Cu(II) Bound to Hydrous Surfaces

EPR Measurements to Characterize Surface Coordination

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Interactions of cations and anions at the interface of humic substances, peptides and of hydrous oxides are of importance in natural water systems, geochemical processes and in colloid chemistry [1]. Such processes can be described by thermodynamic models which account for the partition of the ions between solid surfaces and the solution. The concept of surface complexation has proved to be very successful in these models [2]. The term *surface complexation* implies nothing concerning the molecular structure of the surface complex because the models depend essentially on mass laws with chemical parameters. Stumm et al. [3, 4] postulated the formation of inner sphere surface coordination of metal ions on hydrous oxide surfaces in analogy to corresponding reactions in solution.

This paper describes a model capable of interrelating thermodynamic aspects with spectroscopic properties. From the analysis of Cu(II) EPR spectra (spectroscopic parameters $g_{\parallel}$, $A_{\parallel}$ and $g_{\perp}$ are readily obtained) information about the geometry [5], the number and type of ligands can be derived [6]. In this work it is concluded that $\text{Cu}_{\text{aq}}^{2+}$ ion forms inner sphere type complexes with surface functional groups of hy-

drous $\delta\text{-Al}_2\text{O}_3$, TiO_2 and some types of silica. Figure 1 represents a typical EPR spectrum of Cu^{2+} adsorbed on hydrous $\delta\text{-Al}_2\text{O}_3$. The EPR parameters indicate that a pseudo square geometry around the Cu(II) center is retained.

A linear relationship between thermodynamic complex formation constants of square planar complexes of Cu(II) in aqueous solution and the corresponding EPR parameters $g_{\parallel}$ was found. The overall stability constant

$$(\log K_{\text{tot}} = \sum_{i=1}^n \log K_i)$$

can be estimated:

$$\log K_{\text{tot}} = 84(2.44 - g_{\parallel}). \quad (1)$$

Thus a decrease of the $g_{\parallel}$ value by 0.1 units corresponds to an increase in thermodynamic stability by about 8 orders of magnitude. Cu^{2+} adsorbed on some hydrous oxides exhibits parameters significantly different from those of a frozen solution of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ (Table 1). Estimated surface complex formation constants are listed and compared with K_1 and K_2 obtained by the model of Stumm and Schindler who postulated the formation of inner sphere surface complexes in their thermodynamic models; K_1 and K_2 denote the complex formation constants for the reaction of Cu^{2+} with the surface leading to monodentate and bidentate surface complexes of the type $\equiv \text{MeOCu}$ and $(\equiv \text{MeO})_2\text{Cu}$, respectively. It is important to notice that sur-

Table 1. Estimated stability constants of Cu(II) surface complexes from $g_{\parallel}$ parameters

Oxide	$g_{\parallel}$	$\log K$ (est.)	$\log K_1$ (lit.)	$\log \beta_2$ (lit.)
$\delta\text{-Al}_2\text{O}_3$	2.36	6.8	5.3 [3]	13.0 [3]
Aerosil 300	2.38	5.1	0.8 [11]	2.4 [11]
Si hydrolysis product	2.326	9.6	—	—
TiO_2	2.342	8.3	3.4 [11]	8.4 [11]

Table 2. Ternary surface complexes $(\equiv \text{AlO})_2\text{CuL}_1\text{L}_2$: $g_{\parallel}$ values and estimated formation constants

Ligand L_1L_2	$g_{\parallel}$	$A_{\parallel} [10^{-4} \text{ cm}^{-1}]$	$\log K_i$ (est.)	$\log K_1$ [7]	$\log K_2$ [7]
OH_2OH_2	2.357	148	0		
$\alpha\text{-pic}$	2.300	170	4.8	8.7	6.1
en	2.255	184	8.6	10.7	9.3
gly	2.283	176	6.2	8.6	7.2
bipy	2.295	177	5.2	8.5	5.5
phen	2.288	171	5.8	8.8	6.6
dmg	2.225	192	11.1	12.0	11.4

Fig. 1. EPR spectrum of $\text{Cu}_{\text{aq}}^{2+}$ adsorbed on hydrous $\delta\text{-Al}_2\text{O}_3$, pH = 8.23

face complexes of Cu(II) with hydrous oxides are comparable in strength and nature to complexes in solution.

Ternary complexes are formed on the surface of $\delta\text{-Al}_2\text{O}_3$ of the type $(\equiv\text{AlO})_2\text{Cu}\widehat{\text{L}}_1\text{L}_2(\text{H}_2\text{O})_2$ ($\widehat{\text{L}}_1\text{L}_2$ = bidentate ligand in equatorial position, H_2O in axial position); a decrease of the parameter $g_{\parallel}$ is observed compared to the surface complex $(\equiv\text{AlO})_2\text{-Cu}(\text{H}_2\text{O})_2$ which allows an estimate for the stability constant (K_i) of the reaction $(\equiv\text{AlO})_2\text{Cu}(\text{H}_2\text{O})_2^* + \widehat{\text{L}}_1\text{L}_2^i = (\text{AlO})_2\text{Cu}\widehat{\text{L}}_1\text{L}_2^i$ from the relationship (Table 2)

$$\log K_i = 84(g_{\parallel}^* - g_{\parallel}^i). \quad (2)$$

By comparison with literature values [7] it can be seen that the formation constants estimated are comparable in their sequence and magnitude. The behaviour of ternary ligands can assist in determining structural elements of the surface complexes. ^1H - and ^{14}N -ENDOR studies were performed which strongly support the interpretation of the EPR results. The concept of surface coordination as introduced by this EPR model implies important consequences for the extension to numerous other systems. In Fig. 2 various kinds of adsorbents (ion-exchange resins, charcoal, zeolites, layer silicates, humic substances) are classified by this relationship. There is a dramatic increase in stability in going from a sulfonic acid- to an amine-type ion-exchange resin (EPR data from [8])

Fig. 2. Classification of the stability constants of Cu(II) surface complexes by their $g_{\parallel}$ values for different types of adsorbents given by the relationship of Eq. (1)

which is consistent with the behaviour of corresponding complexes in solution.

Currently Cu(II) adsorption on layer silicates is interpreted by the picture of a $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ or $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ion, respectively, intercalated between layers (see e.g., [9]). The model presented in this study suggests that Cu(II) forms direct bonds to lattice oxygens at the interface (between layers) of the type $(\text{Si},\text{Al})\text{O}_n\equiv\text{Cu}$. The gain in stability is considerable and is comparable with carboxylic acid surface functions of charcoal [8] and fulvic acids [10]. The number of surface functions coordinated to Cu(II) can be determined by

the formation of ternary complexes with ligands coordinating stronger than water but weaker than the surface functional group itself. Plausibly, the number and strength of *surface coordinating* ligands bound to adsorbed Cu(II) strongly influences its activity in biological and catalytical systems.

This study was supported by the Swiss National Science Foundation. The author is grateful to W. Stumm's encouragement and interest.

Received June 13, 1983

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