^{63}Cu Nuclear Magnetic Resonance and Viscosity Studies of Copper (I) Perchlorate in Mixed Solvents Containing Acetonitrile

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^{63}Cu nuclear magnetic resonance and viscosity studies of 0.064 M copper (I) perchlorate solutions have been made at 298 K in binary mixtures of acetonitrile (AN) with dimethylsulphoxide (DMSO), hexamethylphosphotriamide (HMPA), N,N-dimethylacetamide (DMA), nitromethane (NM), propylene carbonate (PC) and 3-hydroxypropionitrile (3 HPN) at several compositions of the mixtures using a 500 MHz NMR Spectrometer and Ubbelohde viscometer, respectively. The chemical shift (δ), linewidth (Δ) and line intensity (I) of the ^{63}Cu NMR signal in these mixed solvents have been measured relative to the ^{63}Cu signal in 0.064 M copper (I) perchlorate ($CuClO_4$) solution in pure AN. The quadrupolar relaxation rates $(1/T_2)_Q$, reorientational correlation times (τ_R) and quadrupolar coupling constants (QCC) of the copper (I) solvates have also been estimated from the data. The QCC values show a big variation in all solvent systems with the change of solvent composition, indicating the formation of mixed complexes. The variation of all NMR parameters with solvent composition shows strong effects of DMSO, HMPA, and DMA on the solvation behaviour of Cu^+ in the first three mixtures, and relatively much weaker effects of PC, NM and 3HPN in the other three mixtures.

Introduction

^{63}Cu NMR studies are still lacking in mixed solvents in spite of the fact that ^{63}Cu and ^{65}Cu are easily observed [1–5] by NMR due to their high natural abundance and magnetogyric ratio close to that of ^{13}C. Since ^{63}Cu NMR studies are interesting and still rare, we report such investigations for $CuClO_4$ in binary mixtures of acetonitrile (AN) with dimethylsulphoxide (DMSO), hexamethylphosphotriamide (HMPA), N,N-dimethylacetamide (DMA), nitromethane (NM), propylene carbonate (PC) and 3-hydroxypropionitrile (3HPN).

Experimental

Copper (I) perchlorate tetraacetonitrile ($CuClO_4 \cdot 4\,AN$), a white crystalline salt was prepared by the method reported in [1, 2, 6, 7]. The salt was stored in a dry box and was handled under anhydrous conditions. AN (99.5%) was dried by the method already reported [8, 9]. DMSO, HMPA, DMA, NM, PC and 3HPN (all AnalaR grade) were dried over 4 Å molecular sieves and distilled under reduced pressure. All NMR spectra were recorded on a Bruker 500 MHz spectrometer using a broadband probe head and 10 mm o.d. sample tubes at a frequency of 132.6135 MHz. Copper (I) perchlorate solutions were prepared by dissolving a constant weight of the salt in a fixed volume of degassed solvent mixture. The concentration of each solution was fixed as 0.064 M. All chemical shifts (δ), linewidths (Δ) and line intensities (I) were referred to 0.064 M $CuClO_4$ in pure anhydrous AN, which was taken as reference solution for all other measurements. This reference solution was measured from time to time to ensure consistency of all ^{63}Cu NMR results. Viscosities of all solutions were measured at 298 K using an Ubbelohde suspended bulb viscometer by the procedure given in [10]. The reproducibility of the viscosity measurements was ±0.1%.

Results and Discussion

$CuClO_4 \cdot 4\,AN$ remains stable for a sufficiently long time in the solid form when stored in a dry box. It also remains stable in solution of AN. The stability of this salt in AN comes from the formation of the complex cation $[Cu(AN)_4]^+$ of nearly tetrahedral symmetry [11]. This complex cation gives a ^{63}Cu NMR signal of linewidth 480 Hz (at half height of the signal) for a 0.064 M $CuClO_4$ solution in AN. The present linewidth of the ^{63}Cu NMR signal, i.e. 480 Hz for 0.064 M $CuClO_4$ in AN, is

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well within the range of previous values (480–540 Hz) reported in [1–5]. In Figs. 1–3 are plotted the chemical shifts (δ), linewidths (Δ) and relative line intensities (I) for ^{63}Cu NMR signals of 0.064 M $CuClO_4$ solutions in binary mixtures of AN with DMSO, HMPA, DMA, NM, PC and 3HPN at different compositions of the mixtures (relative to 0.064 M $CuClO_4$ solutions in pure AN) as functions of mol% cosolvent (S).

^{63}Cu has a large quadrupole moment -0.211×10^{-28} m^2. Therefore the ^{63}Cu NMR signal is observed only in copper (I) complexes where the environment of the copper nucleus is highly symmetrical [1–5]. In such cases also the linewidth (Δ) of the ^{63}Cu NMR signal is large. Fig. 1 shows that the δ values of the ^{63}Cu signal become more and more negative on increase of the concentration of the cosolvent in all cases except in case of 3HPN, where it becomes more positive. The effect is much stronger for DMSO, HMPA, and DMA and weaker for NM and PC. The linewidth (Δ) of the ^{63}Cu NMR signal increases considerably for the DMSO, HMPA, and DMA mixtures even at low cosolvent compositions, while the increase in the linewidth becomes relatively large only at high PC, NM and 3HPN compositions. The effect of DMSO, HMPA, and DMA on the linewidth is even stronger than that of MeOH, DMF, TMPA, and H_2O already reported [1].

The line intensity (I) of the ^{63}Cu NMR signal, which is selected as 1000 for the 0.064 M $CuClO_4$ solution in pure AN, decreases very sharply on addition of even small amounts of DMSO, HMPA, and DMA. The decrease in the line intensity (I), however, becomes pronounced in case of PC, NM, and 3HPN only at high cosolvent compositions in the binary mixtures. The line intensity of the ^{63}Cu NMR signal becomes about 9% at 9.56 mol% HMPA, 6.4% at 24.08 mol% DMSO, 2.5% at 57.06 mol% DMA, 8.0% at 59.05 mol% PC, 2.6% at 89.81 mol% NM, and 3.0% at 91.56 mol% 3HPN in the binary mixtures with AN. If one compares the fall of the intensity at a fixed mol% of the cosolvents in all cases, then the order of the fall is: HMPA>DMSO>DMA>3HPN>PC>NM (Figure 3).

Evaluation of Quadrupolar Relaxation Rates, Reorientational Correlation Times and Quadrupolar Coupling Constants

As shown earlier, the spin lattice relaxation of copper nucleus is governed essentially by the quadrupolar relaxation rate $(1/T_2)_Q$, which in turn depends on the linewidth (Δ), asymmetry factor of the solvation sphere (η) and the reorientational correlation time (τ_R) by the equations [12]

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

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

$$\tau_R = \frac{4\pi r_s^3 \eta_s}{3kT} , \tag{3}$$

where Δ represents the linewidth at half height of the signal, I is the spin 3/2 of the copper nucleus, $(e^2Q\,q/h)$ the quadrupolar coupling constant, and η_s the viscosity of the solution. Equation (1) is applicable when the NMR lineshapes are Lorentzian. Equation (2) is applicable for the limit of extreme narrowing, i.e. when $\omega^2\tau_R^2 \ll 1$, and (3) provides τ_R values which are only an estimate on the molecular level [12].

For complexes of cubic or tetrahedral symmetry, $(1+\eta^2/3)$ can be taken as unity [1, 2]. Since $[Cu(AN)_4]^+$ has tetrahedral symmetry [11], for this ion in pure AN or in binary mixtures of AN with other solvents, this symmetry term can, as before [1, 2], be taken as unity. Using $I = 3/2$, and $(1+\eta^2/3) = 1$, (2) simplifies to the form

$$\left(\frac{1}{T_2}\right)_Q = 3.9478\left(\frac{e^2Qq}{h}\right)^2 \tau_R . \tag{4}$$

Using (1), (3) and (4) and the viscosity (η_s) of 0.064 M $CuClO_4$ solutions measured in the present work and plotted in Fig. 4, the quadrupolar coupling constants have been calculated. The τ_R values were calculated, using (3), by taking r_s values for Cu^+ in various solvent systems obtained from our conductance measurements [13–15]. The τ_R and QCC values for the copper (I) complexes in various solvent systems so obtained are plotted in Figs. 5 and 6 respectively.

The τ_R values for $CuClO_4$ increase uniformly with increase of the cosolvent composition. The QCC values, however, show a significant increase with increase of the cosolvent composition in case of HMPA, DMSO, and DMA even at low cosolvent composition. The formation of mixed complexes generally gives large QCC values. In case of HMPA, DMSO, and DMA as cosolvents, the formation of mixed complexes of the form $[Cu(AN)_{4-i}S_i]^+$ (i = 1–3) thus takes place even at low cosolvent composition. Since the increase in linewidth on addition of cosolvent was accompanied by a chemical shift and decrease of line intensity, the ligand exchange between $[Cu(AN)_4]^+$ and the mixed species seems to take place

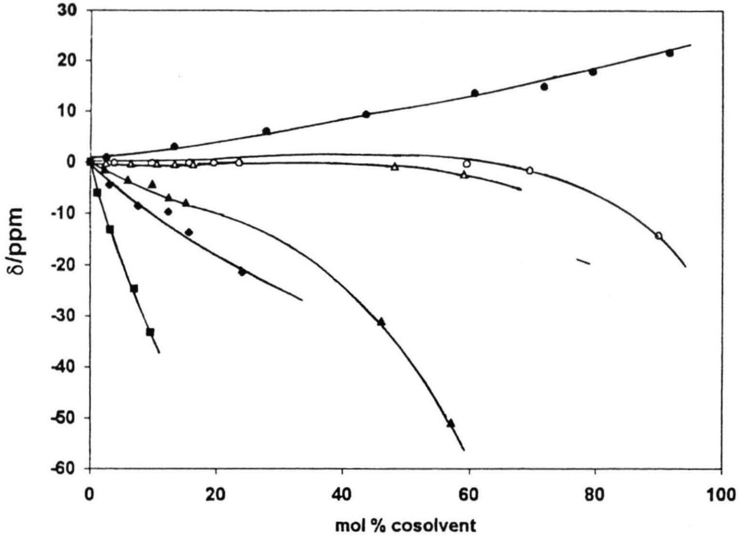

Fig. 1. Chemical shift of the ^{63}Cu NMR signal (δ) versus mol% cosolvent in 0.064 M $CuClO_4$ in AN+ cosolvent mixtures at 298 K. ◆ – AN+DMSO; ■ – AN+-HMPA; ▲ – AN+DMA; △ – AN+PC; ○ – AN+NM; ● – AN+3HPN.

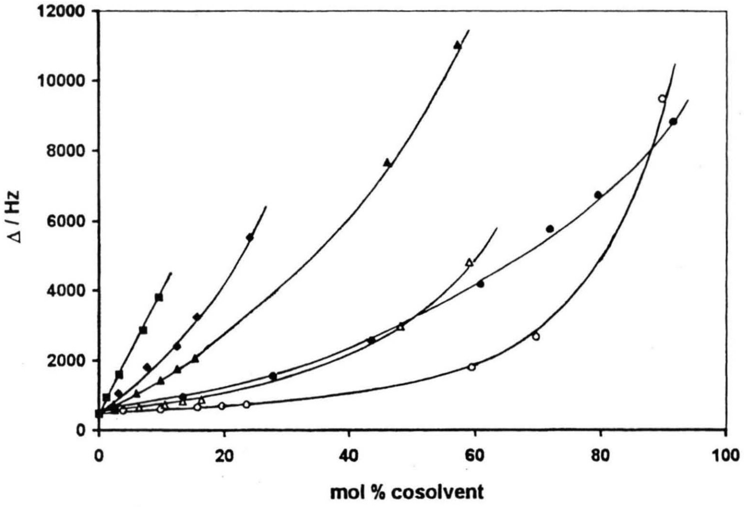

Fig. 2. Linewidth (Δ) of the ^{63}Cu NMR signal versus mol% cosolvent in 0.064 M $CuClO_4$ in AN+ cosolvent mixtures at 298 K. Symbols as in Figure 1.

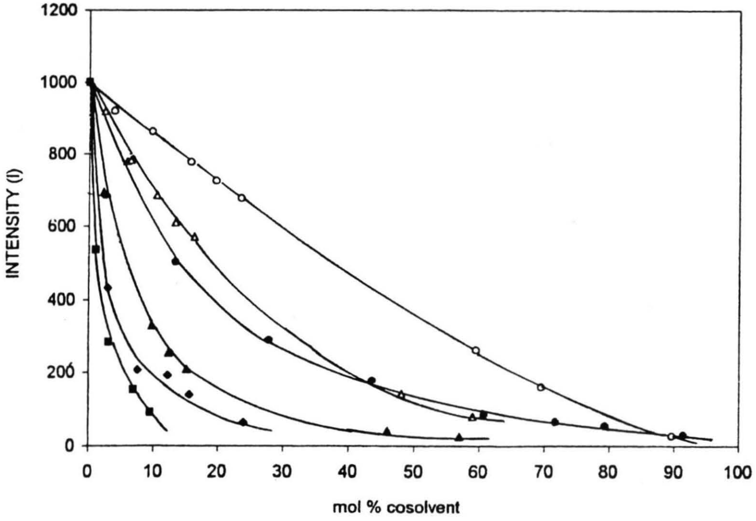

Fig. 3. Intensity of the ^{63}Cu NMR signal (I) versus mol% cosolvent in 0.064 M $CuClO_4$ in AN+ cosolvent mixtures at 298 K. Symbols as in Figure 1.

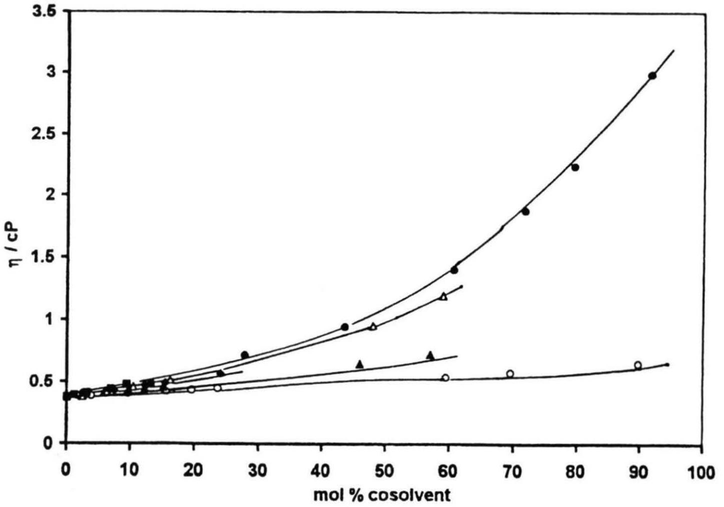

Fig. 4. Viscosity of 0.064 M $CuClO_4$ solutions versus mol% cosolvent in AN+ cosolvent mixtures at 298 K. Symbols as in Figure 1.

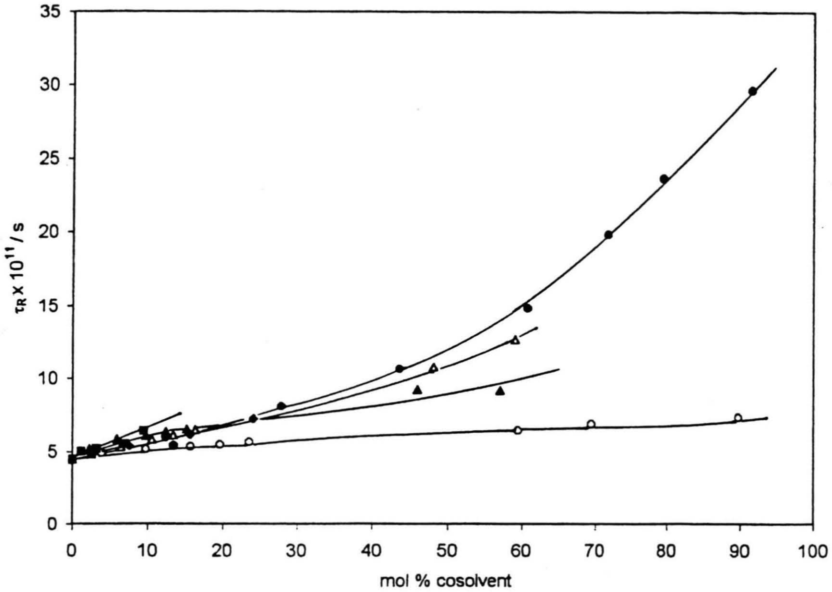

Fig. 5. Reorientational correlation times (τ_R) of copper (I) solvates versus mol% cosolvent in AN+ cosolvent mixtures at 298 K. Symbols as in Figure 1.

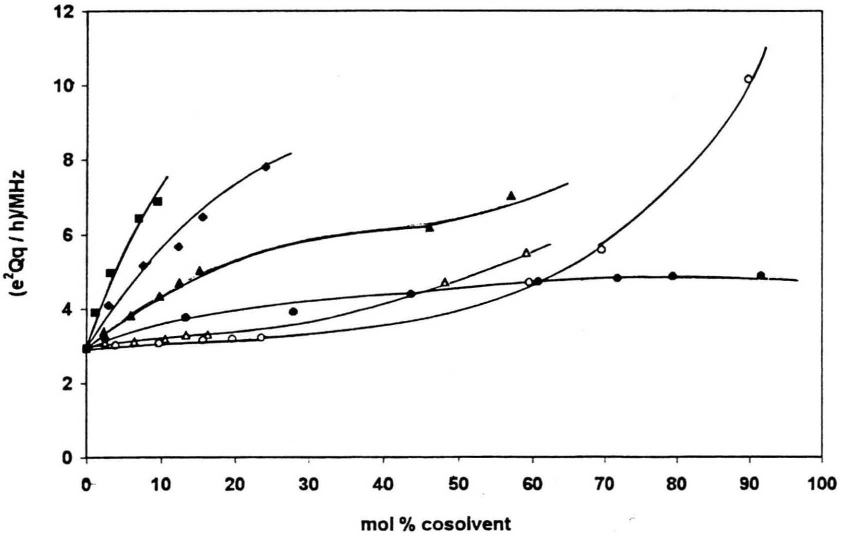

Fig. 6. Quadrupolar coupling constants ($e^2Q\,q/h$) for copper (I) solvates versus mol% cosolvent in AN+ cosolvent mixtures at 298 K. Symbols as in Figure 1.

at moderately slow rate on the NMR time scale. The exchange, however, is not too slow to give separate NMR signals for each mixed species. The QCC values show that the formation of mixed species at low PC, NM and 3HPN as cosolvents is relatively less at low cosolvent compositions but becomes pronounced at high cosolvent compositions (Figure 6).

For the solutions studied, the possibility of line broadening due to the presence of paramagnetic copper (II) ion was ruled out by running the UV/VIS absorption spectra of the solutions, where no peak in the visible region corresponding to copper (II) ions was detectable. At cosolvent mol percentages higher than used in the present study, traces of copper (II) ions, however, were formed due to disproportion of copper (I) to copper (II), which could be detected by the absorption spectra. Such solutions were thus not employed for our NMR studies. The solvent mixture compositions were restricted upto regions in which copper (I) solutions remained stable without having any copper (II) impurity.

Conclusion

The NMR results show that even small quantities of HMPA, DMSO, and DMA have strong effects on the solvation behaviour of Cu^+ in AN. PC, NM, and 3HPN, on the other hand, show effects which are much weaker at low compositions of the cosolvents and become pronounced in the cosolvent-rich region of the mixtures.

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