Electrostatic origin of element selectivity during rare earth adsorption

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Abstract

Rare earths are fundamental components of modern technologies. They are separated and extracted from aqueous solutions using surfactants at oil-water interfaces. Heavier lanthanides are more easily extracted than lighter lanthanides, even though the ions are chemically very similar. Using X-ray fluorescence to measure interfacial densities of two lanthanide ions (Er³⁺ and Nd³⁺) near floating (Langmuir) monolayers, and theoretical arguments, we show that the density of cations adsorbed at the interface has a step-function dependence on the bulk solution concentration. The threshold bulk concentration of erbium (Z=68) is an order of magnitude lower than that of neodymium (Z=60), and erbium is preferentially adsorbed when the bulk solution contains both erbium and neodymium. Electrostatic effects arising from the interface dielectric mismatch, ionic correlations and size of the ions explain this sharp adsorption curve and selectivity.
**Introduction**

Lanthanides are rare earths used in modern technologies\(^1\text{-}^3\), in medicine\(^4\) and in biology\(^5\).

Lanthanides are recovered from aqueous solutions via solvent extraction. The process, which is used in mining and refinement of rare earth metals, in nuclear fuel reprocessing (actinide separation), and in the cleanup of toxic waste, works by placing the aqueous solution in contact with an oil phase, with amphiphiles at the interface\(^1\). Despite decades of research\(^2\text{-}^3\), there is very little understanding of fundamental aspects of the process. One example is the lanthanides’ nearly ubiquitous trend of increased extraction efficiency as a function of atomic number\(^1\), in spite of the fact that all lanthanides have the same outer shell and are therefore chemically similar. While there have been no experiments that shed light on the nanoscale origin of this selectivity, proposed explanations include metal hydration differences\(^6\), and adsorption competition with other salts present in the solution\(^7\). The selectivity may be rooted in the ‘lanthanide contraction’\(^8\), which is the decrease in ionic radii \(r\) of elements in the lanthanide series as the atomic number \(Z\) increases\(^9\).

Indeed, the size of metallic multivalent ions is important in many phenomena including the interaction between emulsions containing lanthanides dispersed in an oil phase\(^8\text{-}^10\), as well as their adsorption to oppositely charged floating monolayers where they induce lateral ordering that depends on the atomic number \(Z\)\(^11\). Interestingly, at very low or zero monovalent salt, lanthanum chloride (LaCl\(_3\)) and other multivalent metallic salts induce a sharp transition in strongly charged polyelectrolytes\(^12\) from an extended charged state to a collapsed electrically neutral ionic structure. This transition is due to correlations that develop from the “condensation” (adsorption) of ions to the polyelectrolyte, which is a function of the ion size and the polyelectrolyte conformation\(^13\text{-}^14\), as observed in simulations of monovalent ions\(^15\), of
multivalent ions\textsuperscript{16} and more recently in simulations that include the dielectric mismatch caused by ion condensation\textsuperscript{17-18}.

We report here that there is a sharp bulk-concentration-dependent transition in the interfacial adsorption of lanthanide ions from a bulk solution in contact with an oppositely charged floating monolayer. We have determined the conditions for such a sharp transition with theoretical arguments, and corroborated the results via Monte Carlo (MC) simulations and X-ray fluorescence near total reflection (XFNTR) experiments. The observed sharp adsorption transition, as opposed to a smooth Langmuir adsorption curve, is explained by the dielectric mismatch at the interface as well as by ion-ion correlations. Experimentally we see an order of magnitude difference in bulk concentration at the adsorption thresholds of two lanthanides, Er\textsuperscript{3+} and Nd\textsuperscript{3+}, whose difference in ionic radius\textsuperscript{9} is minute: $r(\text{Nd}^{3+})/r(\text{Er}^{3+}) \approx 1.06$. The heavier lanthanide ion Er\textsuperscript{3+} adsorbs at lower bulk concentrations, consistent with the known higher extraction efficiency of heavier lanthanides. This adsorption selectivity is revealed in our model when the difference in lanthanide sizes is included.

We present the experimental results first. We used XFNTR to measure the interfacial number densities of two lanthanides, Er\textsuperscript{3+} and Nd\textsuperscript{3+}, adsorbed at floating monolayers of octadecylphosphonic acid (ODPA), as functions of their concentration in the bulk solution. This method is described in Ref. 19, and details of sample preparation and the fluorescence measurements are in the SI\textsuperscript{20}.

We first studied the interfacial lanthanide density when the only lanthanide present in the aqueous subphase is Er\textsuperscript{3+}. With bulk solution concentrations above $\sim 5\times 10^{-8}$M of ErCl\textsubscript{3}, the surface density of erbium measured by XFNTR is roughly constant, at about 0.016 ions/ Å\textsuperscript{2}. However, at lower concentrations the surface density drops quite sharply to essentially zero.
This is shown in Fig. 1 (top); the line through the data is a theoretical prediction, discussed later in this paper.

![Figure 1. TOP: Surface density of Er$^{3+}$ (red triangles) vs. bulk concentration in the aqueous phase. The line connects theoretically calculated values (blue dots); the simulation parameters are given in SI. BOTTOM: Surface density of Nd$^{3+}$ (red triangles) vs. bulk concentration in the aqueous phase. The line connects theoretically calculated values (blue dots); the simulation parameters are given in SI.](image-url)
Nd$^{3+}$ ions in solution likewise show an attraction to ODPA monolayers, but to a lesser extent (Fig. 1). The surface density at high bulk concentrations is about the same as that of Er$^{3+}$ at equivalent concentrations. However, at $\sim$5×10$^{-7}$ M NdCl$_3$ and below, the surface density decreases sharply to zero. Thus, the bulk concentration thresholds of these ions differ by a full order of magnitude.

Figure 2. Surface densities of Er$^{3+}$ and Nd$^{3+}$ when the bulk Er$^{3+}$ concentration is varied while Nd$^{3+}$ concentration is fixed at 10$^{-4}$ M. The lines are polynomial fits, intended only to provide guides to the eye.
Mixtures of Nd$^{3+}$ and Er$^{3+}$ in aqueous solution were also investigated. When there are equal concentrations of Nd$^{3+}$ and Er$^{3+}$ ($10^{-4}$M of NdCl$_3$ and ErCl$_3$), there is five times as much Er compared to Nd at the interface (Fig. 2). When the Er concentration is reduced while the Nd concentration is held constant, there is a continuous decrease in Er surface density and a roughly equal increase in Nd density (i.e. the total surface density is approximately constant). To achieve a 50% reduction in Er surface density (which is also the point at which Er and Nd are present in equal quantities at the surface), the bulk Er concentration must be lower than the bulk Nd concentration by an order of magnitude.

These fluorescence measurements can be used to calculate an average number of ions per ODPA molecule. A previous report\textsuperscript{11} showed that ODPA molecules have an area of \(~0.21\text{nm}^2\) when spread over lanthanide salt solutions. In pure solutions, the data reported here mean that at the top of the “steps” in Fig. 1, there are approximately three ODPA molecules for every lanthanide ion at the interface. Although lanthanides are triply charged and ODPA molecules are singly charged, the above ratio is somewhat fortuitous: given the presence of H$^+$, OH$^-$ and Cl$^-$ ions, it is not necessary that there be exactly three ODPA molecules per lanthanide ion. When both cations are present in the subphase (Fig. 2), the total surface number density remains almost constant while the relative bulk concentrations are varied. If one considers this a measure of the average area for either an erbium or neodymium ion, there is again approximately 1 lanthanide ion per 3 ODPA molecules.
Figure 3. (a) Schematic diagram of the system being simulated. (b) Sample Monte-Carlo simulation setup (smaller 20×20 system shown here for clarity). Upper(lower) hexagonal lattice layer is molecules(lanthanides), red is charged molecules, blue is absorbed lanthanides; white is neutral molecules or empty lanthanide sites. The separation in the z direction is exaggerated here for clarity.

We next explain the monolayer-water-ion interface model used to generate the MC results in Fig. 1. Since we are at an interface, we cannot assume a homogenous dielectric medium with an overall relative dielectric constant ($\varepsilon_r$). The dielectric environment changes dramatically in the vicinity of interface$^{21-23}$, and the presence of dissolved ions also results in a different bulk dielectric constant$^{25}$. For example, at an interface between water ($\varepsilon_{\text{water}}=80$) and air ($\varepsilon_{\text{water}}=1$) the interaction between charges at the interface is governed by the mean dielectric media value ($\varepsilon_{\text{water}}=40$) and even when the head groups are charged and thus totally immersed in water, the concentration of charge is high enough to approach local molarity at which the water dielectric
constant is highly reduced (e.g., $\varepsilon_r \approx 45$ at 3M of NaCl). Moreover, the electrostatic interactions are modified by the concentration of charged groups, including both the charge dissociated from the head groups of the amphiphiles and the charge of the adsorbed ions. Though full atom simulations are the best tool to study electrostatic interactions in systems with dielectric inhomogeneity, they lack a mechanism to dynamically change the degree of charge dissociation of molecules. Therefore, the adsorption of lanthanide ions on surfactant monolayer is determined here self-consistently by extending a Monte Carlo (MC) simulation that accounts for the degree of charge dissociation near a surface to include the surface dielectric mismatch. Indeed, near the interface if one amphiphile dissociates, then due to the strong electrostatic repulsion between the neighboring charges, it will become harder for its immediate neighbors to dissociate. However, if one lanthanide ion is absorbed, due to the electrostatic attraction between positive charged ions and negative charged amphiphiles, it will be easier for nearby amphiphiles to dissociate. Therefore, the actual dissociation and adsorption rates depend on the range of electrostatic correlations, the dielectric environment and the specific arrangement of amphipiles and ions, see Figure 3(a).

In order to use the MC lattice model to determine the fraction of charge dissociated form the amphiphile head groups and the adsorption of ions, we choose hexagonal lattices for both ODPA molecules and lanthanide ions (i.e., we assume commensurability in lateral order, though the amphiphile lattice and the adsorbed multivalent ion lattice are not always commensurable). One layer represents the ODPA molecule headgroups, while the other represents the lanthanide ions (Fig. 3(b)). For the molecular layer, each site can have -1e (dissociated) or 0 (neutral) charge; for the ionic layer, each site can have +3e (adsorbed) or 0 (not adsorbed) charge. Notice that charge neutrality does not have to hold locally between ODPA headgroups and ions, as
discussed earlier. Two nearby sites are separated by $\sigma = 0.5nm$, comparable to the size of hydrated ions. The distance between two layers is approximately the size of the hydrated lanthanide ions, which we set as $\sigma = 0.5nm$, close to the reported Er$^{3+}$ size$^9$.

The MC model introduces several parameters to capture the dielectric inhomogeneity. First, we define the Bjerrum length $l_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r k_BT}$ to indicate the electrostatic strength, where $\varepsilon_r$ is the relative permittivity of the medium, $e$ is the unit charge and $k_BT$ is the thermo energy. The screened electrostatic interaction between two charges separated by a distance $r_{ij}$ is $\frac{e}{k_BT} = l_B \frac{z_i^2 z_j}{r_{ij}^2} e^{-\kappa r_{ij}}$, where $z_i$ is the valence of the i-specie (amphiphile head group or lanthanide), and $\kappa$ is the inverse of Debye screening length. To effectively capture the dielectric inhomogeneity, we then introduce three parameters: $l_B^+ / \sigma$, $l_B^- / \sigma$ and $l_B^{\text{inter}} / \sigma$ to represent the electrostatic strength of positively charged ion/ion interactions, negatively charged molecule/molecule interaction and interlayer molecule/ion interactions, respectively.

The Hamiltonian used in our MC simulations is then given by

$$\frac{H}{k_BT} = -n_+ \ln(c) + \frac{\mu}{k_BT} n_- + l_B^{\text{inter}} \sum_+ - \frac{z_i z_j}{r_{ij}^2} e^{-\kappa r_{ij}} + l_B^+ \sum_+ - \frac{z_i z_j}{r_{ij}^2} e^{-\kappa r_{ij}} + l_B^- \sum_- + \frac{z_i z_j}{r_{ij}^2} e^{-\kappa r_{ij}}$$

Eq. 1

where $n_+$ is the number of adsorbed ions (i.e., how many layer lattice sites have +3 charge), $c$ is the bulk concentration of lanthanide ions, $\kappa = 4\sqrt{\pi l_B c}$ with $l_B$ the bulk dielectric constant of water. Here, $\sum_{+-}$ is the summation over all charged ion/molecule pairs, and the chemical potential $\mu$ that controls the dissociation of acid molecules is a constant given by $\mu/k_BT = -\ln10(pH - pK_a)$.
Before discussing the MC simulation, we discuss an analytical model that helps to rationalize the physical mechanism leading to a sharp adsorption transition. In the Hamiltonian in Eq. 1, the summation terms depend on the lattice configuration of the system. To simplify this Hamiltonian, we define $f$ as the fraction of dissociated sites ($0 \leq f \leq 1$), $f_+$ for positive charged lanthanides ions and $f_-$ for negative charged molecules. Qualitatively,

$$\sum e^{-\kappa r_{ij}} / n_{total} \approx f_i f_j / \sigma_{ij} \quad i, j = +/-$$  \hspace{1cm} \text{Eq. 2}

Note that this scaling argument is a very crude approximation for the case of very low concentration of ions ($\kappa \sigma \ll 1$) since we are setting $\kappa = 0$ and it ignores the lattice configuration by including only the leading term in the $1/r$ electrostatic potential. This approximation differs from the 2D “metallic-like bonding” model assumed to describe the cohesive energy of strongly correlated multivalent ions adsorbed onto a continuously charged surface where the size of the ions is zero, $r = 0$, and $\kappa = 0^{27}$. In ionic systems, a non-zero size of the ions and the discrete charge distribution along the surface are required to evaluate ionic cohesive energies due to correlations, and, as such, Eq. 2 is an approximation of a two-dimensional (2D) “ionic bonding” model where the higher order terms (that only provide a multiplicative factor known as the Madelung constant) are neglected; our approximation is an extension of the two-state thermodynamic model of collapsed polyelectrolytes by multivalent ions $^{14}$, which has been tested by MC simulations$^{16}$, to 2D. The Hamiltonian with this simplification is:

$$\frac{H}{k_B T} \approx -f_+ \ln(c) - 3 l_{\text{inter}}^+ f_+ f_- / d_{\text{inter}} - l_{\text{in}}^- f_- f_- / \sigma_- - 9 l_{\text{in}}^+ f_+ f_+ / \sigma_+$$  \hspace{1cm} \text{Eq. 3}

where the coefficients 3 and 9 are from the charge valence of the lanthanide ions, and $\sigma_- = \sigma_+ = \sigma$ in our model (the ionic size is included in the value of $d_{\text{inter}}$). For any given
concentration $c$, the equilibrium $f_+, f_-$ value is obtained by minimizing $H$. Since $H$ is expressed as a 2nd-order function with two variables, the Hessian matrix is

$$
\mathcal{H}'' = \left[ \frac{\partial^2 H}{\partial f_i \partial f_j} \right] = \begin{bmatrix}
18 l_B^+ / \sigma & -3 l_B^+ / d_{\text{inter}} \\
-3 l_B^+ / d_{\text{inter}} & 2 l_B^+ / \sigma
\end{bmatrix}
$$

If $(l_B^+ / d_{\text{inter}})^2 < 4 l_B^- l_B^+ / \sigma^2$, the Hessian matrix has two positive eigenvalues, and $H$ is positive definite, and thus always has a local minimum at: $f_+ = \ln c / [18 \left( l_B^+ / \sigma - \left( l_B^+ / 2 d_{\text{inter}} \right)^2 / l_B^+ \right)]$, $f_- = 3 l_B^+ \sigma / (2 l_B^- d_{\text{inter}}) \times f_+$. Therefore, $f_+(f_-)$ changes continuously with concentration. However, if $(l_B^+ / d_{\text{inter}})^2 > 4 l_B^- l_B^+ / \sigma^2$, the Hessian matrix has both positive and negative eigenvalues, and $H$ is saddle-like, and has no local minimum. Due to the constrain $0 \leq f_+ \leq 1$, either $f_+(f_-) = 0$ or 1 would give the minimum $H$ of the system. Therefore, $f_+(f_-)$ has a sharp transition from 0 to 1 at some threshold concentration $c_0$. The threshold concentration can be estimated by considering the Hamiltonian in two scenarios:

$$H(f_+ = f_- = 1) \leq H(f_+ = f_- = 0),$$

which gives $\ln(c_0) \approx -3 l_B^+ / d_{\text{inter}} + 1 l_B^- / \sigma + 9 l_B^+ / \sigma$.

It is easy to notice that the threshold concentration will be larger for a smaller interlayer coupling strength.

To summarize, the approximated Hamiltonian in Eq. 3, provides a guideline to predict the sharp transition regime via a simplified relation, $(l_B^+ / d_{\text{inter}})^2 > 4 l_B^- l_B^+ / \sigma^2$. Though the coefficient 4 is not reliable given the approximations in Eq.3, when the terms in the series in Eq. 1 are included, we obtain a condition to predict the sharp transition regime given by $(l_B^+ / d_{\text{inter}})^2 > k l_B^- l_B^+ / \sigma^2$ where the coefficient $k$ must be determined from MC simulations.
The concentration dependent dissociation and adsorption rate are calculated by solving Eq. 1 for various combinations of $l_B^i$, $i= \text{inter, + and -}$ values to compare with the experimental results. Since the bulk concentration of ions is highly diluted, we set the bulk water value to $l_B^\text{water} = 0.7nm$. Now, since the amphiphiles are close to the air-water boundary with $\varepsilon_{\text{average}} \approx 40$, we can approximate $l_B^\text{aq} = 2l_B^\text{water}$ (though could be larger if/when the head group are charged, changes in this value do not change the condition $(l_B^{\text{inter}}/d_{\text{inter}})^2 > kl_B^i l_B^+ /\sigma^2$). According to the experiments, the surface density of ions after the threshold concentration stays constant $(0.016 \text{Er}/\AA^2 \text{ or } 0.013 \text{Nd}/\AA^2)$ at higher bulk concentrations. This means that there are $\sim 3-4$ ODPA molecules per ion. Simulation shows that the surface density only depends on the ratio $l_B^{\text{inter}} / l_B^+$. Larger $l_B^{\text{inter}} / l_B^+$ gives larger surface density and vice versa. In particular, $l_B^{\text{inter}} / l_B^+ = 1.11$ gives a good fit to the observed saturation surface density. Together with the threshold concentration of the sharp transition, we can fit the erbium experimental data with simulation parameters $l_B^+ = 1.769l_B^\text{water}$, $l_B^{\text{inter}} = 1.963l_B^\text{water}$, with adsorption layer distance $d_{\text{inter}}(\text{Er}^{3+}) = \sigma = 0.5nm$ [see Figure 1], which are reasonable values given the large concentration of charge at the interface$^{24}$. Notice, here $(l_B^{\text{inter}}/d_{\text{inter}})^2 = 1.089l_B^- l_B^+ /\sigma^2$ and does not exactly match the analytical coefficient of 4 in the sharp transition criterion $(l_B^{\text{inter}}/d_{\text{inter}})^2 > kl_B^- l_B^+ /\sigma^2$. Overall, this inequality is satisfied only if the $l_B^i$, $i= \text{inter, + and -}$ values are close to each other.

Alternatively, we could fix all three $l_B^i$ values. Then only increasing the interlayer distance would increase the threshold concentration. The reason is that the strength of interlayer interaction decreases with increasing the interlayer distance, thus higher threshold bulk concentration of ions is needed for the transition, as discussed above. Simulation shows that about 7% change of the distance would result in an order of magnitude difference in the threshold concentration. A
distance of $d_{\text{inter}}(\text{Nd}^{3+}) = 1.07\sigma = 0.535\text{nm}$, with $l_B^{\text{inter}}$ and $l_B^+$ unchanged, fits the neodymium experimental data very well [see Figure 1]. The 7% distance difference between Er$^{3+}$ and Nd$^{3+}$ radiuses in the simulations is roughly consistent with the hydrated ionic size difference between them ($\approx 6\%$). This implies that the vastly different threshold concentrations for Er and Nd are due to the different strength of electrostatic interaction resulting from their slightly different hydrated ion sizes.

As shown in Fig. 2, a mixture of Nd and Er does not show any sharp transition with increasing bulk concentration. From the theoretical point of view, the three-component system (Nd, Er and ODPA) has a 3 by 3 Hessian Matrix. The analytical condition for a sharp transition is too complicated to obtain any simple physical insight. Most practical parameters in this system would lead to a positive definite Hamiltonian, which has no sharp transition, consistent with the experimental observation. This is also confirmed by our MC simulations.

In summary, this study shows a strong elemental selectivity in the adsorption of rare earths in aqueous solutions at the interface with amphiphiles. Electrostatic effects arising from the inhomogeneity of the interfacial medium, ionic correlations and small size differences between ions are responsible for this strong selectivity between these two chemically similar ions and for the observed sharp adsorption transitions. The physical reason for the sharp transition is the competition of entropy, which favors non-adsorbed multivalent ions and therefore no surface charge dissociation, with the energy gain when the multivalent metallic ions adsorb. The transition, when occurring in very dilute solutions of multivalent cations and with no monovalent cations, is sharp. It occurs when the surface charge is at a maximum and the adsorption of ions neutralizes the surface charge, reminiscent of the sharp transition of strongly charged chains in multivalent ions. However, in the case of the surface studied here, we find that a highly
restrictive relation between the values of the dielectric constants that quantify the electrostatic interactions between all the components, and/or the size of the multivalent ions, has to be obeyed in order to observe a sharp adsorption transition. This work shows the importance of including dielectric mismatch, ionic sizes and correlations in electrostatic models, and it unifies various models that account for these effects in different contexts to the ubiquitous problem of adsorption of multivalent metallic ions to amphiphiles capable of charge dissociation.

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References

20. See Supplemental Material at [URL will be inserted by publisher] for details of sample preparation, XFNTR measurements, and simulations.


