ligands and form more asymmetric complexes as compared to those formed by mononitriles and thus, the larger quadrupole coupling constant values are obtained using dinitrile as co-solvent. The copper quadrupole coupling constant usually increases with the formation of mixed complexes\(^{26}\). It can be seen from Table 2 and 3 that the quadrupole coupling constants values in all AN + ADN mixtures are larger than the values in pure AN and increase with the increase of mol % co-solvent. The result shows that in each case stable mixed complexes of the form \([\text{Cu(AN)}_x\text{(ADN)}_y]^+\) \((x = 1 - 4)\) are formed due to replacement of AN by ADN molecules from the original complex \([\text{Cu(CH}_3\text{CN)}_4]^+\) formed in pure AN. The mixed copper (I) complexes remain stable at all compositions of the solvent mixtures. The evidence for the stability of these complexes comes from the systematic increase of the \((e^2Qq/h)\) values with the increase of ADN composition. The results show that ADN replaces the AN molecules from the copper (I) complex. The effect of replacement of ADN is stronger in the AN rich region and slows down in the ADN rich region.

Though copper signal line width significantly changes with change of solvent composition in AN and ADN binary mixtures, yet it is difficult to assign the exact solvation number to \(\text{Cu}^+\) in binary mixtures from line width \((\Delta)\) and chemical shift \((\delta)\) data. Gill et al\(^{21}\), however has shown that \(\text{Cu}^+\) signal in acetonitrile and triethylphosphite mixtures shows a coupling with phosphorous atom of the triethylphosphite indicating a coordination number of \(\text{Cu}^+\) as four with respect to triethylphosphite. The coupling pattern as investigated by Gill et al. is shown in Figure 5 where splitting of copper (I) signal into five peaks indicates the coordination.
number as four. The coupling of $^{63}$Cu with $^{31}$P takes place even at every low concentrations of triethylphosphite. The splitting of $^{63}$Cu NMR spectra of the system CuClO$_4$·4AN in AN-TMP at 298 K and 9.4 T as function of the mole fraction of TMP. $X_{\text{TMP}}$: (a) 0.005, (b) 0.01 and (c) 0.04 are represented in Figure 5.

![Figure 5](image)

**Figure 5** – The splitting of copper signal by phosphorous atom at varying composition of triethylphosphite.

### 4.4 CONCLUSION

In AN + ADN mixtures, the $(e^2Qq/h)$ values for copper (I) complexes increase significantly with increase of co-solvent composition. The results show that ADN, nitriles with two -C=N groups in the same molecule has strong tendency to replace AN from the complex ion $[\text{Cu(\text{CH}_3\text{CN})}_4]^+$ forming the mixed complexes of the form $[\text{Cu(AN)}_{4-x}\text{(ADN)}_x]^+$ ( $x = 1 - 4$), in which ADN systematically replaces the AN molecules from the solvation sphere of copper (I) with increase of ADN composition. This shows that ADN (dinitrile) has stronger effect on the solvation of copper (I) than the mononitrile (AN) at the corresponding compositions.
Table 1 - Solvated radii of Cu⁺ (ρ₁) and average solvent radii (ρₛ) in AN and AN + ADN mixtures at 298 K.

<table>
<thead>
<tr>
<th>mol % AN</th>
<th>10⁸ρ₁ (Å)</th>
<th>10⁹ρₛ (Å)</th>
</tr>
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<tbody>
<tr>
<td>100</td>
<td>2.33</td>
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<td>95</td>
<td>2.37</td>
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</tr>
<tr>
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<td>5.3</td>
</tr>
<tr>
<td>75</td>
<td>2.52</td>
<td>5.3</td>
</tr>
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Beyond 25 mol % ADN, Cu NMR could not be recorded due to large broadening of signal.
Table 2 - Linewidth (Δ), reorientational correlation times (τ_R) and quadrupole coupling constants (ε^2Qq/h) of ^{63}Cu NMR signal from 0.064 M [Cu(CH$_3$CN)$_4$]ClO$_4$ solutions in AN and AN + ADN mixtures at 298 K.

<table>
<thead>
<tr>
<th>mol% AN</th>
<th>Δ/Hz</th>
<th>10$^{11}$τ_R / s</th>
<th>(ε^2Qq/h)/MHz</th>
</tr>
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<tbody>
<tr>
<td>100</td>
<td>482</td>
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</tr>
<tr>
<td>85</td>
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<td>3.15</td>
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<td>2285</td>
<td>3.96</td>
<td>6.78</td>
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<tr>
<td>75</td>
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<td>4.54</td>
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Table 3 - Linewidth ($\Delta$), reorientational correlation times ($\tau_R$) and quadrupole coupling constants ($e^2Qq/h$) of $^{65}$Cu NMR signal from 0.064 M [Cu(CH$_3$CN)$_4$]ClO$_4$ solutions in AN and AN + ADN mixtures at 298 K.

<table>
<thead>
<tr>
<th>mol % AN</th>
<th>$\Delta$/Hz</th>
<th>$10^{11}\tau_R$/s</th>
<th>$(e^2Qq/h)$/MHz</th>
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4.5 REFERENCES