

SURFACE COMPLEX FORMATION AT THE ADSORPTION OF Cu^{2+} IONS AND 2,2'-BIPYRIDINE ONTO HIGHLY DISPERSE SILICA

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Abstract

The enhanced adsorption of copper ions onto silica surface from the solution containing 2,2'-bipyridine is explained by ternary surface complex formation. The equilibrium reaction constants of binary and ternary complexes have been calculated using constant capacitance model. The potentiometric titration data were used in order to determine the $\text{H}^+/\text{Cu}^{2+}$ exchange stoichiometry. The adsorption of 2,2'-bipyridine on a copper-containing silica surface has been studied too. The equilibrium of 2,2'-bipyridine binding to immobilized copper ions are well reproduced by the constants for the formation of ternary surface complexes from an aqueous solution containing copper ions and 2,2'-bipyridine. This indicates clearly that under experimental conditions all reactions are reversible and speciation is controlled by the thermodynamics.

Introduction

The presence of organic metal-complex forming agents in solution may significantly affect the adsorption of metal ions onto hydrous oxide surface. Bourg *et al.* [1] found unusual enhancement of the adsorption of Cu^{2+} at the silica surface by 2,2'-bipyridine. This observation was explained by the formation of ternary surface complexes. This effect is very important with respect to many applications because it shows that the affinity of oxide surfaces can be controlled by the adsorption of metal ions. For this reason the system Cu^{2+} , 2,2'-bipyridine, amorphous silica was studied by several groups since the seminal paper of Bourg *et al.* [1] as a model system for surface complex formation. Von Zelewsky and Bemtgen [2] were the first ones that applied EPR to characterize the structure of the surface complexes. They could identify a 1:1 and a 1:2 Cu^{2+} / 2,2'-bipyridine surface complex. The equilibrium constant estimated from the spectral intensities confirmed the stabilization of these complexes at the silica surface found by Bourg *et al.* [1]. Cheah *et al.* [3] published a detailed XAFS and EPR study which proved the structure of the ternary surface complexes proposed in the earlier work.

Ternary surface complexes are obtained either by the adsorption of complexes between metal ions and organic ligands formed in solution or by the successive adsorption of the two components. In an earlier paper we reported the preparation of ternary surface complexes between Cu^{2+} and bipyridine at a SiO_2 surface by these two reaction paths. The complexes have been characterized by their EPR and absorption spectra [4]. No difference was observed between the spectra of the complexes obtained by the two different reactions, indicating that their structure is identical and does not depend on the method of preparation.

In this paper we report a quantitative study of the adsorption of Cu^{2+} and 2,2'-bipyridine onto silica surface as a function of their concentrations and the pH of the

solutions. These data allowed us to determine the equilibrium constants of the formation of binary and ternary surface complexes. In addition we measured the distribution of 2,2'-bipyridine between the solution and a silica surface which was modified beforehand by the adsorption of copper ions. The measured isotherm of bipyridine is well reproduced with the calculated equilibrium constants. This proves that all the reactions in this system are reversible and the speciation is controlled by thermodynamics.

Experimental

Materials

Amorphous highly disperse silica A-300 (Chlorvinyl, Kalush, Ukraine) with surface area 300 m²/g, and reagents NaNO₃, Cu(NO₃)₂ · 6H₂O, 2,2'-bipyridine (bipy) (all p.a., Fluka) were used as received. HNO₃ and NaOH solutions were prepared from Titrisol (Merck). All solutions and suspensions were prepared from doubly distilled water. The temperature was kept constant 25 ± 0.2 °C and ionic strength was fixed with 0.1 M NaNO₃.

Acid-base titration of silica suspensions

The stock suspension of silica with concentration 10 g/L in 0.1 M NaNO₃ was prepared and stirred for 2 weeks. Afterward, 30 ml of this suspension and 30 ml 2mM HNO₃ were placed in special thermostated reactor equipped with a combine glass electrode from pH-meter Metrohm 713, tip of automatic titrator Dosimat Metrohm 665, magnetic stirrer, and tubes for argon bubbling. The pH-meter and automatic titrator were connected and managed with computer by special titration program. This mixture was titrated with 5 mM NaOH. After each addition of base equilibrium was assumed if subsequent EMF measurements taken in 15 min intervals did not differ by more than 0.1 mV. The concentration of free hydrogen ions was obtained from EMF measurements with using Nernst equation for solutions with constant ionic strength. Coefficients in this equation were determined from the calibration titration of samples without of silica. Acid-base titration of suspensions containing of copper ions or copper ions with 2,2'-bipyridine (Cu: bipy 1:1, 1:2 and 1:3) were carried out in a similar manner. In these experiments the result concentration of silica was 5 g/L, copper ions - 0.5 mM and bipy - 0.5, 1.0 and 1.5 mM respectively.

Adsorption of copper ions, bipyridine and their complexes

The series of samples were prepared by mixing of 10 ml of stock suspension of silica and 10 ml 1 mM solutions of copper nitrate and 2,2'-bipyridine for the study of pH-dependence of adsorption from individual solutions. The suspensions with the same ratios Cu²⁺: bipy as for potentiometric titration were prepared to study the adsorption from mutual solutions.

The pHs of these suspensions were adjusted to desirable values over the range 3-8. These suspensions were stirred for 1 h, then pH were tested, and silica was separated with centrifugation (5 000 rpm, 10 min). The concentrations of copper ions in supernatant solutions were determined using atomic absorption spectrophotometry (AAS-30, Karl Zeiss, Germany). The concentrations of bipy were measured by UV spectrophotometry (Specord M-40, Karl Zeiss, Germany) as complex with copper ions 1:1 which is formed with an excess amount of Cu²⁺ (5 mM) and characterized with 2 maxima at 300 nm ($\epsilon=15500$) and 310 nm ($\epsilon = 15800$) [5]. The copper ion and bipy adsorption values were calculated as the difference between initial and equilibrium concentrations.

Preparation of silica modified by copper ions

The 5 g silica was added to 500 ml of 0.1 M NaNO₃ solution containing 2 mM Cu(NO₃)₂. The pH was adjusted to 5.8-5.9 by dropwise addition of 1 mM NaOH solution to the stirred suspension. The suspension was stirred under argon (protection from CO₂) for 1 week. This time was necessary to attain equilibrium between dry silica and solution containing sodium and copper nitrates. The pH was tested periodically and readjusted if

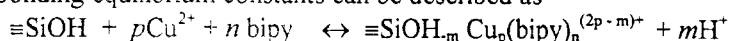
necessary. After centrifugation the concentration of adsorbed copper ions was calculated from the decrease of Cu^{2+} in the supernatant solution. It was found to be 0.57 mmol/l or 0.057 mmol/g SiO_2 corresponding approximately to 30% of total amount of Cu^{2+} in the suspension. This corresponds to a surface loading of 1 Cu^{2+} adsorbed per 8.77 SiOH -group. The mean distance between two adsorbed Cu^{2+} ions is 3.34 nm as calculated from the area available for 1 Cu^{2+} assuming a homogeneous distribution.

Adsorption of bipy on silica modified with copper ions

Samples of the prepared suspension, 20 ml each, were placed in centrifuge tubes. After centrifugation (5000 rpm, 10 min) supernatant solution was completely removed from the solid. A known amount of a bipyridine solution (0.5 - 10 mmol/l, pH 6) was added to each of the samples and the total volume of suspension was completed up to 20 ml. The pH value of each sample was controlled and adjusted to pH 6.0 if necessary. After the samples were stirred for 60 min, the pH was checked. It did not change significantly in all experiments. Then the suspension was centrifuged and concentrations of bipyridine and Cu^{2+} were determined in the supernatant equilibrium solutions.

Speciation in the solution and suspension

The speciation in solutions and suspensions is calculated with the program GRFIT [6]. GRFIT solves solution speciation problems in homo- and heterogeneous systems. It is specially written for evaluating concentrations, thermodynamical equilibrium constants and capacities, or site densities, depending on the chosen double-layer model. We choose as a model of surface ionization and complex formation the constant capacitance model (CCM) [7] because all our experiments were made at strong constant ionic strength. At the treatment of the potentiometric titration data with GRFIT program the concentrations of active surface groups and capacitance of double electric layer are fitted. Then, these values are used in the calculations of equilibrium reaction constants. The surface reactions and corresponding equilibrium constants can be described as



$$\beta = \frac{\{\equiv\text{SiOH}_m\text{Cu}_p(\text{bipy})_n^{(2p-m)+}\} [\text{H}^+]^m}{\{\equiv\text{SiOH}\} [\text{Cu}^{2+}]^p [\text{bipy}]^n} e^{(2p-m)F\Psi/RT}$$

where $m = 0, 1, 2$; $n = 0, 1, 2$; $p = 0, 1$.

Moreover this program allows us to calculate the concentration of the species in solution and on the surface if the composition of the system (total concentrations and pH) and the chemical model (reaction stoichiometry) are known.

Results and discussion

The results of potentiometric titration of the silica suspension (in absence and presence of copper ions and bipy) were used for the calculation of the quantity of protons adsorbed on surface or released from surface at the dissociation (Q , mmol/l):

$$Q = \frac{v_A A - v_B B + (v_0 + v_A + v_B) \times (K_w / [\text{H}^+] - [\text{H}^+])}{(v_0 + v_A + v_B)}$$

where v_A , v_B are the volumes of added acid or base with concentrations A and B , respectively; v_0 is the initial volume of silica suspension (in l); $K_w = [\text{H}^+][\text{OH}^-] = 10^{-13.78}$, and $[\text{H}^+]$ - concentration of protons determined from EMF measurements. The curves Q as functions of pH are shown in Fig. 1. In this figure the positive values of Q mean the releasing of protons from surface and negative values of Q mean the uptake of protons from solution. The proton adsorption on silica surface in the pH range being

studied is practically not observed. The releasing of protons is a result of dissociation of silanol groups and the intrinsic dissociation constant determined by equation is calculated:

$$\equiv\text{SiOH} \leftrightarrow \equiv\text{SiO}^- + \text{H}^+ ; \quad k_{\text{int}} = \frac{\{\equiv\text{SiO}^-\} [\text{H}^+]}{\{\equiv\text{SiOH}\}} \exp(-F\Psi/RT)$$

Ψ is the surface potential. The calculated value of dissociation constant of silanol groups ($\log k_{\text{int}} = -6.90 \pm 0.03$) is in a good agreement with literature data [8,9]. This constant was fitted with using of concentration of silanol groups 0.5 mM/g and capacitance 1.2 F m⁻². As for point of zero charge (PZC) we observe an interval in the pH range 2 - 3 in which silica surface is practically electroneutral on the whole. The value of PZC from 2 [8-11] to 2.9 [12] are quoted.

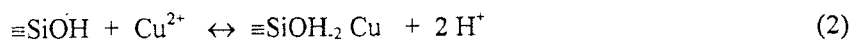
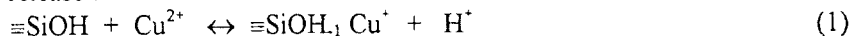
In Fig.1 potentiometric titration data of silica suspension in presence of copper ions or copper- bipyridine complexes are also present. The comparison of these titration curves with titration curve of silica alone allowed us to calculate the concentrations of protons released at the adsorption of copper ions or their complexes with bipy on silica surface.

The concentration of each species in solution (in the absence of silica) was calculated (GRFIT, "Solution speciation") as a function of pH using the complex formation and acidity constants represented in Table 1. This calculation shows that in solution with ratio Cu : bipy 1:1 the main complex is Cu(bipy)²⁺, and in solutions with ratios Cu : bipy 1: 2 and 1:3 the predominant species is complex Cu(bipy)₂²⁺ over the range of pH 3-8.

The results of adsorption study of Cu²⁺ and bipy onto silica surface are shown in Figs.2 and 3. The adsorption data were used to fit adsorption constants of the surface complex formation reactions using the values of site density and double layer capacitance fitted at the titration of silica suspension.

Adsorption of Cu²⁺ ions

The copper ions adsorption as a function of pH is shown in Fig.2. The adsorption of copper ions begins at pH >4 and abruptly increases at pH > 5. We supposed that surface complexation of Cu²⁺ ions by silica involves bond formation with surface silanol groups and proton release :



The calculated equilibrium complex formation constants for reactions (1) and (2) and all other ones are represented in Table 1.

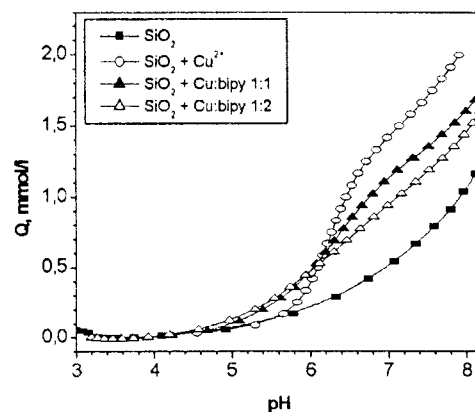


Fig.1 Potentiometric titration of silica suspension and its mixture with solutions containing Cu²⁺, and Cu²⁺- bipyridine with ratios 1:1 and 1:2.

Table 1

The complex formation reactions in solution and onto silica surface and corresponding equilibrium constants

Reaction	logK ^{int}
$\text{Bipy} + \text{H}^+ \leftrightarrow \text{bipyH}^+$	4.43 [13]
$\text{Bipy} + 2\text{H}^+ \leftrightarrow \text{bipyH}_2^{2+}$	5.93 [13]
$\text{Cu}^{2+} + \text{bipy} \leftrightarrow \text{Cu}(\text{bipy})^{2+}$	8.00 [13]
$\text{Cu}^{2+} + 2 \text{bipy} \leftrightarrow \text{Cu}(\text{bipy})_2^{2+}$	13.50 [13]
$\text{Cu}^{2+} + 3 \text{bipy} \leftrightarrow \text{Cu}(\text{bipy})_3^{2+}$	16.90 [13]
$\equiv\text{SiOH} \leftrightarrow \equiv\text{SiO}^- + \text{H}^+$	-6.90±0.03
$\equiv\text{SiOH} + \text{Cu}^{2+} \leftrightarrow \equiv\text{SiOCu}^+ + \text{H}^+$	-4.20±0.03
$\equiv\text{SiOH} + \text{Cu}^{2+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{SiOCuOH} + 2\text{H}^+$	-10.36±0.03
$\equiv\text{SiOH} + \text{bipy} \leftrightarrow \equiv\text{SiOH}(\text{bipy})$	2.01±0.03
$\equiv\text{SiOH} + \text{H}^+ + \text{bipy}^+ \leftrightarrow \equiv\text{SiOH}(\text{Hbipy})^+$	6.49±0.04
$\equiv\text{SiOH} + \text{Cu}^{2+} + \text{bipy} \leftrightarrow \equiv\text{SiOHCu}(\text{bipy})^+$	9.88 ± 0.03
$\equiv\text{SiOH} + \text{Cu}^{2+} + \text{bipy} \leftrightarrow \equiv\text{SiOCu}(\text{bipy})^+ + \text{H}^+$	5.02 ± 0.03
$\equiv\text{SiOH} + \text{Cu}^{2+} + \text{bipy} + \text{H}_2\text{O} \leftrightarrow \equiv\text{SiOCuOH}(\text{bipy}) + 2\text{H}^+$	-3.26 ± 0.08
$\equiv\text{SiOH} + \text{Cu}^{2+} + 2\text{bipy} \leftrightarrow \equiv\text{SiOHCu}(\text{bipy})_2$	15.67 ± 0.03
$\equiv\text{SiOH} + \text{Cu}^{2+} + 2\text{bipy} \leftrightarrow \equiv\text{SiOCu}(\text{bipy})_2^+ + \text{H}^+$	10.20 ± 0.03
$\equiv\text{SiOH} + \text{Cu}^{2+} + 2\text{bipy} + \text{H}_2\text{O} \leftrightarrow \equiv\text{SiOCuOH}(\text{bipy})_2 + 2\text{H}^+$	2.26 ± 0.09

The $[\text{H}^+]/\{\text{Cu}^{2+}\}$ exchange stoichiometry of these reactions were determined using the potentiometric titration data. The potentiometric curve (Fig.1) of silica suspension containing Cu^{2+} ions passes higher than a curve of silica titration, which is evidence of proton release at the Cu^{2+} ion adsorption onto the silica surface. To determine the ratio of H^+ released concentration to Cu^{2+} ion adsorbed concentration we modeled the titration curve with the GRFIT program. We took into account proton release at the dissociation of silica itself and two reactions of Cu^{2+} ion binding with silanol groups on Eqs. (1) and (2). The best agreement between experimental and calculated titration curves as well as agreement between experimental and calculated adsorption curves were observed at the formation on the surface both complexes. On the one hand, we supposed that a second proton was formed at the hydrolysis of adsorbed copper ions that is released from water molecules in the coordination sphere of a hydrated Cu^{2+} ion. The possibility of formation of such complexes is confirmed by us [4] and others [14] on ESR spectra of copper ions adsorbed on silica. The intensity of the ESR signal in such spectra is less than could be expected from total concentration of adsorbed copper. Apparently some part of copper exists on the surface as hydroxocomplexes which are inclined to formation of polynuclear diamagnetic clusters. On the other hand, the concentration of silanol groups 0.5 mM/g corresponds to their distribution, 1 $\text{SiOH} / \text{nm}^2$, and the distance between two silanol groups approximately 1.13 nm. This distance is larger than necessary for the formation of complex with participation of two silanol groups. Although it is impossible to exclude the

irregular distribution of silanol groups on the surface and the presence of surface area with closer arrangement of these groups. So we can mark this complex as $\{\equiv\text{SiOH}_2\text{Cu}\}$ or $\{\equiv\text{SiOCuOH}\}$.

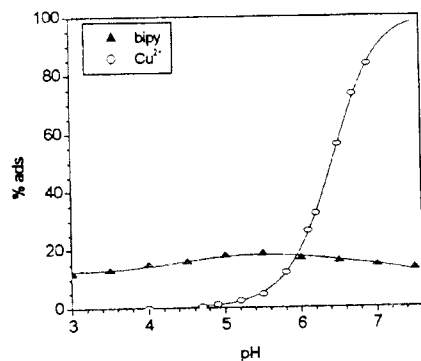


Fig.2 Adsorption of Cu^{2+} and bipy from individual aqueous solution as a function of pH ($C_{\text{Cu}} = 0.5 \text{ mM}$, $C_{\text{bipy}} = 0.5 \text{ mM}$, $C_{\text{SiO}_2} = 5 \text{ g/l.}$).

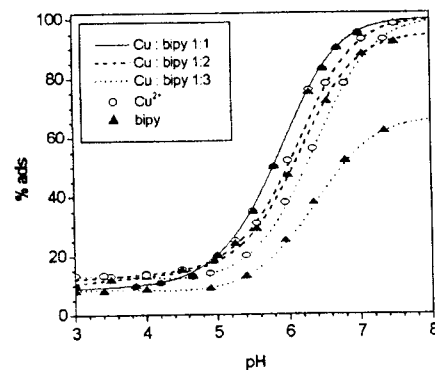
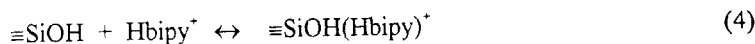
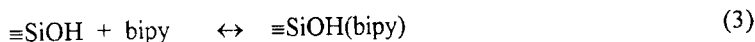


Fig.3 Adsorption of Cu^{2+} ions and bipy from solutions with different ratios as a function of pH ($C_{\text{Cu}} = 0.5 \text{ mM}$, $C_{\text{bipy}} = 0.5; 1.0; \text{ and } 1.5 \text{ mM}$, $C_{\text{SiO}_2} = 5 \text{ g/l.}$).

Adsorption of 2,2'-bipyridine

The bipyridine adsorption on silica surface from aqueous solutions as a function of pH is shown in Fig.2. We assumed formation of 2 binary complexes and calculated their equilibrium reaction constants according with equations (3) and (4) with using GRFIT program :



The formation of these complexes is confirmed by UV reflectance absorption spectra. We isolated several samples of adsorbed bipyridine from solutions with different pH and observed in UV reflectance spectra absorption band at $\sim 280 \text{ nm}$ which is characteristic for neutral bipy molecule and at $\sim 300 \text{ nm}$ inherent for protonated form of bipyridine.

Adsorption of copper - 2,2'-bipyridine complexes

The results of the adsorption study of copper ions and bipyridine from solutions with molar ratio 1:1, 1:2 and 1:3 are present in Fig.3. At the adsorption from mutual solutions an essential increase in copper ion adsorption is observed. At low pH 3 - 5 the adsorbed concentrations Cu^{2+} and bipy remain almost constant. At pH > 5 the percentage of adsorbed copper ions and bipy rapidly increases with pH. The almost full agreement of Cu^{2+} and bipy adsorption from solution with ratio 1:1 suggests that the main adsorbed species is the complex $\text{Cu}(\text{bipy})^{2+}$. The fraction of adsorbed bipy from solution with ratio 1:2 is slightly less than that of adsorbed copper ions. It can arise from simultaneous adsorption of $\text{Cu}(\text{bipy})^{2+}$ and $\text{Cu}(\text{bipy})_2^{2+}$. The molar fraction adsorption of bipy from solution with ratio 1:3 is approximately less by a factor of 1.5 than adsorption of copper ions suggesting that complex $\text{Cu}(\text{bipy})_2^{2+}$ is predominantly adsorbed on silica surface. The comparison of these data with potentiometric data indicates that the interaction of complex

ions with surface in pH range from 3 to 4 is not accompanied by release of protons, at the increase of pH one proton releases per adsorbed copper ion and at pH > 6.5 slightly enhancement of released proton concentration is observed. The last is evidence that reaction with release of 2 protons is possible.

Together with binary complex formation reactions for Cu^{2+} (1), (2) and for bipy (3), (4) on silica surface we assumed the following reactions of ternary complex formations and calculated the corresponding equilibrium constants:

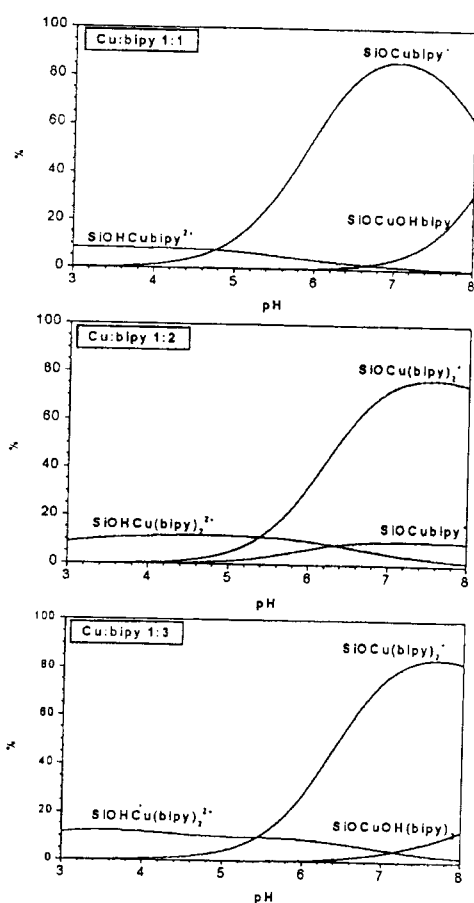
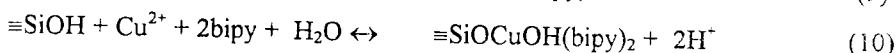
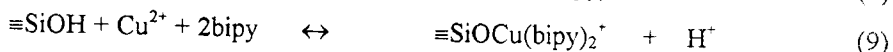
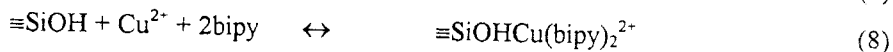
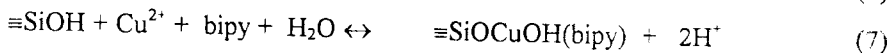
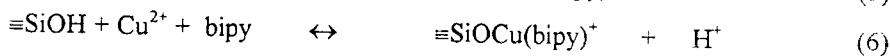
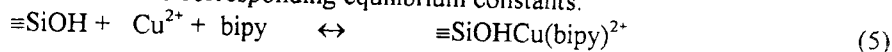


Fig.4 Surface speciation of copper-bipyridine complexes.

Using these constants we calculated the composition of adsorption layer onto silica surface in dependence of pH and composition of solutions containing Cu^{2+} and bipy (Fig.4). It was found that at the adsorption from solutions containing copper ions and bipy in different ratios only ternary complexes are formed onto silica surface. We observed in the reflectance spectra of these samples in UV-region the absorption bands inherent to complex ions $\text{Cu}(\text{bipy})^{2+}_n$ and in visible region - absorption bands of d-d transitions of copper ions containing the nitrogen donor atoms in coordination sphere [4].

Adsorption of 2,2'-bipyridine at the silica modified with copper ions

The results of the adsorption, measured for 2,2'-bipyridine on the surface of silica modified with copper ions are presented in Table 2. The experimental data are the concentrations of 2,2'-bipyridine and Cu^{2+} in the equilibrium solutions after adsorption. The values show that with increasing the 2,2'-bipyridine total concentration the amount of adsorbed copper ions decreases. The reason for the desorption of Cu^{2+} is the decrease of the free Cu^{2+} concentration due to the formation of relatively stable copper - 2,2'-bipyridine complexes in solution. The free bipy concentrations [bipy], which are also given in

Table 2, are calculated from measured total concentration of Cu^{2+} and 2,2'-bipyridine and the pH of the solution using the equilibrium constants of the protonation of bipy and the complex formation reactions with copper ions [13].

Table 2

Initial and equilibrium concentrations of bipy and copper ions
($\{\text{SiOH}\} = 5 \text{ mmol/l}$; $\{\text{Cu}\} = 0.57 \text{ mmol/l}$; pH 6; 0.1 M NaNO_3)

C_{bipy} , mmol/l	$C_{\text{bipy}}/\{\text{Cu}\}_{\text{total}}$	Total equilibrium bipy concentration, mmol/l	Total equilibrium Cu (II) concentration, mmol/l	$-\log[\text{bipy}]$ free *
0.50	0.877	0.108	0.157	7.78
0.56	0.982	0.126	0.135	7.12
0.60	1.053	0.142	0.133	6.47
0.75	1.316	0.217	0.150	5.62
0.84	1.474	0.255	0.156	5.37
1.15	2.018	0.439	0.192	4.46
1.30	2.280	0.569	0.216	4.00
1.70	2.982	0.960	0.264	3.50
2.00	3.510	1.275	0.307	3.32
3.20	5.614	2.308	0.380	2.90
4.00	7.018	3.02	0.431	2.75
6.00	10.526	4.68	0.470	2.50
8.00	14.035	6.35	0.515	2.30
10.0	17.544	8.062	0.522	2.20

* - calculated from experimental total equilibrium concentrations *bipy* and *Cu(II)* using the program GRFIT.

Earlier we assumed that the adsorption of copper ions on silica surface from solutions at $\text{pH} > 4$ could be modeled postulating the formation of two surface complexes with the stoichiometry $\{\equiv\text{SiOH}_1\text{Cu}^+\}$ and $\{\equiv\text{SiOH}_2\text{Cu}\}$ if the surface coverage was lower than 0.23 % of monolayer. We should mention that at higher Cu^{2+} loading surface precipitation of copper hydroxide species was observed even at a surface coverage as low as 0.8 % [14]. At pH 6 $\{\equiv\text{SiOCu}^+\}$ accounts approximately 60% of total amount of adsorbed copper ions. In a study of the interaction of 2,2'-bipyridine with a surface modified by adsorbed Cu^{2+} one has in addition to the formation of the ternary Cu^{2+} - 2,2'-bipyridine surface complexes to consider the adsorption of 2,2'-bipyridine by active sites of the silica surface. The stoichiometry and the equilibrium constants for this process were determined in an independent experiment by measuring the adsorption of bipy as a function of pH. Using the constants in Table 1 we calculated the isotherm for 2,2'-bipyridine and Cu^{2+} adsorption in this experiment. Figure 5 shows the experimental data points and the calculated curve (solid line). The good agreement clearly indicates that, under the conditions of our experiment, pH 6, $[\text{Cu}^{2+}]_{\text{tot}} < 9 \{\text{SiOH}\}_{\text{tot}}$, all the reactions are reversible at the silica surface and the speciation is controlled by thermodynamics within the time scale of the experiment.

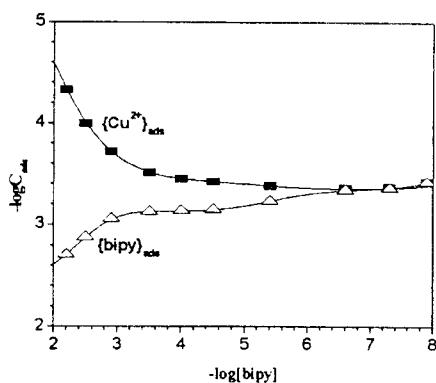


Fig.5 Experimental (points) and Calculated (solid line) isotherm of Bipyridine adsorption on copper-containing silica surface: $\{\text{SiOH}\} = 0.5 \text{ mmol/g}$, $\{\text{Cu}\} = 0.57 \text{ mmol/g}$, $\{\text{bipy}\}_{\text{total}} = 0.5 - 10 \text{ mmol/l}$, pH 6.0.

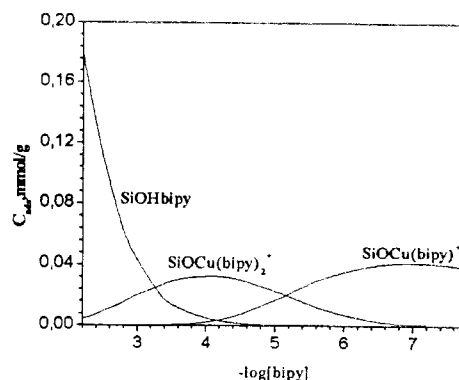
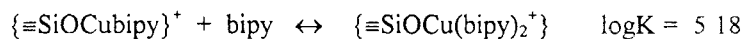
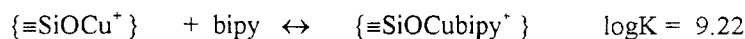


Fig.6 The surface distribution of bipyridine complexes onto copper-containing silica ($\{\text{SiOH}\} = 0.5 \text{ mmol/g}$, $\{\text{Cu}\} = 0.057 \text{ mmol/g}$, pH 6.0).

The distribution of surface bipy complexes as a function of free bipy concentration is shown in Fig.6. Different complexes of bipy are formed at the surface of copper-containing silica as a function of increasing bipy concentration. At low bipy concentrations, lower or about equal to the amount of adsorbed Cu^{2+} , the complex $\{\equiv\text{SiOCubipy}^+\}$ is formed. Under these conditions the adsorption of bipy is strongly enhanced by the Cu^{2+} at the surface. At higher bipy concentrations the complex $\{\equiv\text{SiOCu}(\text{bipy})_2^+\}$ is formed on the surface. However, the amount of this species at the surface is small, because a significant part of adsorbed copper ions goes into solution as $\text{Cu}(\text{bipy})_n^{2+}$ ($n = 1, 2, 3$). At even higher bipy concentrations the copper ions disappear practically completely from the surface and excess bipyridine forms the binary surface species $\{\equiv\text{SiOHbipy}\}$ and $\{\equiv\text{SiOH Hbipy}^+\}$ with surface silanol groups. The UV reflectance spectra of the samples also confirm the formation of these complexes. We isolated several samples that correspond to different compositions of adsorption layer and observed in UV spectra two adsorption bands at 300 and 310 nm inherent for complexes $\text{Cu}(\text{bipy})^{2+}$ and $\text{Cu}(\text{bipy})_2^{2+}$ and one band at 280 nm, which is characteristic for bipyridine not bound with copper ions [15]. The concentrations of complexes in which bipy is bound to the complex $\{\equiv\text{SiOCuOH}\}$ are very small; they never exceed $0.1 \mu\text{mol/g}$.

From the results of our measurements, we can deduce the equilibrium constants for the binding of bipyridine onto Cu^{2+} immobilized to the silica surface by thermodynamic cycle. The constants show that the bipyridine prefers strongly to be bound to Cu^{2+} at the surface rather than directly to the SiOH sites :



A comparison with the corresponding complex formation constants in solution indicates that the 1:1 complex formation is more favorable at the surface ($\log K = 9.22$)

than in solution ($\log K = 8.00$). This result is direct evidence of the additional stability of the ternary surface complexes. The affinity for the second bipy molecule is slightly less favorable than that in solution. The introduction of second bipy molecule into coordination sphere of the complex $\{\equiv\text{SiOCubipy}^+\}$ is sterically hindered and requires of substantial rearrangement of the structure of ternary surface complex.

Another interesting equilibrium constant that might be deduced from the results, is the one for the formation of the ternary surface complexes of Cu^{2+} and bipy, starting from adsorbed bipyridine and adsorbed Cu^{2+} . This reaction corresponds to a redistribution of the molecules at the surface. In these reaction the number of educt species is equal to the number of product species. Hence, the equilibrium constants for this reaction is independent of the concentration scale respectively the standard state used:

$$\{\equiv\text{SiOCu}^+\} + \{\equiv\text{SiOHbipy}\} \leftrightarrow \{\equiv\text{SiOCubipy}^+\} + \{\equiv\text{SiOH}\} \quad \log K_{1,\text{sur}} = 7.2$$

$$\log K_{1,\text{surf}} = \frac{\{\equiv\text{SiOCubipy}^+\} \{\equiv\text{SiOH}\}}{\{\equiv\text{SiOCu}^+\} \{\equiv\text{SiOHbipy}\}}$$

$$\{\equiv\text{SiOCubipy}^+\} + \{\equiv\text{SiOHbipy}\} \leftrightarrow \{\equiv\text{SiOCu}(\text{bipy})_2^+\} + \{\equiv\text{SiOH}\} \quad \log K_{2,\text{surf}} = 3.2$$

$$\log K_{2,\text{surf}} = \frac{\{\equiv\text{SiOCu}(\text{bipy})_2^+\} \{\equiv\text{SiOH}\}}{\{\equiv\text{SiOCubipy}^+\} \{\equiv\text{SiOHbipy}\}}$$

The constants of the reaction at the surface are smaller than those for the reactions in solution. This gives some hint into the influence of the solvation on complex formation. We think that this decrease of the stability is mainly due to a reduced hydrophobic effect of bipy in the surface layer. The free bipyridine molecules in which the aromatic cycle are hydrophobic are destabilized by unfavorable solvation in aqueous solution, which supports complex formation under these conditions. This effect is less pronounced for bipyridine adsorbed onto silica surface.

Summary

Our measurements of adsorption of 2,2'-bipyridine onto a hydrous silica surface, which previously modified by Cu^{2+} , shows clearly that the equilibria are controlled by the same equilibrium constants as ternary surface complex formation. This indicates that all the surface reactions in this system are thermodynamically controlled, at least under the conditions of our experiment. This means especially low copper ions surface coverage to suppress the formation of $\text{Cu}(\text{OH})_2$ phases at the surface. Under these conditions equilibrium constants for many different surface processes can be obtained using thermodynamic cycle.

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