Kurze Mitteilungen

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Ternary Surface Complexes
2. Complex Formation in the System Silica-Cu(II)-2,2' Bipyridyl *

Preliminary Communication

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Abstract

The adsorption of Cu(II) at the silica-water interface in the presence of 2,2′-bipyridyl (bipy) can be explained in terms of formation of ternary surface complexes $(\geqslant Si-O)_nCu(bipy)_k^{(2-n)+}$ where (n, k) = (1,1), (1,2) and (2,1). The surface complexes formed with $Cu(bipy)_k^{2+}$ are markedly more stable than those formed with $Cu^{2+}_{(aq)}$.

In a previous paper [1] we reported evidence of the formation of the ternary surface complexes $(\geqslant Si-O)Cu(en)^+$ and $(\geqslant Si-O)_2Cu(en)^0$ (en: ethylenediamine). As in the related system oxalate-Cu(II)-en [2], the stability constants of these ternary or "mixed" complexes could be obtained by decreasing the formation constants of the binary complexes $(\geqslant Si-O)Cu^+$ and $(\geqslant Si-O)_2Cu^0$ by factors governed mostly by statistics. As a consequence of this statistical control we noted [1] that the adsorption of Cu(II) at the oxide-water interface is impeded by addition of the dissolved ligand. Recent investigations [3–6] actually report numerous examples for impediment or even prevention of metal ion adsorption by dissolved ligands.

Studies on the stability of ternary complexes in solution [2,7] have shown that $Cu(bipy)^{2+}$ (bipy: 2,2′-bipyridyl) exhibits a higher affinity for oxygen donor ligands (such as oxalate) than Cu^{2+}_{aq}. One would thus expect that the ternary surface complexes $(\geqslant Si-O)_nCu(bipy)_k^{(2-n)+}$ are more stable than the corresponding binary complexes $(\geqslant Si-O)_nCu^{(2-n)+}$. Such an enhanced stability of the ternary surface complexes should in turn result in an enhancement of the adsorption of Cu(II) at oxide surfaces upon addition of bipy.

The present paper reports the results of a study of the effect of bipy on the adsorption of Cu(II) at the silica-water interface. It offers, to our knowledge, the first quantitative interpretation of enhancement of metal ion adsorption by dissolved ligands.

Experimental

(a) Survey: Samples of 2.40 g of silica were introduced in 50 ml of solutions of the composition $[Cu(II)]_{total} = 1.884 \times 10^{-4}$ *M*, $[bipy]_{total} = Qx[Cu]_{total}$ (with Q = 0.45, 0.9 and 1.8 for different sets of experiments). The experiments were performed in 0.1 *M* $NaNO_3$. The solutions were then brought to appropriate log $[H^+]$ values by addition of 10 ml of solutions of NaOH or HNO_3. The suspensions were equilibrated for a period of 30 min. at 25 ± 0.05 °C after which $[H^+]$ was obtained from emf measurements with a glass electrode. The suspensions were protected from atmospheric carbon dioxide by bubbling purified and presaturated nitrogen. In order to control the liquid junction potential, the connection between the test solution and the reference electrode was made by a "*Wilhelm*"-type salt bridge [8,9]. The supernatant liquid was decanted after centrifugation and the total amount of Cu(II) adsorbed was obtained as detailed earlier [1]. The adsorption of Cu in the absence of bipy was measured as described previously [10].

On the basis of our experience with en it was assumed that adsorption of bipy at silica is negligible under the chosen experimental conditions.

(b) Materials: Silica "Aerosil 300", from Degussa (BET specific surface S = 248 ± 5 m²/g) was used without further treatment. The total amount C_0 of reactive surface OH groups was determined as described previously [11]: C_0 = 0.73 mole/kg (0.1 *M* $NaNO_3$). This corresponds to a density of 1.77 OH groups/100 (Å)². Under the experimental conditions chosen only a very small fraction of C_0 is used for the formation of surface complexes. However, deprotonation according to:

$$\geqslant Si-OH \rightleftarrows \geqslant Si-O^- + H^+ \qquad (1)$$

must be taken into account. The empirical equation

$$\log\{\geqslant Si-O^-\} = (-\log[H^+] - 10.19)/3.27 \qquad (2)$$

was obtained from potentiometric titration of the silica sample.

(c) The acidity constant of $Hbipy^+$ and the stability constants of $Cu(bipy)_k$ complexes are listed in Table 1.

Table 1: Auxiliary Equilibrium Constants *

Stability constants of Cu(II)-bipy complexes	Acidity constant of 2,2′-bipyridyl (bipy)
$\log\beta_1$ = 8.0 $\log\beta_2$ = 13.60 $\log\beta_3$ = 17.08	$\log K_a$ = 4.49

* From *Anderegg* [12] (20 °C, 0.1 *M* $NaNO_3$).

Results and Discussion

As expected the presence of bipy modifies dramatically the speciation (dissolved—adsorbed) of Cu(II), the adsorption of Cu starting to occur at lower − log$[H^+]$values (Fig. 1). This change in the adsorption behaviour of Cu(II) indicates that Cu-bipy complexes are respon-

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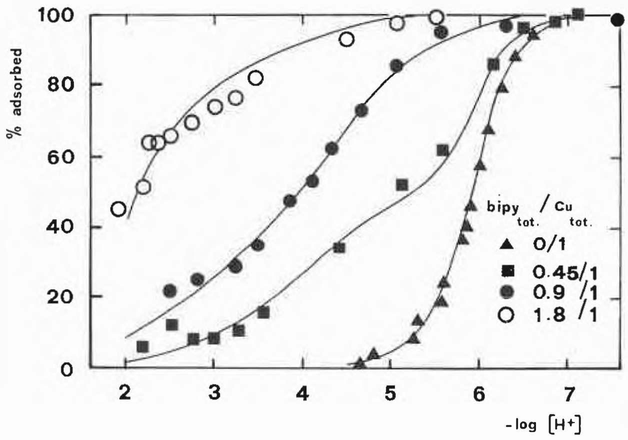

Fig. 1: Adsorption of Cu(II) (0.1 *M* $NaNO_3$, 25°C) at silica as a function of log $[H^+]$. The curves correspond to calculations using equation (7) and the constants given in Table 2.

sible for the surface reactions. The pertinent surface equilibria are:

$$>\mathrm{Si{-}OH} + \mathrm{CuL_k^{2+}} \rightleftarrows (>\mathrm{Si{-}O})\mathrm{CuL_k^{+}} + \mathrm{H^+} \qquad (3)$$

$$^{*}K^{s}_{1(\mathrm{CuL_k})} = \{(>\mathrm{Si{-}O})\mathrm{CuL_k^{+}}\}[\mathrm{H^+}]/\{>\mathrm{Si{-}OH}\}[\mathrm{CuL_k^{2+}}] \qquad (3a)$$

$$2>\mathrm{Si{-}OH} + \mathrm{CuL_k^{2+}} \rightleftarrows (>\mathrm{Si{-}O})_2\mathrm{CuL_k^{0}} + 2\mathrm{H^+} \qquad (4)$$

$$^{*}\beta^{s}_{2(\mathrm{CuL_k})} = \{(>\mathrm{Si{-}O})_2\mathrm{CuL_k^{0}}\}[\mathrm{H^+}]^2/\{>\mathrm{Si{-}OH}\}^2[\mathrm{CuL_k^{2+}}] \qquad (4a)$$

[ ]: Concentrations of species in the aqueous phase (mole/dm^3)
{ }: Concentrations of surface species (mole/kg)

where L = 2,2′-bipyridyl and k = 0, 1 or 2. The percentage of Cu(II) species adsorbed is then given by:

$$\%\ \mathrm{Cu_{adsorbed}} = \frac{100\,\dfrac{A}{V}\displaystyle\sum_{n=1}^{n=2}\sum_{k=0}^{k=2}\{(>\mathrm{Si{-}O})_n\mathrm{CuL_k^{(2-n)+}}\}}{[\mathrm{Cu}]_{\mathrm{total}} + \dfrac{A}{V}\{\mathrm{Cu}\}_{\mathrm{total}}} \qquad (5)$$

where A is the weight of silica (kg) and V the volume of the solution (dm^3). Defining the ratio:

$$R_{n,k} = \frac{^{*}\beta^{s}_{n(\mathrm{CuL_k})}}{^{*}\beta^{s}_{n(\mathrm{Cu})}} \qquad (6)$$

(where n = 1 or 2 and k = 0, 1 or 2) and using equations (3a) and (4a), equation (5) transforms into:

$$\%\ \mathrm{Cu_{adsorbed}} = \frac{100\,\dfrac{A}{V}\displaystyle\sum_{n=1}^{n=2}\sum_{k=0}^{k=2} R_{n,k}\,^{*}\beta^{s}_{n(\mathrm{Cu})}\beta_k\{>\mathrm{Si{-}OH}\}^n[\mathrm{Cu^{2+}}][\mathrm{L}]^k[\mathrm{H^+}]^{-n}}{[\mathrm{Cu}]_{\mathrm{total}} + \dfrac{A}{V}\{\mathrm{Cu}\}_{\mathrm{total}}} \qquad (7)$$

The best fit of the experimental data (Fig. 1) was obtained for the following set of values of $R_{n,k}$.

$\log R_{1,1} = 2.7 \pm 0.3$ $\quad \log R_{2,1} = 3.6 \pm 0.3$
$\log R_{1,2} = 5.3 \pm 0.3$ $\quad (\log R_{2,2} < 1.3)$

The corresponding stability constants are given in Table 2. It is seen that $^{*}\beta^{s}_{n(\mathrm{CuL_k})}$ increases with k for a given value of n. The low stability of $(>\mathrm{Si{-}O})_2\mathrm{Cu(bipy)}^0$ is probably due to steric hindrance. The uncertainty on $^{*}\beta^{s}_{2(\mathrm{Cu(bipy)_2})}$ arises from the fact that $(>\mathrm{Si{-}O})\mathrm{Cu(bipy)}^+$, $(>\mathrm{Si{-}O})_2\mathrm{Cu(bipy)}^0$ and $(>\mathrm{Si{-}O})\mathrm{Cu(bipy)}_2^+$ are the dominating species (Fig. 2).

Table 2: Formation Constants of Surface Complexes (25 °C, 0.1 *M* $NaNO_3$)

Binary complexes:
$\log {}^{*}K^{s}_{1(\mathrm{Cu})} = -4.89 \pm 0.23$ $\quad \log {}^{*}\beta^{s}_{2(\mathrm{Cu})} = -10.18 \pm 0.04$

Ternary complexes:
$\log {}^{*}K^{s}_{1(\mathrm{Cu\,bipy})} = -2.2 \pm 0.3$ $\quad \log {}^{*}\beta^{s}_{2(\mathrm{Cu\,bipy})} = -6.6 \pm 0.3$
$\log {}^{*}K^{s}_{1(\mathrm{Cu(bipy)_2})} = 0.4 \pm 0.3$ $\quad (\log {}^{*}\beta^{s}_{2(\mathrm{Cu(bipy)_2})} < -8.9)$

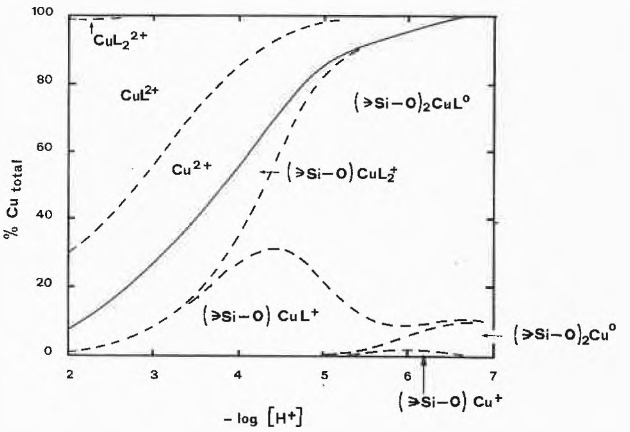

Fig. 2: Effect of log $[H^+]$ on the speciation of Cu(II). (L = bipy). $[\mathrm{bipy}]_{\mathrm{total}} = 0.9\ [\mathrm{Cu}]_{\mathrm{total}}$.

The high values obtained for the ratios $R_{n,k}$ (with the exception of $R_{2,2}$) indicate that, as in the case of dissolved ternary complexes [2,7], ligands containing oxygens as donor atoms form more stable complexes with $\mathrm{Cu(bipy)_k^{2+}}$ than with $\mathrm{Cu^{2+}_{(aq)}}$. The effect is even larger for ternary surface complexes as one can see by comparing log R = 3.6 (for $(>\mathrm{Si{-}O})_2\mathrm{Cu(bipy)}^0$) and log R = 0.43 (for oxalate-Cu-bipy^0) [2]. The presence of a π-acceptor ligand enhances the ability of Cu^{2+} species to compete with protons for adsorption at an oxide-water interface.

These results, along with those of the previous paper in this series, suggest that the rules that govern the stability constants of mixed complexes in solution are applicable to ternary surface complexes.

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