

## The Surface Chelate Effect

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The binding of metal ions to monolayer assemblies is important in many disciplines. The ability of surface functional groups to selectively bind certain metal ions has shown their utility in chemical sensing<sup>1,2</sup> and environmental cleanup.<sup>3</sup> Metal ions bound to surface groups have been used for the immobilization of protein molecules for purification,<sup>4,5</sup> sensing,<sup>6,7</sup> and two-dimensional crystallization.<sup>8</sup> In the so-called “molecular beaker epitaxy” developed by Mallouk<sup>9</sup> and others,<sup>10,11</sup> metal ion binding to surface phosphate groups is used to form multilayer films. Similar strategies have been extended to other ligands, such as pyridine, carboxylate, and sulfonic acid.<sup>12,13</sup> For example, layer-by-layer assemblies could be produced by first attaching a monolayer of 11-mercaptoundecanoic acid (HS-(CH<sub>2</sub>)<sub>10</sub>-COOH) to a gold substrate followed by the sequential adsorption of Cu<sup>2+</sup> ions and 11-mercaptoundecanoic acid to form multilayer films.<sup>14</sup>

In the examples listed above, the thermodynamics of metal ions binding to surface ligand groups is a key issue, but this issue has not been addressed in past studies. It should be noted that one may not simply extrapolate solution-phase metal coordination chemistry to surfaces. One distinguishing factor related to the coordination of metal ions to surfaces is that the surface functional groups can be arranged in a two-dimensional array. We set out to explore how this two-dimensional arrangement may lead to an inherent chelate effect, which we will call the “surface chelate effect”.

To establish the surface chelate effect, we measured the binding constants of Cu<sup>2+</sup> ions to surface -COOH groups<sup>14</sup> using a self-assembled monolayer (SAM) of 16-mercaptohexadecanoic acid (HS-(CH<sub>2</sub>)<sub>15</sub>-COOH) (MHA). There has been some inconsistency in the literature in regards to the formation of thiol monolayers with -COOH terminal groups. Arnold et al. showed the necessity of using very dilute solutions of MHA to form well-ordered monolayers, not multilayers.<sup>15</sup> We followed this procedure for monolayer formation by using 0.02 mM ethanolic solutions of MHA that contained 10% acetic acid. The acid helps prevent multilayer formation as well as protonate the carboxyl groups. The gold substrates were prepared by thermal evaporation of 100 nm of Au onto polished Si(100) with a 10 nm Cr adhesion layer. The samples were cut into 1.5 cm<sup>2</sup> pieces and immersed in thiol solutions within 3 h of Au deposition. After a total reaction time of ≥ 16 h for the formation of the SAM, each sample was removed and rinsed extensively with ethanol. A water contact angle of nearly zero indicated a hydrophilic surface due to the terminal carboxyl groups. Grazing angle FTIR showed a CH<sub>2</sub> asymmetric stretching frequency of 2918 cm<sup>-1</sup>, characteristic of a well-ordered, close-packed film.

To deduce the magnitude of the surface chelate effect, we compare the surface formation constant to solution-phase data. It is known that the molecules succinic acid (HOOC-(CH<sub>2</sub>)<sub>2</sub>-COOH) and glutaric acid (HOOC-(CH<sub>2</sub>)<sub>3</sub>-COOH) are able to chelate bivalent metal ions by forming seven- and eight-membered rings, respectively. The formation constant of Cu<sup>2+</sup> with these molecules is much larger than that of acetic acid.<sup>16</sup>

SAM samples were incubated in solutions composed of 0.5 mM Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O and either succinic or glutaric acid at various concentrations. This involved equilibrating a solution of Cu<sup>2+</sup> ions with an excess of competing reagent (succinic or glutaric acid). All solutions were buffered to a pH of 6.0 with MES buffer (4-morpholinoethanesulfonic acid).<sup>17</sup> The *K*<sub>soln</sub> value is quite large (~2000 M<sup>-1</sup> for succinic acid), so it can be assumed that nearly all of the Cu<sup>2+</sup> is bound to the chelating acid. After 1 h, the MHA SAM-covered sample was added to the solution. The sample was incubated with the solution for 15 min and then rinsed extensively with ethanol and dried under an argon stream. We found that the surface saturated with Cu<sup>2+</sup> after the first minute; a 15 min reaction time assured saturation. Ethanol was used as the rinsing solvent as was previously reported,<sup>14,18</sup> and we did not observe a decrease in surface Cu coverage with increased rinsing time. We used ethanol instead of water because a decrease in surface Cu<sup>2+</sup> was indeed observed when the surface was rinsed with H<sub>2</sub>O.

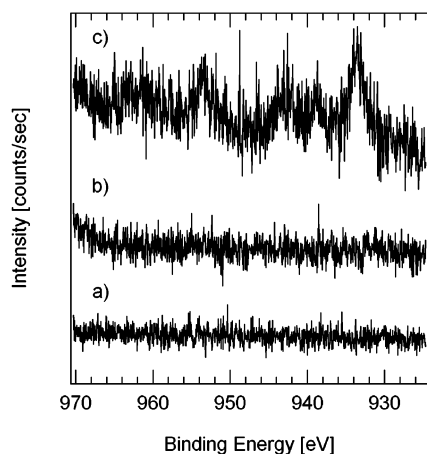
The formation constant (*K*<sub>soln</sub>) for the binding of Cu<sup>2+</sup> to an acid molecule in the solution phase is shown in eq 1. Similarly, the surface binding constant (*K*<sub>surf</sub>) is given by (2), where [Surf] and [Cu-Surf] represent the unoccupied and occupied surface sites, respectively, for Cu<sup>2+</sup> adsorption. As shown below, one surface site consists of two adjacent -COOH groups. Combining the two yields eqs 3.

$$K_{\text{soln}} = \frac{[\text{Cu} - \text{Acid}]}{[\text{Cu}^{2+}][\text{Acid}]} \quad (1)$$

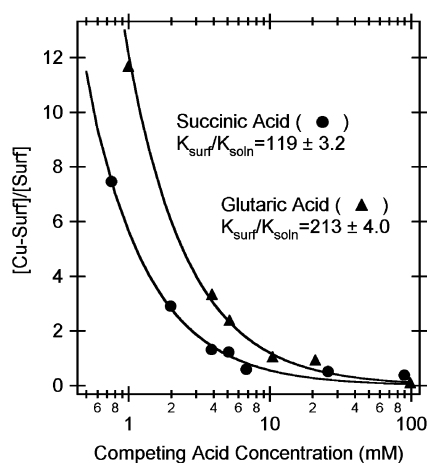
$$K_{\text{surf}} = \frac{[\text{Cu} - \text{Surf}]}{[\text{Cu}^{2+}][\text{Surf}]} \quad (2)$$

$$\frac{[\text{Cu} - \text{Surf}]}{[\text{Surf}]} = \frac{K_{\text{surf}}[\text{Cu} - \text{Acid}]}{K_{\text{soln}}[\text{Acid}]} \quad (3)$$

X-ray photoelectron spectroscopy (XPS) was used to follow the binding of Cu<sup>2+</sup> to the MHA SAM. Figure 1 shows high-resolution spectra of the Cu 2p region from various samples. It has been previously shown that Cu<sup>2+</sup> on the surface may be reduced to Cu<sup>1+</sup> by photoelectrons.<sup>18</sup> Therefore, we reduced the Al X-ray anode power to 50 W and minimized scan time. Some reduction was still observed, but we did not notice any loss in total Cu peak area upon prolonged X-ray exposure. Figure 1a shows a background spectrum from a mercaptohexadecane (HS-(CH<sub>2</sub>)<sub>15</sub>-CH<sub>3</sub>) SAM which was exposed to a pure Cu<sup>2+</sup> solution. As expected, no copper adsorbed to this monolayer. Spectrum b in Figure 2 shows a MHA sample that was exposed to a Cu<sup>2+</sup> solution at a pH of 2. No copper was seen bound to this sample either. Previously reported values for the p*K*<sub>a</sub> of surface acid groups on MHA SAMs range from 4.5 to 7.7.<sup>19</sup> All surface carboxyl groups should be protonated at pH = 2, which explains the lack of copper adsorption. Li et al. studied the effect of pH on Cd<sup>2+</sup> adsorption on carboxylic acid terminated



**Figure 1.** XPS spectra in the Cu 2p region for (a) a mercaptohexadecane SAM exposed to  $\text{Cu}^{2+}$ , (b) a MHA SAM exposed to  $\text{Cu}^{2+}$  (pH = 2), and (c) a MHA SAM exposed to  $\text{Cu}^{2+}$  (pH = 6.0).



**Figure 2.** Ratios of occupied/unoccupied surface sites for  $\text{Cu}^{2+}$  adsorption on MHA SAM vs succinic or glutaric acid concentration in the solution phase. The solid curves are fits of the data to eq 3, yielding the indicated ratios in formation constants.

SAMs and found the deposition of multilayer Cd containing species at pH  $\geq 8$ .<sup>20</sup> We also observed multilayer formation as well as the precipitation of  $\text{Cu}(\text{OH})_2$  at pH  $> 8$ . For these reasons, our competitive binding experiments were done at a pH of 6.0. Spectrum c in Figure 1 is from a MHA sample that was exposed to a solution of  $\text{Cu}^{2+}$  at pH = 6.0. The Cu 2p<sub>3/2</sub> peak at 933.5 eV as well as the presence of shake up peaks is characteristic of Cu in the +2 state.<sup>21</sup> On the basis of the Cu<sub>2p</sub> and O<sub>1s</sub> peak intensities, we obtain an atomic Cu/O ratio of  $0.233 \pm 0.023$ . This is close to the ratio of 0.25 expected for one copper atom bound to two surface acid groups, forming a dimeric structure.<sup>14</sup> Note that there is no adsorption of free acids from the solution because the C 1s signal remains constant.

A series of solutions were prepared in which the concentration of the competing acid was varied. The initial  $\text{Cu}^{2+}$  concentration was kept constant. The Cu/O atomic ratio was determined from XPS for each sample. The difference between 0.233 and the atomic ratio for each sample was directly related to the number of unoccupied sites. A plot of the ratio of occupied/unoccupied sites versus competing acid concentration is shown in Figure 2 for both succinic and glutaric acid. The solid curves are fits to eq 3, which yield the ratios of  $K_{\text{surf}}/K_{\text{soln}} = 119 \pm 3.2$  for succinic acid and  $213 \pm 4.0$  for glutaric acid. The ratio of these two numbers, 1.8, is in qualitative agreement with the ratio of  $\sim 1.5$  for solution-phase

binding constants of succinic and glutaric acid.<sup>16</sup> The greater formation constant of metal ions binding to surface carboxylic groups than those of succinic and glutaric acids in the solution phase establishes a strong surface chelate effect. The chelate effect refers to the greater stability of metal complexes of multidentate ligands than those of unidentate ligands. Consider the coordination of two carboxylic groups to one  $\text{Cu}^{2+}$ . In the case of acetic acid, this involves two bimolecular reactions steps. However, in the case of a bidentate ligand, such as succinic or glutaric acid, the coordination of the second ligand is a unimolecular reaction. Thus, there is tremendous statistical advantage for the bidentate in the formation of the second reaction step. Energetic gain or penalty associated with the formation of the cyclic metal–bidentate bond is usually of less significance than the statistical gain. Indeed, the reaction rate for the second coordination bond formation and, thus, the overall equilibrium constant involving bidentate can be orders of magnitude higher than that of unidentate. Such a statistical advantage should be further enhanced when one considers the binding of the  $\text{Cu}^{2+}$  to a two-dimensional array of surface ligands, provided that binding to two surface carboxylic groups is geometrically allowed on the SAM surface. After the coordination to one surface carboxylic group, there is a great propensity for the metal ion to bind to one of the six neighboring carboxylic groups within an ordered monolayer. The surface chelate effect may be further enhanced by the well-known possibility of a precursor state to chemisorption in surface chemistry.

We believe the surface chelate effect demonstrated here is of general significance to adsorption on molecular surfaces and should depend strongly on chemical functionality and monolayer structure. This effect can be advantageously incorporated into the design of monolayer-based technologies, such as those previously discussed.

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