Molecular Scale Description of Anion Competition on Amine-Functionalized Surfaces

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Supporting Information

ABSTRACT: Many industrial and biological processes involve the competitive adsorption of ions with different valencies and sizes at charged surfaces; heavy and precious metal ions are separated on the basis of their propensity to adsorb onto interfaces, often as anionic ion clusters (e.g., [MCl₄]⁻). However, very little is known, both theoretically and experimentally, about the competition of factors that drive preferential adsorption, such as charge density or valence, at interfaces in technologically relevant systems. There are even contradictory pictures described by interfacial studies and real life applications, such as chlorometalate extractions, in which charge diffuse chlorometalate ions are extracted efficiently even though charge dense chloride ions present in the background are expected to occupy the interface. We studied the competition between divalent chlorometalate anions (PtCl₆²⁻ and PdCl₄⁻) and monovalent chloride anions on positively charged amine-functionalized surfaces using in situ specular X-ray reflectivity. Chloride anions were present in vast excess to simulate the conditions used in the commercial separation of heavy and precious metal ions. Our results suggest that divalent chlorometalate adsorption is a two-step process and that the divalent anions preferentially adsorb at the interface despite having a charge/volume ratio lower than that of chloride. These results provide fundamental insight into the structural mechanisms that underpin transport in phases that are relevant to heavy and precious metal ion separations, explaining the high efficiency of low charge density ion transport processes in the presence of charge dense anions.

1. INTRODUCTION

The advanced energy and electronic technologies of today rely on relatively rare elements, such as lanthanides, actinides, and platinum group metals (PGMs). Most of these elements are refined, recycled, and reprocessed via solvent extraction and ion exchange processes.‡ Although some of these separation technologies can be considered mature, they are not adequate for the exponentially growing volumes of heavy metal production and recycling around the globe. A breakthrough in these technologies will require a molecular scale understanding of the processes beyond the classical pictures assumed from the macroscopic properties.

A fundamental aspect of most separation technologies is that they involve preferential ion adsorption on, or transfer through, interfaces.§ For example, during solvent extraction, hydrated ions in an aqueous phase are transferred into an organic phase, usually with the aid of amphiphilic extractant molecules that form reverse micellar structures around the target ions to solubilize them in the organic phase.¶ Very little is known, however, about the molecular scale structures that form at interfaces during ion separations, with the exception of a few recent X-ray/neutron scattering and reflectivity studies of interfacially adsorbed lanthanide cations at complexing amphiphiles.¶ Even less is known about the structure of anionic species that interact electrostatically with positively charged surfaces that are relevant to separations.

Unlike the adsorption of metal cations, which is driven by dative (i.e., coordinating) interactions with ligating groups on the surface, anions are extracted via a competitive “anion exchange” mechanism. For example, the production of Pt and Pd involves the preferential extraction of the PtCl₆²⁻ and PdCl₄⁻ anions over Cl⁻, which is usually in excess by several orders of magnitude.¶ Other heavy metal ions, such as the actinides, can also be separated as the chlorometalate species when in the presence of very high chloride concentrations.¶ Extraction is performed using an anion exchanger, often a quaternary amine, which either is tethered to a solid support or is in a water-immiscible organic liquid phase. Thus, extraction pivots on the preferential adsorption of the chlorometalate anion onto a solid—liquid or liquid—liquid interface consisting of positively charged organic groups. The efficiency of this process, like in all anion exchange separations, depends on the ability of the chlorometalate anion to compete effectively with chloride for adsorption onto the charged interface.

Received: September 21, 2016
Published: October 7, 2016
The very fast kinetics and high efficiencies of extraction of the chlorometalate from highly concentrated chloride aqueous phases imply that these charge diffuse ions are preferentially adsorbed at positively charged interfaces compared to chloride. Singly charged chlorometalate anions, such as AuCl$_4^{-}$, are even more charge diffuse and thus even more preferentially extracted. This relationship between charge density and extraction has been known in the separations community for decades and underpins many anion separations processes. However, from an interfacial perspective, this observation presents a dichotomy as ions with high charge density, such as chloride, are expected to interact more strongly with charged surfaces than ions with low charge density, such as chlorometalate. For instance, both theory and simulations suggest that the charge/volume ratio plays an important role in the competition of ions with different valencies, particularly in the high surface charge regime. This ratio roughly expresses the combined effects of electrostatic energy and entropy at the interface. Higher valence ions are expected to preferentially adsorb at the interface because of the electrostatic forces, and the entropic effects favor the adsorption of smaller ions. Although in theoretical and computational studies (under ideal conditions) a larger charge/volume ratio leads to stronger adsorption, in reality, hydration, van der Waals interactions, and nonideal surface properties should also play significant roles. For instance, the preferential extraction of PtCl$_6^{2-}$ (2/139 = 0.0144 e$^-$/Å$^3$) and PdCl$_4^{2-}$ (2/106 = 0.0189 e$^-$/Å$^3$) over Cl$^-$ (1/24 = 0.0417 e$^-$/Å$^3$), whose charge/volume ratio is more than twice those of the metalate anions, suggests that the charge/volume ratio does not always determine preferential adsorption (volumes are calculated using atomic radii). It is important to note that the extraction efficiency is ultimately related to the final structures in the organic and aqueous phases, rather than the interfacial complexes. However, efficient extraction is unlikely to occur if Cl$^-$ blocks the interfacial adsorption of chlorometalate anions. Clarifying this apparent contradiction between the interfacial picture of the competitive adsorption of ions at a charged interface and chlorometalate extraction improves our understanding of these complex interfaces significantly, particularly those used in the separation of heavy and precious metal ions.

With a goal of addressing this dichotomy, we probe the structure at the interface between an amine-functionalized silicon substrate and an aqueous solution having high concentrations of chloride ions and minute concentrations of platinum group chlorometalate ions (reflecting the conditions in separations processes). Studying a model system at the solid−liquid interface to understand some aspects of an extraction process at the liquid−liquid interface has two advantages. First, the kinetics of these separation processes can be very fast, making it very difficult to catch observable structures at the liquid−liquid interface on reasonable time scales, unless some “arrested” metastable structures are formed. Second, a real extraction system involves too many complex interactions, such as ion−extractant interactions, extractant−extractant interactions, and interactions with organic and aqueous solvents. Therefore, it is usually not possible to completely isolate a certain effect. Studying fixed amine surfactants isolates the interfacial amine−anion interactions, allowing direct observation of the competition between the anions that is independent of other effects. The results of this study provide a benchmark for improving our understanding of more complex systems. Also, this simple model system can be interpreted in the context of biological, geochemical, or other systems in which competitive ion adsorption plays an important role. In particular, experimental studies of the electric double layer (EDL) structure of concentrated electrolytes are scarce, and recent studies suggest that these systems might be more complicated than generally assumed.

X-ray reflectivity (XR) probes the laterally averaged interfacial structure perpendicular to the surface normal with subnanometer spatial resolution. Although XR is not element specific, the strong electron density contrast between chloride (18 e$^-$ for Cl$^-$) and chlorometalate (116 and 182 e$^-$ for PdCl$_4^{2-}$ and PtCl$_6^{2-}$, respectively) anions allows for reasonably accurate determination of the surface chlorometalate concentrations. Despite the relatively low bulk concentrations and charge density of chlorometalate versus chloride, interfacial adsorption of PtCl$_6^{2-}$ and PdCl$_4^{2-}$ is highly favored, accounting for the high efficiency of ion transport processes that target these ions. We were also able to determine the maximal metalate coverage, providing important insights into the energy−entropy balance during the competition.

2. EXPERIMENTAL SECTION

All chemicals were purchased from Sigma and used without further purification. Silicon samples were cleaned in a piranha solution (7/3 sulfuric acid/hydrogen peroxide) at 120 °C for 30 min. Then they were rinsed with deionized (DI) water three times for 5 min each and finally dried with nitrogen. (3-Aminopropyl)triethoxysilane (APTES) solutions were freshly prepared in anhydrous toluene (~1.0% (w/w)). Clean silicon substrates were placed in these solutions for 1 h at room temperature. To prevent evaporation of the solvent during the reaction, the top of the Petri dish was closed. After surface functionalization, the samples were rinsed with excess toluene and dried with nitrogen.

Chlorometalate solutions were prepared from palladium(II) chloride and hexachloroplatinate acid by dissolving appropriate amounts in background solutions (5 M LiCl or 3 mM NaCl at pH 1 as described in the text). The pH of the solutions was controlled with 1 M HCl. In addition to simulating industrial conditions, these concentrations also ensure that the chlorometalate speciation is fixed at PtCl$_6^{2-}$ and PdCl$_4^{2-}$.

The XR measurements were taken at beamlines 33-IDD and 12-IDD of the Advanced Photon Source (APS) at Argonne National Laboratory. A thin film sample cell (Figure 1) and PILATUS detector were mounted on a six-circle diffractometer (a modified Huber psi-C diffractometer at 12-IDD and a Newport Kappa diffractometer at 33-IDD). The incident beam size was focused to

![Image](https://example.com/image.png)

Figure 1. Depiction of the thin film sample cell and X-ray scattering geometry. The Kel-F sample cell holds the silicon substrates with the help of a kapton film (yellow lines) secured by an O-ring and compression from the sides (not shown) to prevent fluid leakage. When the fluid is injected, the kapton film puffs up, allowing quick concentration equilibration. Immediately before the measurement, the kapton film was collapsed to leave a liquid film (a few micrometers thick) over the substrate.)
~80 μm vertically. The horizontal size was set to 0.5 mm by a pair of slits. The specular reflectivity signal was recorded as a function of the vertical momentum transfer \(q_z = (4\pi/\lambda) \sin(\theta/2)\), where \(\lambda\) is the wavelength of the X-rays (0.60 Å at 33ID-D and 0.73 Å at 12ID-D) and \(2\theta\) is the scattering angle. The beam damage due to the X-rays was identified carefully by repetitive measurements on the same spot, and the final measurements were limited to shorter time intervals. Samples were shifted perpendicular to the beam to a fresh spot between measurements. We also studied 0.5 mM PtCl\(_6^{2-}\) in a 3 mM NaCl background solution (Figure 2c). However, a comparable measurement with PdCl\(_4\) was not taken because the speciation of PdCl\(_4\) cannot be fixed to PdCl\(_{2.5}\) at low Cl\(^{-}\) concentrations.29

The concentration-dependent measurements were taken on a single APTES film for each metalate. All experiments begin with the background solution and progress from low to high chlorometalate concentrations. After each measurement, the sample chamber is thoroughly flushed, by puffing up the kapton film, with the new solution and allowed to equilibrate for at least 10 min, and the sample is translated to a fresh spot. After the solution is fully exchanged, interfacial equilibration is expected to occur in less than a few minutes.30 This provides a reliable background subtraction to identify the effects of increasing the bulk metalate concentration on the interfacial concentration. The intensity of the XR signal \((R)\) decreases in a manner proportional to \(q^{-4}\) even at an ideal flat surface; this is known as the Fresnel reflectivity \((R_F)\).23,25 Normalizing \(R\) to \(R_F\) enhances visualization of the Kiessig fringes (the minima and maxima in XR data due to the electron density gradients at the interface).23

Before discussing the results obtained from the model-dependent fits, we investigate the qualitative behavior of the XR signal in panels a and b of Figure 2 as a function of increasing metalate concentration. Two major trends can be observed in both Pd and Pt data. The minima in the XR curves shift to higher \(q\) values in 0.5 mM metalate solutions (blue squares) compared to those in the background (black circles). However, as the concentration increases to 5 and 50 mM (green diamonds and red triangles, respectively), the minima move in the opposite direction (to smaller \(q\) values). Because \(q\) represents reciprocal space, these results suggest that the interfacial structure (APTES and ions) becomes thinner compared to the background solution at 0.5 mM metalate, counterintuitively implying desorption of ions. However, as the metalate concentration increases further, the thickness increases as expected. Also, the amplitude of the Kiessig fringes increases significantly in the 5 and 50 mM solutions, implying that the density contrast at the interface is also increasing.

### 3. RESULTS AND DISCUSSION

We measured the XR at the APTES–electrolyte interface for concentrations of 0.5, 5, and 50 mM PdCl\(_4^{2-}\) and PtCl\(_6^{2-}\) in 5 M LiCl as shown in panels a and b of Figure 2, respectively. Before injecting the metalate anions, we measured the XR with the 5 M LiCl background solution (black circles in each plot). We also studied 0.5 mM PtCl\(_6^{2-}\) in a 3 mM NaCl background solution (Figure 2c). However, a comparable measurement with PdCl\(_4\) was not taken because the speciation of PdCl\(_4\) cannot be fixed to PdCl\(_{2.5}\) at low Cl\(^{-}\) concentrations.29

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#### 3.1. APTES in 5 M LiCl

We first discuss APTES films in background solutions without any metalate ions. Figure 3 shows the EDP of the APTES film structure obtained from fitting the top reflectivity data set in Figure 2a. The films used

![Figure 2](image_url) Specular XR intensity normalized to Fresnel reflectivity as a function of the vertical momentum transfer \((q)\) from aqueous–APTES interfaces at different bulk metalate concentrations in (a and b) 5 M LiCl and (c) 3 mM NaCl solutions. The solid black lines show the fits to the data (symbols) as discussed in the text.

![Figure 3](image_url) Electron density profile (EDP) of APTES on silicon in 5 M LiCl (solid red line). The green solid lines show the same EDP without interfacial roughness. The bottom left inset is the molecular model of APTES. The superimposed cartoon depiction of the APTES film structure with Cl\(^{-}\) adsorption is deduced from the EDP.
Table 1. Best Fit Parameters for the XR Data and Fits Shown in Figure 2a

<table>
<thead>
<tr>
<th></th>
<th>silicon oxide</th>
<th>first APTES layer</th>
<th>second APTES layer</th>
<th>adsorption layer</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>L (Å)</td>
<td>σ (Å)</td>
<td>L (Å)</td>
<td>σ (Å)</td>
</tr>
<tr>
<td>PdCl$_4^{2-}$ in 5 M Cl$^-$</td>
<td>0</td>
<td>0.68</td>
<td>12.9</td>
<td>2.2</td>
</tr>
<tr>
<td>0.5 mM</td>
<td>0.58</td>
<td>12.9</td>
<td>2.2</td>
<td>0.57</td>
</tr>
<tr>
<td>5 mM</td>
<td>0.68</td>
<td>12.9</td>
<td>2.2</td>
<td>0.57</td>
</tr>
<tr>
<td>50 mM</td>
<td>0.68</td>
<td>12.9</td>
<td>2.2</td>
<td>0.51</td>
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<tr>
<td>PdCl$_4^{2-}$ in 3 M Cl$^-$</td>
<td>0</td>
<td>0.68</td>
<td>12.4</td>
<td>1.8</td>
</tr>
<tr>
<td>0.5 mM</td>
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<td>0.57</td>
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<tr>
<td>5 mM</td>
<td>0.68</td>
<td>12.4</td>
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<tr>
<td>50 mM</td>
<td>0.68</td>
<td>12.4</td>
<td>1.8</td>
<td>0.58</td>
</tr>
<tr>
<td>PtCl$_2$$^+$ in 3 mM Cl$^-$</td>
<td>0</td>
<td>0.69</td>
<td>10.3</td>
<td>2.2</td>
</tr>
<tr>
<td>0.5 mM</td>
<td>0.69</td>
<td>10.3</td>
<td>2.2</td>
<td>0.49</td>
</tr>
<tr>
<td>error (μ)</td>
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<td>0.04</td>
<td>0.01</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The silicon electron density and the Si–SiO interface roughness are fixed to 0.71 e$^-$/Å$^3$ and 1.5 Å, respectively, for all samples. The superphase density is fixed to 0.36 e$^-$/Å$^3$ for the 5 M LiCl background solutions and 0.33 e$^-$/Å$^3$ for the 3 mM NaCl background solution. All the parameters were allowed to float within reasonable limits for zero metalate concentration background samples. Then, the silicon oxide parameters and APTES layer thicknesses are fixed (marked with a superscript a) for the measurements with metalate ions. The uncertainties shown in the bottom row are estimates from the least-squares fitting of the background solutions; they are very similar and usually smaller for other fits in which some of the parameters are fixed.

with other samples also have the same qualitative EDP with only slight differences in the densities and thicknesses (Table 1 and Figure 4). The ~6 Å lengths of each APTES layer match quasi-bilayer formation.\(^{34}\) We modeled the film with two separate boxes and allowed the parameters to vary freely. The fits show that the second layer is ~10–20% less dense than the first. A multilayer surfactant is representative of interfaces in commercial liquid–liquid extraction systems,\(^{3}\) where atomically flat monolayers are unusual.

A separate layer was assigned for the adsorbed Cl$^-$ ions. As shown in Figure 3, this layer has almost the same density as the previous layer and is only ~3 Å thick. Indeed, it is possible to obtain an identical EDP using a single box (with an ~8 Å thickness) for the top APTES layer and the Cl$^-$ layer.\(^{35}\) However, this extra slab allows an easier comparison between different samples with varying metalate concentrations. Nevertheless, all the results presented here can be reproduced with three-slab models with no qualitative differences (see the Supporting Information for details).

The APTES coverage, calculated from the EDP in Figure 3, is ~24 Å$^2$/molecule in the first layer and ~29 Å$^2$/molecule in the top layer. The same analysis of the APTES film used for PtCl$_2$$^+$ adsorption (Figure 2b) gives values of ~22 and ~27 Å$^2$/molecule for the first and second APTES layer, respectively. The APTES film used in the NaCl background solution, which was prepared on a silicon substrate from a different batch during an earlier beamtime, has coverages of ~30 and ~32 Å$^2$/molecule. Because the APTES films are prepared under ambient conditions, different relative humidity levels during the preparation are likely responsible for the slight differences in the films.\(^{36,37}\) These coverages are used to estimate the surface charge, assuming that all the amine groups at the top surface are protonated, and therefore positively charged in the highly acidic (pH 1) solution.

3.2. Chloride Desorption from the Surface with Metalate Injection. When 0.5 mM metalate is injected into the 5 M LiCl background solution, the minima in the reflectivity signal (Figure 2, blue squares) shift toward higher values of q, suggesting a decrease in the thickness of the interfacial layer. A comparison of the EDPs calculated by fitting the XR data (Figure 4) shows that this is due to a decrease in the electron density of the slab assigned to the adsorbed anions.

This decrease in the EDP must be caused by a net decrease in the number of adsorbed ions or by thinning of the APTES with the size of the molecule calculated by the MMFF94 force field (Figure 3, inset).\(^{31}\) Contrary to most well-known self-assembly processes, such as octadecyltrichlorosilane (OTS),\(^{32,33}\) APTES self-assembly is not self-limiting after the formation of the first layer; the APTES Si has three Si–O groups that can attach to the surface or self-polymerize, and the hydrocarbon chain is too short to block the formation of APTES–APTES bonds. Therefore, the thickness of the film increases with reaction time (Figure 3).\(^{34}\) Our synthesis parameters matched well with previous reports that show
film. The injection could dislodge physisorbed APTES molecules; this is unlikely because the film is thoroughly washed during preparation and first injected with the background solution. The presence of metalate ions could rearrange the APTES layer. This could change the shape of the EDP but would conserve the total amount of interfacial electrons. The data show a net decrease in the number of interfacial electrons, making this scenario unlikely. Finally, the metalate ions could break some of the Si–O bonds, thinning the film; this is also unlikely, especially because this strong chemical interaction would need to occur without enough chlorometalate adsorption to increase the electron density. Therefore, it is most likely that these changes arise from desorption of adsorbed ions.

Interestingly, the subtraction of the background EDP from the 0.5 mM EDP gives a very similar differential EDP for both metalate anions (Figure 4, inset), suggesting that the effect is approximately the same for both PdCl₄²⁻ and PtCl₆⁻² Cl⁻ anions desorb from the surface and are not replaced by metalate anions. This behavior is reflective of the identical bulk phase liquid–liquid extraction equilibria for PdCl₄²⁻ and PtCl₆⁻²−.

\[
PdCl₄^{2⁻} + 2[ClHA] = [PdCl₆HA₂]²⁻ + 2Cl⁻
\]

\[
PtCl₆^{2⁻} + 2[ClHA] = [PtCl₆HA₂]²⁻ + 2Cl⁻
\]

where A is the amine extractant.

Why do Cl⁻ ions leave the surface after the introduction of the metalate? Most likely, metalate anions are attracted to the surface and disturb the Cl⁻ ions in the Stern layer. However, metalate anions cannot be adsorbed, possibly because of their hydration (Figure 4, inset schematic). Because XR is sensitive to the gradient in the EDP, the few metalates that are not adsorbed exactly at the surface (and therefore cannot form a well-defined layer) do not create enough contrast to be directly measured. Assuming charge compensation, this is the simplest explanation. Also, the almost identical differential EDPs for both metalates (Figure 4, inset) suggest that there is no significant metalate adsorption on the Stern layer, which would result in observable differences due to their dissimilar electron densities. It is known that, on negatively charged mineral surfaces, divalent cations adsorb as outer sphere and extended outer sphere complexes with little effect on the total electron density profile. Hence, it is not surprising that divalent anions behave similarly at a positive potential. In this picture, ~4% of the Cl⁻ ions leave the surface at a bulk metalate concentration of 0.5 mM; it is also assumed that for every two chloride ions leaving the Stern layer, one metalate is adsorbed in the diffuse layer. However, in liquid–liquid ion extraction systems using amine/ammonium extractants, partial or complete dehydration of the anion is necessary to complete transport from one phase to another via the interface. Therefore, under conditions where ion extraction is known to proceed rapidly (i.e., at higher metalate concentrations that reflect process conditions), there should be evidence of penetration of the anion from the diffuse layer into the Stern layer.

3.3. Chlorometalate Adsorption at the Stern Layer.

Increasing the metalate concentration in the bulk to 5 and 50 mM causes the minima in the XR data to shift to smaller values of q and increases the Kiessig fringe amplitudes (Figure 2, green diamonds and red triangles); this is direct evidence of the adsorption of metalate anions on the Stern layer. Figure 5 shows the electron density profiles derived for these higher relative metalate concentrations, including the measurement in a 3 mM NaCl background (Figure 2c), which has a relative metalate concentration of 0.17.

The differential EDPs (Figure 5b,c) provide important insights into the adsorption of metalate anions as a function of the relative metalate concentration. The integration of each curve gives the change in the electron density per unit area at the interface; this can be converted to the coverage of metalate anions by using the number of electrons they have. We can normalize each of the coverages to the available number of sites obtained from the APTES molecular areas, assuming full coverage (θ = 1) when two APTES molecules are occupied by one metalate (Figure 6). It is important to note that XR provides EDPs that are convoluted with the experimental resolution (π/q_max ~ 4 Å in these experiments). Therefore, the differential EDPs are too broad to determine the exact position of the ions. However, the area under the EDP is a more robust parameter.

Figure 6 summarizes all the results obtained from the XR experiments. The first remarkable result is that, after calculating the number densities and normalizing with respect to the surface charge, there is no significant difference between PdCl₄²⁻ and PtCl₆⁻² adsorption at the interface over a relative concentration range of three decades. The charge/volume ratios of PdCl₄²⁻ and PtCl₆⁻² are 45 and 35% Cl⁻, respectively. PdCl₄²⁻ has a planar shape, while PtCl₆⁻² is octahedral. Apparently, these factors do not create a significant difference.
in their competition against chloride at the APTES–water interface. This is a surprising result because computer simulations suggest that PdCl$_4^{2-}$ and PtCl$_6^{2-}$ have different hydration shells,$^{39,40}$ which are expected to affect interfacial interactions,$^{41-43}$ due to the differences in their molecular geometries. This multitude of seemingly contradictory phenomena underscores the importance of further research into the molecular-level interactions of highly concentrated electrolyte solutions at charged interfaces.

The black solid line in Figure 6 represents the case in which the relative metalate concentrations at the surface and in the bulk are the same. The results suggest that metalate adsorption at the interface is significantly favored at a metalate/chloride ratio of $ \lesssim 0.1$. At a concentration ratio of 0.17, the measured surface concentration is almost the same as the bulk concentration. This strongly suggests that the metalate coverage saturates significantly below the theoretical limit of 2NH$_4^+$ + M$^{2+}$, which assumes the complexation of two amine groups with one metalate. The data were fit with a Langmuir isotherm (blue dashed lines), which shows that only approximately one-third of the available sites are occupied by metalate anions at high metalate concentrations. The fit does not provide absolute adsorption free energy because we use relative concentrations without any activity coefficients. However, it helps to qualitatively visualize the fact that the interfacial metalate concentration starts to become saturated at high relative concentrations.

The preferential adsorption of the metalate anions onto the ammonium surface is qualitatively reflective of their rapid kinetics and high extraction efficiency seen in analogous liquid–liquid extraction systems.$^9$ However, there is a great paucity of quantitative kinetic data for these systems that can provide insight into the absolute interfacial mechanisms associated with the extraction of Pt and Pd under these conditions. This is in part due to the rapid kinetics, making interfacial reactions difficult to deconvolute from diffusion-controlled processes. However, with the advent of new microfluidic techniques that couple rapid mixing with well-defined interfacial areas,$^{14}$ extraction studies should now be able to access absolute interfacial kinetic values in these rapidly evolving systems. Such studies would be invaluable for comparison with the surface structures presented herein.

4. CONCLUSIONS

We studied the competitive adsorption of platinum and palladium chlorometalate anions on amine-functionalized surfaces in highly concentrated chloride solutions; the conditions were reflective of commercial heavy and precious metal ion extractions. XR reflectivity data clearly show that the metalate anions are able to adsorb to the surface even at relative metalate/chloride concentrations of $10^{-3}$ in the bulk, suggesting that energetics due to Coulombic interactions play an important role in this regime and favor divalent over monovalent anions regardless of the charge/volume ratio; this is contrary to the expectations from MC simulations and mean field theories.$^{13,14}$ Hydration of the ions may be mainly responsible for this difference between experiment and theory. Nevertheless, this is consistent with the well-known very rapid extraction kinetics for these metalate species. At higher relative concentrations, metalate anion coverage levels off after occupying one-third of the available sites, indicating that entropic effects (mainly driven by the smaller volume of chloride ions)$^5$ play a critical role in determining the maximal coverage.

These results show that at low relative concentrations, a low charge/volume ratio does not prevent metalates from being adsorbed to the interface, explaining their efficient liquid/liquid extraction. On the other hand, entropic effects keep the maximal possible coverage low at high metalate concentrations. We can speculate that in a solvent extraction process, where ions are transferred into an organic phase from the aqueous phase by forming reverse micellar structures (contrary to forming a static interfacial structure as in our experiment), limited surface coverage may help prevent third-phase formation that occurs after high loading of metals at the interface. Such a relation could explain the inversely proportional relation between the charge/volume ratio and the extraction efficiency in chlorometalate anions.

Both platinum and palladium chlorometalate adsorption have two regimes. At very low metalate concentrations, they are adsorbed on the diffuse layer without forming a well-defined structure and cause an apparent decrease in the interfacial electron density. As the concentration increases, metalate ions are adsorbed at the interface preferentially over chloride, suggesting that the electrostatic interactions dominate for most technologically relevant concentrations. At very high metalate/chloride relative concentrations, entropic effects become important and limit the maximal coverage of the metalates. These observations will help to develop a better understanding of interfacial processes that include the competitive adsorption of ions with different charges and sizes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b03479.
Details of the models used to fit XR data and atomic force microscopy (AFM) characterization of APTES films (PDF)

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

XR experiments were conducted at Sector 12-IDD and Sector 33-IDD of the Advanced Photon Source at Argonne National Laboratory. This work and the use of the Advanced Photon Source are supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Biosciences and Geosciences, under Contract DE-AC02-06CH11357. We thank Lynda Soderholm for her comments on the manuscript. We also thank Paul Fenter and Sang Soo Lee for fruitful discussions and access to their atomic force microscope.

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