

A Comparative Nuclear Magnetic Resonance Study of the Solvation of CuClO_4 in Binary Mixtures of Acetonitrile with Pyridine and Picolines at 298 K

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^{63}Cu nuclear magnetic resonance (NMR) and viscosity studies of 0.064 M CuClO_4 solutions have been reported in binary mixtures of acetonitrile (AN) with pyridine (Py) and 2, 3, and 4-picolines (2,3,4-Pic) at 298 K using a Bruker 500 MHz NMR spectrometer and an Ubbelohde viscometer, respectively. Chemical shift δ and linewidth Δ for the ^{63}Cu signals have been recorded referenced to a 0.064 M CuClO_4 solution in anhydrous AN. The copper quadrupole coupling constants (e^2Qq/h) have been calculated in all cases. The variation of the δ and e^2Qq/h values as a function of mol fraction of the co-solvent show that all these bases interact with Cu^+ more strongly than AN. They replace AN from the Cu^+ complexed with AN in the form $[\text{Cu}(\text{AN})_4]^+$ and form a mixed complex of the type $[\text{Cu}(\text{AN})_4 - x(\text{S})x]^+$ ($x = 1-4$) where S stands for the base. At relatively high mole fraction of the co-solvents, the mixed solvated complex gradually changes to a more symmetrical complex of the type $[\text{Cu}(\text{S})_4]^+$ which remains stable in the solution. The solvating effect of 2-Pic and 4-Pic is observed to be stronger than that of Py and 3-Pic.

Key words: ^{63}Cu NMR; Pyridine; Picolines; Chemical Shift; Linewidth; Quadrupole Coupling Constant.

1. Introduction

The stabilization of copper(I) salts in solutions leads to applications in the hydrometallurgical purification of copper and silver [1–3]. Therefore, stabilization of concentrated copper(I) solutions is industrially a useful subject. The stabilization of Cu^+ salts in solutions depends upon the extent and nature of the interaction between Cu^+ and the solvent molecules, i.e. the solvation of Cu^+ ions. This interaction can be electrostatic (like in Na^+), $d\pi-p\pi$ type (like in Cu^+ and Ag^+) or through the coordination from the lone pair on the nitrogen atom of a base molecule (like in Li^+ and Cu^+). We spent several years in finding a more suitable solvent system to be used as a medium for the solvation and hence stabilization of copper(I) salts. In our previous papers [4–8], we investigated the solvation of Cu^+ in binary mixtures of acetonitrile (AN) with other nitriles [5, 8] and with a large number of organic solvents [4, 5, 7] using ^{63}Cu nuclear magnetic resonance (NMR) measurements by evaluating the copper quadrupole coupling constants e^2Qq/h . In one of our

recent papers [8], we reported the solvation behaviour of Cu^+ in n-butyronitrile (BTN) and iso-butyronitrile (iso-BTN), i.e. two isomeric solvents, by the same technique. We observed that the difference of NMR parameters in the two isomers was experimentally and precisely measurable by the use of a 500 MHz spectrometer. We wanted to extend now our studies to other similar solvent systems. In continuation with our previous ^{63}Cu NMR studies in isomeric solvent, we report herein some studies that lead to the investigation of solvation behaviour of ^{63}Cu in binary mixtures of AN with pyridine (Py) and picolines (2,3,4-Pic) by the evaluation of e^2Qq/h .

2. Experimental

2.1. Materials

As standard, Tetraacetonitrile copper(I) perchlorate ($[\text{Cu}(\text{AN})_4]\text{ClO}_4$) was used and all other ^{63}Cu NMR measurements were prepared by the method reported earlier [9, 10]. However, the salt was stored in a dry

box and was handled under anhydrous conditions. Acetonitrile (AN), pyridine (Py), and picolines (2,3,4-Pic) of analytical grade > 99.0% (E. Merck) were further purified as reported in [11].

2.2. Equipment and Method

All ^{63}Cu NMR measurements as reported earlier [6, 8] were performed on a Bruker 500 MHz narrow bore spectrometer at 298 ± 1 K using a broadband probe head and non-rotating sample tubes at 132.612 MHz. Typical parameters for the run were 300 scans of 4 K points with 45° pulse angle, a relaxation delay of 0.05 s, and a spectral window of 20 kHz. The other details of the experiments and a typical shape of the ^{63}Cu NMR spectrum in AN and Py mixtures are already reported in one of our papers [4] and by Ochsenbein and Schlaefer [12]. In all cases similar types of spectra like in the AN-Py mixture were obtained. Chemical shifts δ and linewidths Δ for ^{63}Cu NMR signals were measured relative to 0.064 M $[\text{Cu}(\text{AN})_4]\text{ClO}_4$ in AN. For the reference solution, the ^{63}Cu signal was at 482 Hz and the δ value was set to 0.0 ppm. In order to ensure the consistency of the measurements, the NMR signal of the reference solution was periodically measured. The uncertainty in the δ values were estimated at ± 0.1 ppm and ± 20 Hz, respectively. Viscosities of all binary solvent mixtures and that of the 0.064 M CuClO_4 solutions were measured at 298 ± 0.1 K using an Ubbelohde viscometer with the uncertainty estimated at ± 0.001 mPa s.

3. Results and Discussion

The characteristic effects on the linewidth due to contamination as moisture and copper (II) salts were ensured to be absent before undertaking the experimental measurements. The ^{63}Cu NMR signal at 482 Hz in the present measurements for the 0.064 M CuClO_4 solution falls within the range 480–550 Hz as reported in the literature [12, 13] and was found to be within the limit of experimental error.

The plots in Figure 1 compare the effect of Py, 2-Pic, 3-Pic, and 4-Pic on the ^{63}Cu chemical shift of copper(I) complexes coordinated to AN. One of the interesting observations arising from these data is that the addition of pyridines and picolines to a 0.064 M CuClO_4 solution in AN results in the following increasing order of the down field shift: $\text{Py} < 3\text{-Pic} < 2\text{-Pic} < 4\text{-Pic}$, and this is also the order of their basicity (4-Pic, $pK_a = 6.03$; 2-Pic, $pK_a = 5.96$; 3-Pic, $pK_a = 5.68$; and Py, $pK_a = 5.25$) [14]. This result shows that the solvation of Cu^+ by all these bases is due to an interaction of Cu^+ with the availability of the lone pair on the base molecules and not due to a $d\pi$ - $p\pi$ type of interaction.

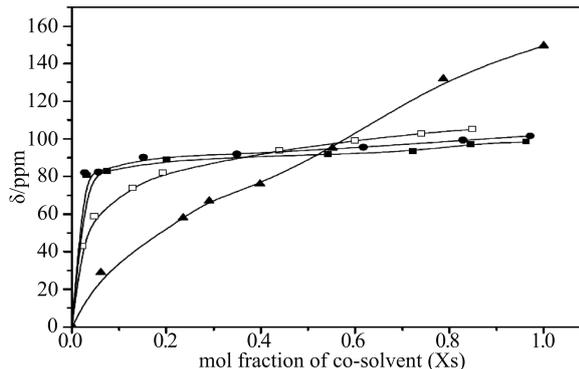


Fig. 1. Chemical shift δ for ^{63}Cu NMR signals from 0.064 M CuClO_4 solution vs. mol fraction X_s of co-solvent in AN + co-solvent mixtures at 298 K: AN + Py (\square), AN + 2-Pic (\blacksquare), AN + 3-Pic (\blacktriangle), and AN + 4-Pic (\bullet).

A further point of significant interest is that the δ value in this solvent region rises very sharply on the addition of 2-Pic and 4-Pic, whereas it can be seen increased relatively smoothly in the presence of 3-Pic and Py. In view of the above, this can be interpreted as indicating the sensitive of the solvated copper(I) ion complex to changes in its solvation interaction in the presence of a co-solvent. In other words, it is likely to be due to the replacement of AN molecules from the original complex $[\text{Cu}(\text{AN})_4]$ in pure AN by the co-solvent. However, the data seem to support the exchange of the solvent molecule occurring in the region of < 0.4 mol fraction of the co-solvent relatively effectively in respect of 2-Pic and 4-Pic followed by Py and 3-Pic. Above > 0.4 mol fraction of the co-solvent, since no significant change occurs in the δ value in the presence of 2-Pic and 4-Pic and Py as well, it appears to indicate the formation of a stable solvated entity strongly coordinated by both AN and the co-solvent. In case of 3-Pic, however, since the δ value increases consistently over the whole composition range of the solvent, we would expect it to correspond to the formation of a less stable solvated entity of the copper(I) ion.

In previous ^{63}Cu NMR studies [4–8], we found that the chemical shifts of AN were positive and

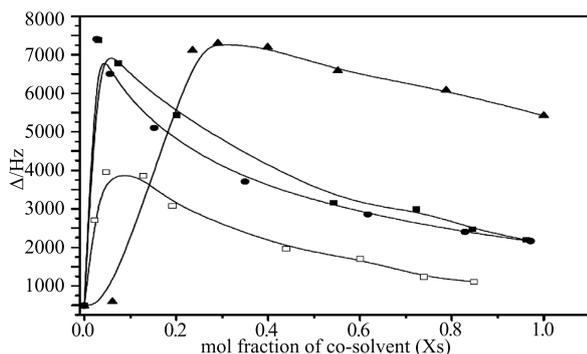


Fig. 2. Linewidth Δ for ^{63}Cu NMR signals from 0.064 M CuClO_4 solution vs. mol fraction X_s of co-solvent in AN + co-solvent mixtures at 298 K: AN + Py (\square), AN + 2-Pic (\blacksquare), AN + 3-Pic (\blacktriangle), and AN + 4-Pic (\bullet).

increased with the increase of mol fraction of various organic nitriles used as co-solvent. In each case, stable mixed complex ions of the form $[\text{Cu}(\text{AN})_{4-x}(\text{S})x]^+$ ($x=1-4$) were found formed due to the replacement of AN molecules from the original complex $[\text{Cu}(\text{AN})_4]^+$ in pure AN by the co-solvent (S). However, the negative δ values were observed for ^{63}Cu NMR signals in binary mixtures of AN with various organic solvents [4–6], which were suggested to support the existence of mixed solvated complex $[\text{Cu}(\text{AN})_{4-x}(\text{S})x]^+$ ($x=1-4$) of poor stability over the whole solvent composition range due to the rapid replacement of AN by the added co-solvent. Interestingly, even the complexes of the form $[\text{Cu}(\text{S})_4]^+$, where S stands for co-solvent, were found to be not stable in all solvents except Py and triethylphosphite (TEP).

In Figure 2, we report on the variation of linewidth as a function of solvent composition. The value can be seen rising relatively sharply to a maximum value of 7 kHz at ~ 0.1 mol fraction of Py, 2-Pic, and 4-Pic and then falls off gradually with the further increase of the co-solvent composition. In case of 3-Pic, however, the maximum can be seen at around 0.3 mol fraction of co-solvent.

3.1. Evaluation of Quadrupole Coupling Constants (e^2Qq/h)

The spin lattice relaxation of the copper nucleus is essentially governed by the quadrupole relaxation rate $(1/T_2)Q$ which can be obtained from the linewidth Δ

and its dependence on the symmetry factor of the solvation sphere η and the reorientational correlation time τ_R according to the following relations [13]:

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

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

where Δ represents the linewidth at half height of the signal, and I is the nuclear spin for the copper nucleus ($I=3/2$).

Equation (1) is applicable when the NMR line shapes are Lorentzian, whereas (2) is applicable for the limits of extreme narrowing when $\omega^2 \cdot \tau_R^2 \ll 1$. Since the η values for all these systems were not available, the factor $1 + \eta^2/3$ in (2) could not be evaluated. For the symmetrical complex $[\text{Cu}(\text{AN})_4]^+$ of tetrahedral geometry in pure AN, η is zero. In mixed solvents, where the replacement of AN by any of the other co-solvent forms a tetrahedral complex of the type $[\text{Cu}(\text{AN})_{4-x}(\text{S})x]^+$ ($x=1-4$), η can have a non-zero value but too small to be significant.

Setting $I=3/2$ for ^{63}Cu nucleus and $1 + \eta^2/3 = 1$ as before [5, 7], (2) simplifies to (3) from which e^2Qq/h can be calculate:

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

Further, when the size of the solute molecule r_i is much larger than that of the solvent molecule r_s , the reorientational correlation time τ_R in (3) can be calculated from the relation [13]

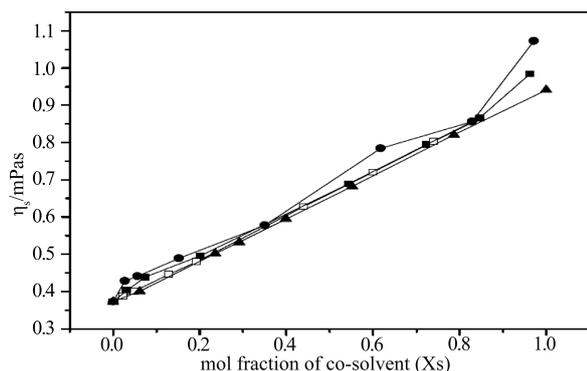
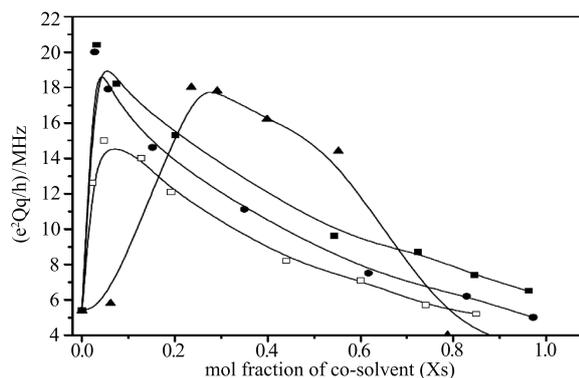
$$\tau_R = \frac{4\pi r_i^3 \eta_s}{3kT}, \quad (4)$$

where r_i stands for the radius of the spherical solvated ion or solute molecule and η_s for the viscosity of the solution. For ions and the solvent molecules of comparable size, $r_i - r_s$ and the actual reorientational correlation time τ_R is calculated by applying a microviscosity factor f_{GW} suggested by Gierer and Wirtz [15] in (4). Thus the following relation becomes valid for the calculation of actual τ_R values:

$$\tau_R = \frac{4\pi r_i^3 \eta_s}{3kT} \left[6 \frac{r_s}{r_i} + \left(1 + \frac{2r_s}{r_i}\right)^{-3}\right]^{-1}. \quad (5)$$

Table 1. Solvated radii (r_i in Å) for Cu^+ and the solvent radii (r_s in Å) values for AN + Py, AN + 2-Pic, AN + 3-Pic, and AN + 4-Pic mixtures at 298 K.

X_s	AN + Py		AN + 2-Pic		AN + 3-Pic		AN + 4-Pic	
	r_i	r_s	r_i	r_s	r_i	r_s	r_i	r_s
0.0000	4.9	2.33	4.9	2.33	4.9	2.33	4.9	2.33
0.0225	4.9	2.34	4.9	2.35	4.9	2.35	4.9	2.35
0.0480	4.9	2.35	4.9	2.37	5.0	2.37	5.0	2.37
0.1280	4.9	2.39	4.9	2.43	5.1	2.42	5.0	2.42
0.1920	4.9	2.42	5.0	2.47	5.2	2.47	5.1	2.47
0.4400	5.0	2.51	5.0	2.62	5.2	2.61	5.1	2.61
0.6000	5.0	2.59	5.0	2.73	5.2	2.72	5.2	2.72
0.7400	5.0	2.61	5.1	2.76	5.3	2.75	5.2	2.75
0.8480	5.0	2.64	5.1	2.81	5.3	2.80	5.2	2.80

Fig. 3. Viscosity η_s for 0.064 M CuClO_4 solutions vs. mol fraction X_s of co-solvent in AN + co-solvent mixtures at 298 K: AN + Py (\square), AN + 2-Pic (\blacksquare), AN + 3-Pic (\blacktriangle), and AN + 4-Pic (\bullet).Fig. 4. Quadrupole coupling constant (e^2Qq/h) for ^{63}Cu NMR signals from 0.064 M CuClO_4 solution vs. mol fraction X_s of co-solvent in AN + co-solvent mixtures at 298 K: AN + Py (\square), AN + 2-Pic (\blacksquare), AN + 3-Pic (\blacktriangle), and AN + 4-Pic (\bullet).

Using the r_i and r_s values reported in Table 1, the microviscosity factor was estimated and found to lie between 0.24–0.28, which is in good agreement with the literature value [6, 7]. From Table 1, it can be seen that the r_i and r_s values in all cases are comparable to each other, which shows the applicability of (5) above.

Using (1), (3), (5), the solution viscosity η_s for 0.064 M CuClO_4 from Figure 3, the solvated radii for the Cu(I) ion from conductance data, and the r_i value averaged at various compositions, the quadrupole coupling constants e^2Qq/h for the copper(I) ion in AN + co-solvent systems have been calculated; the (e^2Qq/h) and τ_R values have been summarized in Table 2.

Figure 4 shows the values of (e^2Qq/h) plotted against the mol fraction of the co-solvent. It is immediately apparent that e^2Qq/h varies similar to the observed linewidth Δ (Fig. 2). Thus, e^2Qq/h achieves a maximum value as the solvent composition approaches to ~ 0.1 mol fraction of Py, 2-Pic, and 4-Pic.

Also in the case of the AN + 3-Pic system, the data show a maximum at 0.3 mol fraction. Thus, we find a marked correlation of the solvent composition depending on linewidth Δ and quadrupole coupling constant e^2Qq/h . The decrease from the maximum value to a small value can be due to the formation of mixed complexes of lower symmetry. This observation is supported by evaluating the intensity of the signal with change of mol fraction of the co-solvent which is 100% in pure AN and decreases to about 10% at 0.1 mol fraction of co-solvent and then again increases to 80% in pure Py and picolines indicating that all Cu^+ are solvated by four AN molecules. The very low value of intensity in the co-solvent rich region indicates that the mixed complexes are not all tetracoordinated. There can be a lot of bi-coordinated and tri-coordinated complexes formed which are insensitive to the NMR signal. Gill et al. [4] reported the NMR quadrupole coupling constants of AN + Py and AN + 4-Pic mixtures which

Table 2. Reorientational correlation time ($\tau_R \times 10^{11}$) and ⁶³Cu quadrupole coupling constant (e^2qQ/h) in MHz from solutions of CuClO₄ in binary mixtures of Py and 2,3,4-Pic at 298 K.

X_s	AN + Py		AN + 2-Pic		AN + 3-Pic		AN + 4-Pic		
	τ_R	(e^2qQ/h)	τ_R	(e^2qQ/h)	τ_R	(e^2qQ/h)			
0.0000	1.29	5.4	1.29	5.4	1.29	5.4	1.29	5.4	(5.4)*
0.0225	1.34	12.6	1.32	15.8	1.37	5.6	1.30	15.5	(15.2)*
0.0480	1.39	15.0	1.34	18.2	1.45	6.1	1.37	18.3	(17.9)*
0.1280	1.55	14.0	1.53	17.1	1.71	9.7	1.63	15.8	(15.3)*
0.1920	1.67	12.1	1.60	15.7	1.89	14.9	1.74	13.9	(13.6)*
0.4400	2.32	8.2	2.33	11.5	2.58	15.6	7.42	9.9	(9.5)*
0.6000	2.66	7.1	2.67	9.3	3.10	9.2	2.79	7.6	(7.5)*
0.7400	2.96	5.7	2.93	8.7	3.51	6.9	3.15	6.8	(6.8)*
0.8480	3.19	5.2	3.22	7.4	3.97	4.3	3.57	6.0	(6.1)*

* These values are available in [7].

also confirms the precision of the present measurements. It has been observed from conductance measurements that ClO₄⁻, being a large ion, is poorly solvated by dipolar aprotic solvents. Since all the solvent systems used in the present work are dipolar aprotic solvents, the solvation of ClO₄⁻ is not considerable [16, 17].

4. Conclusions

In all AN + base mixtures, the (e^2Qq/h) values for copper(I) complexes increase significantly with an increase of co-solvent compositions reaches to maximum values even at very low co-solvent mole fraction and then start decreasing. The results show that

all bases used as co-solvents have a strong tendency to replace AN from the complex ion [Cu(AN)₄]⁺ found in pure AN, forming mixed complexes of the form [Cu(AN)_{4-x}(S)_x]⁺ ($x = 1-4$) with lower symmetry, e.g. [Cu(AN)_{2-x}(S)_x]⁺ and [Cu(AN)_{3-x}(S)_x]⁺. As the mole fraction of the bases increases, the mixed complexes change to more symmetrical (tetra coordinated) complexes [Cu(S)₄]⁺ indicated by their relatively low (e^2Qq/h) values.

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