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### Quadrupole coupling constant studies of Cu(I) in binary mixtures of acetonitrile with N,N-dimethylacetamide and Adiponitrile

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#### ABSTRACT

Copper(I) nuclear magnetic resonance (NMR) studies of 0.064 M  $\text{CuClO}_4$  have been made in binary mixtures of acetonitrile (AN) with N,N-dimethylacetamide (DMA) and adiponitrile (ADN) co-solvents containing 100, 95, 90, 85, 80 and 75 mol % of acetonitrile at 298 K using Brüker 500 MHz NMR spectrometer. Chemical shift ( $\delta$ ) and linewidth ( $\Delta$ ) for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  signals have been recorded relative to 0.064 M  $\text{CuClO}_4$  solution in pure anhydrous AN. Quadrupole relaxation rates  $(1/T_2)_Q$ , reorientational correlation times ( $\tau_R$ ) and copper quadrupole coupling constants ( $e^2Qq/h$ ) have been calculated in all cases. The variation of these NMR parameters has been examined as a function of mol % of co-solvent to compare the relative effects of co-solvents on the solvation behaviour of copper (I) and hence on the stabilization of copper (I) complexes formed. The variation of quadrupole coupling constant with solvent composition shows that the ( $e^2Qq/h$ ) values in all composition increases with the increase of mol % of co-solvent, which indicates the formation of mixed complexes of the form  $[\text{Cu}(\text{CH}_3\text{CN})_{4-x}(\text{S})_x]^+$  ( $x = 1-4$ ) due to the replacement of AN molecules by the co-solvent molecules (S) from the original complex  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  formed in pure AN. Comparison of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  NMR signals in pure AN shows that  $^{63}\text{Cu}$  is more sensitive nucleus while  $^{65}\text{Cu}$  yields slightly narrower signals.

**Key words:** Quadrupole coupling constant, Acetonitrile, N,N-dimethylacetamide, Adiponitrile

#### INTRODUCTION

The uncomplexed copper(I) ion is unstable in water and immediately disproportionates into copper(II) and metallic copper [1]. The presence of strongly coordinating anions such as halides or cyanide and some dipolar aprotic solvents, however, largely increases the stability of copper(I) [2]. Thus the disproportionation constant of Cu(I) decreases from ca.  $10^6 \text{ dm}^3 \text{ mol}^{-1}$  in water [3] to nearly unity in dimethylsulphoxide [4,5], becomes ca.  $10^{-14} \text{ dm}^3 \text{ mol}^{-1}$  in pyridine [6] and ca.  $10^{-21} \text{ dm}^3 \text{ mol}^{-1}$  in acetonitrile [7]. The stabilization of Cu(I) in two latter solvents is due to the formation of a strong solvation complex  $[\text{CuS}_4]^+$ , of nearly tetrahedral symmetry [8]. In binary mixtures of acetonitrile with several co-solvents including water, copper(I) is remarkably stable upto very high concentrations of the co-solvent [9,10]. The solvation behaviour of copper(I) in mixed solvents containing AN as a component have been studied by using conductance, viscosity, transference number and EMF measurements [11–16]. All these studies indicated, a strong preferential solvation of the 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, 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 ( $\delta$ ) or relaxation time ( $\tau$ ) as well as from quadrupole coupling constant ( $e^2Qq/h$ ). In some favorable cases the number of solvent molecules in the first coordination sphere can also be directly deduced from coupling patterns of the NMR signals [17].

Copper has two stable isotopes,  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , which have large quadrupole moments but very favorable 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 meager due to several difficulties [18–22]. Firstly,  $^{63}\text{Cu}$  NMR studies can be carried out using only diamagnetic copper salts. For this purpose copper (I) salts have to be prepared 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,  $^{63}\text{Cu}$  nucleus has a large quadrupole moment ( $-0.211 \times 10^{-28} \text{ m}^2$ ) due to which  $^{63}\text{Cu}$  NMR signal is usually very broad in pure solvents and becomes even broader in mixed solvents because of the strong field gradient, therefore we restrict our studies upto 25 mol % of co-solvent. Fourthly,  $^{63}\text{Cu}$  NMR signal can be observed only in those cases where  $\text{Cu}^+$  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  $[\text{Cu}(\text{AN})_4]\text{ClO}_4$  or  $[\text{Cu}(\text{AN})_4]\text{BF}_4$  which produce tetracoordinated copper (I) complex ions in solution are shown to be the most suitable salts for  $^{63}\text{Cu}$  NMR studies. For bicoordinated and tricoordinated copper (I) complexes in solution,  $^{63}\text{Cu}$  NMR signal, however, cannot be observed. The symmetry at the copper site is thus very important for  $^{63}\text{Cu}$  NMR measurements. In this paper, we present some interesting Cu NMR results in binary mixtures of acetonitrile (AN) with N,N-dimethylacetamide (DMA) and adiponitrile (ADN) as co-solvents to through light on the following aspects:

- (1) Which of two isotopes i.e.  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , gives more symmetrical copper (I) complexes and hence better NMR signals and less line width?
- (2) Effect of the Guttmann donor number on the solvation of copper(I), which is significantly large in case of DMA than AN (AN = 14.1 and DMA = 27.8).
- (3) Effect of number of  $-\text{C}\equiv\text{N}$  groups in each solvent molecule on stabilization of copper(I) salts.

## MATERIALS AND METHODS

Tetraacetonitrile copper(I) perchlorate  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  used for all NMR measurements was prepared by the method reported earlier [18,23]. The salt was stored in a dry box and was handled under anhydrous conditions. Acetonitrile (AN), N,N-dimethylacetamide (DMA) and adiponitrile (ADN), (99.5 %, all from E. Merck) were purified as reported earlier [24]. Cu NMR measurements were made at  $298 \pm 1 \text{ K}$  using 10 mm NMR tubes on a Bruker 500 MHz spectrometer using a broadband probe head and non rotating sample tubes at 132.612 MHz and 142.057 MHz frequencies. Copper(I) solutions were prepared by fixing the salt concentration as 0.064 M. All chemical shifts ( $\delta$ ) and linewidths ( $\Delta$ ) were measured relative to 0.064 M  $\text{CuClO}_4$  in pure anhydrous AN, which was taken as a standard reference solution for all other measurements. For the reference solution,  $\Delta$  for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  was 482 Hz and 422 Hz, respectively, and  $\delta$  values in all cases were set as 0 ppm for measuring  $\delta$  values in all other cases. The reference solution was measured from time to time to ensure consistency of all NMR measurements. The uncertainty in  $\delta$  and  $\Delta$  values were estimated as  $\pm 0.1 \text{ ppm}$  and  $\pm 20 \text{ Hz}$  respectively. Viscosities of all binary mixtures and 0.064 M  $\text{CuClO}_4$  solutions were measured at  $298.15 \pm 0.01 \text{ K}$  using Ubbelohde suspended level viscometer. The uncertainty of viscosity measurements were  $\pm 0.001 \text{ mPa}\cdot\text{s}$ .

## RESULTS AND DISCUSSION

In this work, we have investigated the solvation behaviour of  $[\text{Cu}(\text{AN})_4]\text{ClO}_4$  in AN and its binary mixtures with DMA and ADN using Cu NMR studies. The chemical shift ( $\delta$ ) and linewidth ( $\Delta$ ) have been measured for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  NMR signals using 0.064 M  $[\text{Cu}(\text{AN})_4]\text{ClO}_4$  solutions in binary mixtures of AN with DMA and ADN at different compositions of the mixtures. In all measurements 0.064 M  $\text{CuClO}_4$  solution in pure AN was taken as reference solution for which the chemical shift ( $\delta$ ) value was set as 0 ppm. The  $\Delta$  values thus obtained are reported in Table 1 and 2. The linewidth found increased significantly with the water content of the AN. Trace amounts of copper (II) as impurity in  $[\text{Cu}(\text{AN})_4]\text{ClO}_4$  also increased the linewidth of the copper signal considerably. It was, therefore ensured that AN used was completely free from water and the trace amounts of copper (II) salt. The linewidth of the  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  NMR signals in pure AN from various samples were reproducible within the experimental error.

### 3.1 Evaluation quadrupole coupling constants ( $e^2Qq/h$ )

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 the copper (I) complexes in AN + co-solvent binary mixtures. The spin lattice relaxation of copper nucleus is essentially governed by the quadrupole relaxation rate  $(1/T_2)_Q$ , which is extracted 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 [25]

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

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

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. Equation (2) is applicable for the limits of extreme narrowing when  $\omega^2 \cdot \tau_R^2 \ll 1$ . 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  $[\text{Cu}(\text{AN})_4]^+$  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 co-solvent molecules (S) forming tetrahedral complexes of the type  $[\text{Cu}(\text{AN})_{4-x}(\text{S})_x]^+$  ( $x = 1-4$ ),  $\eta$  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 [19,26], equation (2) simplifies to equation (3)

$$\left(\frac{1}{T_2}\right)_Q = 3.9478 \left[\frac{e^2Qq}{h}\right]^2 \tau_R \quad (3)$$

from which  $(e^2Qq/h)$  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 [25]

$$\tau_R = \frac{4\pi r_i^3 \eta_s}{3kT} \quad (4)$$

where  $r_i$  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 [27] 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 as

$$f_{GW} = \left[6 \frac{r_s}{r_i} + \left(1 + \frac{2r_s}{r_i}\right)^{-3}\right]^{-1} \quad (5)$$

where  $r_i$  is the radius of the solute or solvated ion and  $r_s$  is the radius of the solvent molecule. In the macroscopic limit when  $r_i \gg r_s$ , 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 [28]. For the ions and molecules of comparable size, the actual reorientational correlation time  $\tau_R$  can be calculated by applying microviscosity correction to  $\tau_R$  in equation (4). The following relation then becomes valid for the calculation of actual  $\tau_R$  values.

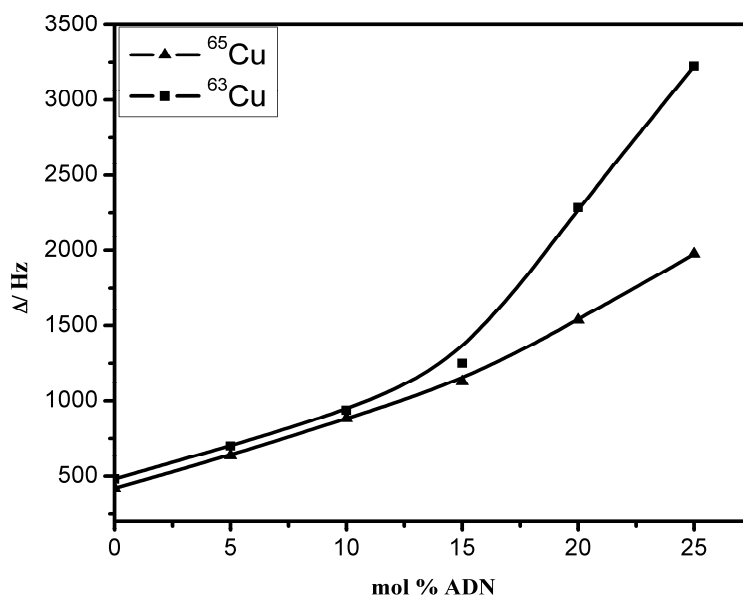
$$\tau_R = \frac{4\pi r_i^3 \eta_s}{3kT} \left[ 6 \frac{r_s}{r_i} + \left( 1 + \frac{2r_s}{r_i} \right)^{-3} \right]^{-1} \quad (6)$$

Using equations (1), (3), (6) and the solution viscosity ( $\eta_s$ ) for 0.064 M  $\text{CuClO}_4$ , the copper quadrupole coupling constants ( $e^2Qq/h$ ) in AN + DMA and AN + ADN binary mixtures have been calculated by taking solvated radii ( $r_i$ ) for  $\text{Cu}^+$  from conductance data and the averaged  $r_i$  values at various compositions in different solvent mixtures. Using these  $r_i$  values, the  $\tau_R$  values have been calculated using equation (6). The copper quadrupole coupling constants for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  complexes evaluated by this method are reported in Tables 1 and 2.

The copper quadrupole coupling constant usually increases with the formation of mixed complexes. It can be seen from Tables 1 and 2 that the quadrupole coupling constant values in all AN + DMA and AN + ADN mixtures are larger than the values in pure AN and increase with the increase of co-solvent composition. The result shows that in each case stable mixed complexes of the form  $[\text{Cu}(\text{AN})_{4-x}(\text{S})_x]^+$  ( $x = 1-4$ ) are formed due to the replacement of AN by co-solvent molecules from the original complex  $[\text{Cu}(\text{AN})_4]^+$  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 co-solvent composition. The results show that co-solvent molecules replaces the AN molecules from the copper (I) complex. This effect of replacement of co-solvent is stronger in AN rich region of binary mixture.

**Table 1.** Linewidth ( $\Delta$  / Hz) and quadrupole coupling constant ( $e^2Qq/h$  / MHz) of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  NMR signal from 0.064 M  $\text{CuClO}_4$  in AN and AN + ADN mixtures at 298 K

mol % AN	$^{63}\text{Cu}$		$^{65}\text{Cu}$	
	$\Delta$ / Hz	( $e^2Qq/h$ ) / MHz	$\Delta$ / Hz	( $e^2Qq/h$ ) / MHz
100	482	5.06	422	4.7
95	699	5.18	635	4.9
90	938	5.29	885	5.04
85	1250	5.62	1127	5.24
80	2285	6.78	1537	5.56
75	3223	7.51	1976	5.85



**Figure 1.** Line width ( $\Delta$ ) for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  NMR signals from 0.064 M  $\text{CuClO}_4$  solution vs mol % of ADN in AN + ADN binary mixtures at 298 K

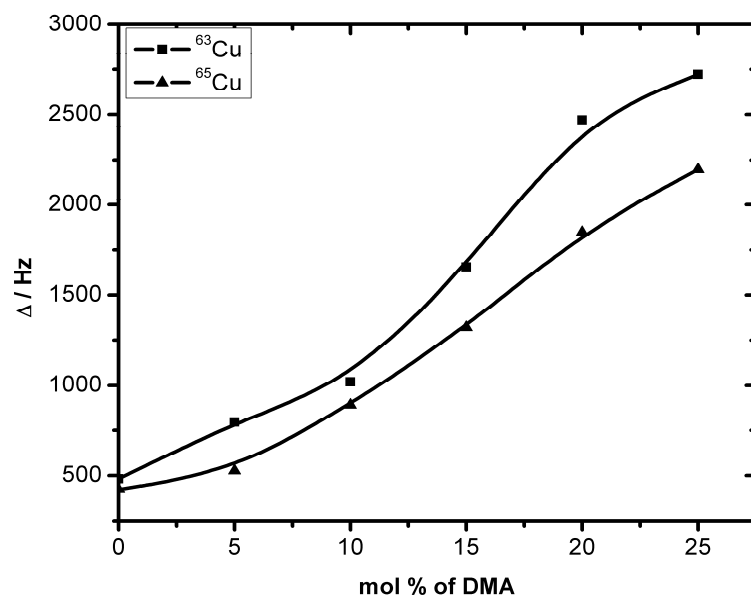


Figure 2. Line width ( $\Delta$ ) for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  NMR signals from 0.064 M  $\text{CuClO}_4$  solution vs mol % of DMA in AN + DMA binary mixtures at 298 K

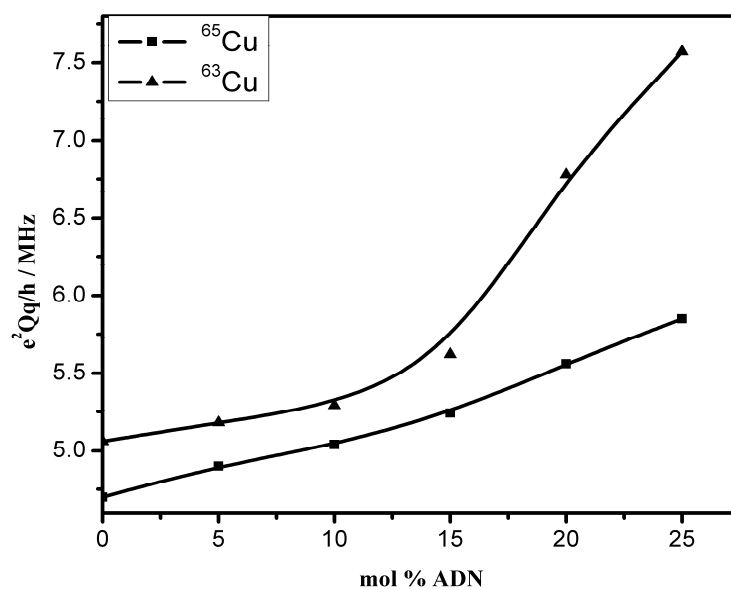


Figure 3. Quadrupole coupling constant ( $e^2Qq/h$ ) for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  NMR signals from 0.064M  $\text{CuClO}_4$  solution vs mol % of ADN in AN + ADN binary mixtures at 298 K

Table 2. Line width ( $\Delta$  / Hz) and quadrupole coupling constant ( $e^2Qq/h$  / MHz) of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  NMR signal from 0.064 M  $\text{CuClO}_4$  in AN and AN + DMA mixtures at 298 K

mol % AN	$^{63}\text{Cu}$		$^{65}\text{Cu}$	
	$\Delta$ / Hz	$(e^2Qq/h)$ / MHz	$\Delta$ / Hz	$(e^2Qq/h)$ / MHz
100	482	5.06	422	4.7
95	795	6.35	527	5.17
90	1020	7.00	891	6.54
85	1655	8.62	1321	7.73
80	2469	10.17	1848	8.63
75	2722	10.32	2196	9.27

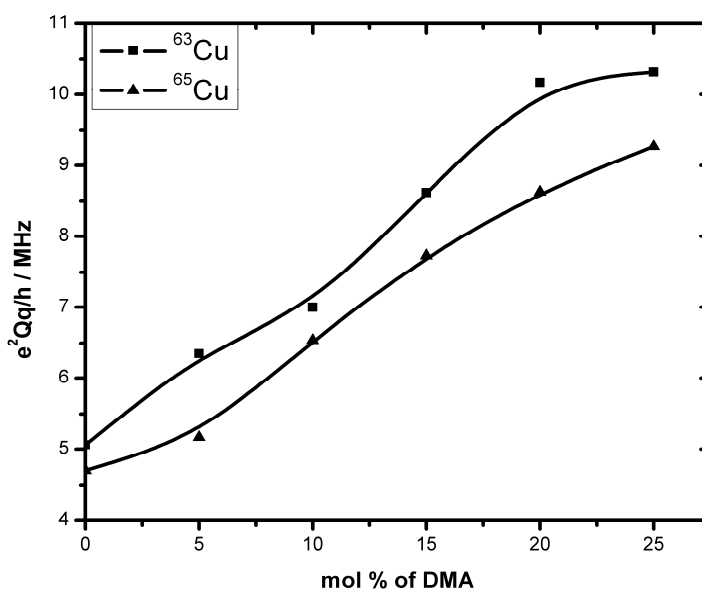


Figure 4. Quadrupole coupling constant ( $e^2Qq/h$ ) for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  NMR signals from 0.064M  $\text{CuClO}_4$  solution vs mol % of DMA in AN + DMA binary mixtures at 298 K

### CONCLUSION

In all AN + DMA and AN + ADN mixtures, the ( $e^2Qq/h$ ) values for copper(I) complexes increase significantly with increase of co-solvent composition. Increase in ( $e^2Qq/h$ ) values for  $^{63}\text{Cu}$  nucleus is more than  $^{65}\text{Cu}$  nucleus. The results show that ADN (nitriles with two  $-\text{C}\equiv\text{N}$  groups in the same molecule) and DMA (significantly different Guttmann donor numbers, AN = 14.1 and DMA = 27.8) 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  $[\text{Cu}(\text{AN})_{4-x}(\text{S})_x]^+$  ( $x = 1-4$ ), in which co-solvent systematically replaces the AN molecules from the solvation sphere of copper(I) with increase of co-solvent composition and form more asymmetric complexes.

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