Nanoscale view of assisted ion transport across the liquid–liquid interface

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During solvent extraction, amphiphilic extractants assist the transport of metal ions across the liquid–liquid interface between an aqueous ionic solution and an organic solvent. Investigations of the role of the interface in ion transport challenge our ability to probe fast molecular processes at liquid–liquid interfaces on nanometer-length scales. Recent development of a thermal switch for solvent extraction has addressed this challenge, which has led to the characterization by X-ray surface scattering of interfacial intermediate states in the extraction process. Here, we review and extend these earlier results. We find that trivalent rare earth ions, Y(III) and Er(III), combine with bis(hexadecyl) phosphoric acid (DHDP) extractants to form inverted bilayer structures at the interface; these appear to be condensed phases of small ion–extractant complexes. The stability of this unconventional interfacial structure is verified by molecular dynamics simulations. The ion–extractant complexes at the interface are an intermediate state in the extraction process, characterizing the moment at which ions have been transported across the aqueous–organic interface, but have not yet been dispersed in the organic phase. In contrast, divalent Sr(II) forms an ion–extractant complex with DHDP that leaves it exposed to the water phase; this result implies that a second process that transports Sr(II) across the interface has yet to be observed. Calculations demonstrate that the budding of reverse micelles formed from interfacial Sr(II) ion–extractant complexes could transport Sr(II) across the interface. Our results suggest a connection between the observed interfacial structures and the extraction mechanism, which ultimately affects the extraction selectivity and kinetics.

solvent extraction | interfacial transport | structure | dynamics

The transfer of metal ions from aqueous to organic phases underlies the process of solvent extraction. Ongoing developments of this process are aimed at optimizing the efficiency and kinetics of the separation and recovery of base, rare earth, and precious metals (1), as well as the reprocessing of spent nuclear fuel and nuclear waste (2). In the latter case, for example, the efficient separation of trivalent minor actinides (Am/Cm) from lanthanides in spent nuclear fuel would reduce the demands imposed on the geological repositories proposed for the long-term storage of nuclear waste (2). Although the interaction of metal ions with solutes at the organic–aqueous interface is likely to determine the efficiency and kinetics of extraction (3), little is known about the mechanism of ion transport across this interface. Conventional hydrodynamic analysis assumes that ions diffuse across the interface on the nanoscale, although interfacial instabilities are predicted and observed on larger spatial scales (4). Here, we extend recent investigations of solvent extraction on the nanoscale to relate the observed interfacial intermediates to the extraction mechanism and efficiency, as well as suggest a role for nonequilibrium interfacial instabilities on the nanoscale.

Metal ion extraction is assisted by the formation of supramolecular complexes with a soluble organic extractant (5). Acidic organo-phosphorous extractants are used extensively and will be studied here (1). They are amphiphilic molecules with a

phosphoric acid head group that binds to metal ions and hydrophobic alkyl tail groups that provide sufficient solubility in the organic phase. After extraction into the organic phase, metal ions are found in supramolecular ion–extractant complexes in the form of either coordination complexes or reverse micelles (6–8).

Studies of the kinetics of metal ion extraction indicate that ions and extractants interact at or near the organic–aqueous interface (3, 9). Different authors have suggested that the extractant binds metal ions either in the aqueous phase near the interface, or in the organic phase near the interface, or at the interface itself. For instance, the mass transfer with chemical reaction (MTWCR) mechanism (9) postulates that acidic extractants are transferred into the aqueous boundary layer near the organic–aqueous interface, where they are deprotonated and interact with metal ions to form aqueous ion–extractant complexes, which subsequently diffuse into the organic phase. MTWCR has achieved partial success in describing the extraction kinetics of divalent metal ions with organo-phosphorous extractants (10, 11). On the other hand, it has been suggested that when the interface is occupied by stronger amphiphiles that exclude the extractants, the extractants in the organic phase near the interface can form ion–extractant complexes when fingers of water that contain metal ions reach into the organic phase (12). Somewhat between these two cases, there is evidence that the amphiphilic character of extractants leads to their interaction with ions directly at the interface (13–16); these studies include the suggestion that reverse micelles of extractants that enclose metal ions can form at the

Significance

The selective separation of targeted metal ions is utilized for environmental remediation, mining of rare earth and base metals, as well as the separation and isolation of long-lived radionuclides from nuclear waste. During the process of solvent extraction, organic extractant molecules complex with metal ions to assist their transfer from an aqueous to an organic phase. The structure of ion–extractant complexes at the interface, as well as the mechanism of ion transport across the interface, are generally unknown but are relevant for improving the kinetics and efficiency of this industrial process. Here, we describe experiments that reveal different ion–extractant complexes for divalent and trivalent ions, and discuss their consequences for the extraction process.

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interface (17). Largely missing from these investigations has been the application of experimental techniques that can locate and identify metals, extractants, and ion–extractant complexes in the liquid–liquid interfacial region, although recent X-ray and neutron scattering studies have begun to do just that (18–22).

Here, we use interface-sensitive X-ray scattering and fluorescence techniques to locate and identify interfacial species in model extraction systems. The challenge of measuring fast ion transport processes with slow X-ray techniques formerly led us to develop a thermal process that switches between fast and slow rates of extraction (19). This allowed us to characterize intermediate states in the extraction process of a trivalent lanthanide Er(III) and a divalent main group ion Sr(II). One such state consisted of supramolecular erbium–extractant complexes condensed into an inverted bilayer structure in the form of a two-dimensional layer of Er ions sandwiched between two layers of extractant (19). These Er–extractant complexes were formed at the dodecane–water interface within the timescale of minutes used to toggle the thermal switch, and possibly much faster. Similar experiments with strontium ions revealed, instead, a conventional monolayer of extractants with bound Sr(II) ions located on the aqueous side of the interface (20), with no obvious route to transfer ions into the organic phase. Nevertheless, toggling the thermal switch led to extraction of both types of ions, although a larger fraction of erbium than strontium was extracted.

The unexpected structure of inverted bilayers at an organic solvent–water interface is confirmed by the X-ray studies presented here of a model solvent extraction system with Y(III) cations. The inverted bilayer structure contains hydrophobic alkyl tail groups in direct contact with water—illustrated later in Fig. 1—instead of the conventional arrangement of amphiphiles in which polar head groups are in contact with water. The stability of this unconventional interfacial structure is confirmed by molecular dynamics (MD) simulations. Comparing the results from these three ions, Y(III), Er(III), and Sr(II), suggests that the electronic configuration of the ion is secondary or irrelevant, whereas the ion charge or oxidation state plays the primary role in determining the extraction mechanism. The form of the interfacial ion–extractant complexes provides insight into the mechanism of ion transport across the interface, which is discussed in the context of dynamical distortions of the interface.

In recent years, MD simulations have clarified the role of interfacial fluctuations in the case of ion transport across bare electrochemically controlled interfaces, although the mechanism of transport under these conditions remains under investigation (23). The degree to which interfacial fluctuations play an important role in the extractant-assisted ion transport processes discussed here is also an open issue.

Results

Our experimental system consists of a macroscopically flat liquid–liquid interface between a dilute, acidic aqueous solution of metal chlorides [where the metal ion is Y(III), Er(III), or Sr(II)] and a dilute organic solution of the extractant bis(hexadecyl) phosphoric acid (DHDP) ($[\text{CH}_3(\text{CH}_2)_{15}\text{O}]_2\text{POOH}$) (10^{-4} M) in *n*-dodecane $[\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3]$. In the absence of metal ions, the extractant DHDP will form a high-density, ordered monolayer at the dodecane–water interface below an adsorption temperature $T_0 = 38.2^\circ\text{C}$, which varies with pH (19). Under these conditions, DHDP molecules are close-packed with the long axis of the molecule oriented perpendicular to the interface, similar to those shown in Fig. 1D. As the temperature is raised above T_0 , DHDP desorbs from the interface, leaving behind a disordered partial monolayer (19). When metal ions are present, we have shown previously that changing the temperature from above to below T_0 retards the passage of ions from the water to the dodecane phase, thereby acting as a thermal switch for ion extraction; similarly, the rate of extraction is enhanced if the temperature is raised from below to above T_0 (19). By preparing a model extraction system under conditions with normal rates of

extraction ($T > T_0$), then reducing the temperature to below T_0 to retard the rate of extraction, ion–extractant complexes formed in the midst of extraction when $T > T_0$ can be trapped at the interface when $T < T_0$. This metastable interfacial state is then characterized with X-ray reflectivity and X-ray fluorescence near total reflection (XFNTR).

Fig. 1A shows X-ray reflectivity data, which measures the electron density profile of the liquid–liquid interface (Fig. 1B), and cartoons that represent molecular ordering at the interface. Two different structures were measured for multiple Er samples: a structure labeled Er_{HD} that contains a high-density of Er ions and one labeled Er_{LD} with a low density of Er ions. Inverted bilayer structures at the interface (Fig. 1E and F) can be identified by a unique experimental signature in the low Q_z region of the data, as exhibited in Fig. 1A by the Y(III) and Er(III) samples. As shown previously, X-ray reflectivity data of this form cannot be due to a conventional monolayer, bilayer, or trilayer with DHDP head groups exposed to the water subphase (19). Instead, the head groups are located in the middle of an inverted bilayer (Fig. 1E and F). As shown in Fig. 1B for the Y and Er_{HD} structures, the peak in electron density in the middle of the bilayer structure is a region of high electron density, which is due to the location of electron-dense components [phosphoric acid head groups and Y(III) or Er(III) ions]. The uneven shoulders of this peak represent the alkyl chains of the two DHDP layers. The absence of a peak just at the interface, at $z \approx 0$, indicates an absence of DHDP head groups that are directly exposed to the water subphase, in contrast to the conventional expectation that polar head groups of amphiphiles should interact with water. On the other hand, measurements of systems with Sr(II) exhibit a conventional monolayer (Fig. 1D) with a peak in the electron density at $z \approx 0$ representing Sr ions bound to DHDP head groups exposed to the water subphase, as well as a shoulder representing tail groups exposed to the dodecane (Fig. 1B).

Quantitative analysis of the X-ray reflectivity utilizes a representation of the interfacial structure in terms of slabs of uniform electron density, an example of which is shown in Fig. 1B as a dashed-line profile, which is roughened by capillary waves to produce the solid lines in Fig. 1B. Each slab represents a different region of the interfacial layer, such as the head groups or tail groups. Table 1 shows that most of the tail group electron densities vary from 0.30 to $0.33 \text{ e}^- \cdot \text{\AA}^{-3}$, values that are characteristic of all-*trans* close-packed crystalline or rotator phases of alkanes (24). Exceptions include the terminal portion of DHDP tail groups in the upper leaflet (in contact with dodecane), which has a lower electron density that reveals molecular disorder near the end of the alkyl chains (24). The other exception is the lower density liquid-like tail groups observed in the lower leaflet of the Er_{LD} measurement. Table 1 and Fig. 1B show that inverted bilayers containing Y ions were structurally similar to the high-density Er_{HD} inverted bilayers.

The tail group thickness of the DHDP monolayer bound to Sr(II) is $20 \pm 1 \text{ \AA}$, given by the sum of the thicknesses of slabs 2 and 3, which matches the all-*trans* length, $20.6 \text{ \AA}$, of the DHDP tail groups. This indicates that the tail groups are arranged as shown roughly in Fig. 1D, although the disorder near the terminal methyl group is not shown. Similar thickness values are observed for the lower leaflet of the Y and Er_{HD} inverted bilayers. Smaller thicknesses of $18\text{--}19 \text{ \AA}$, as observed for the low-density Er inverted bilayer, may correspond to chains tilted on the order of 25° from the interfacial normal. Even smaller values, as observed for slab 3 of the Y and Er_{HD} inverted bilayers, require a fourth slab to account for the rest of the tail group. In these cases, good fits to the data require four slabs.

Additional information on the ionic content of the interface is provided by XFNTR, which measures the total number of a specific ion (Y, Er, or Sr) per interfacial area (25, 26). Although ions within a distance of roughly 15 nm from the interface can contribute to this measurement, the small bulk concentration of ions ($\sim 10^{-7} \text{ M}$ for Y and Er solutions) limits the measurable signal to those ions within the interfacial structure. The line shown in Fig. 1C is the result of data analysis described in *X-Ray Fluorescence*

Fig. 1. (A) The variation of X-ray reflectivity $R(Q_z)$ with wave vector transfer Q_z (perpendicular to the interface) normalized to the calculated Fresnel reflectivity $R_F(Q_z)$, as measured from the interface between metal (Y, Er, Sr) chlorides in water (pH 2.5 for Y and Er, pH 5.3 for Sr) and 10^{-4} M DHDP in dodecane. Samples were prepared as described in the text and measured at a temperature a few degrees below each sample's adsorption transition T_o . The upper three curves were shifted for clarity, although $R/R_F \rightarrow 1$ as $Q_z \rightarrow 0$ for all measurements. Curves labeled Er_{HD} and Er_{LD} refer to high-density and low-density Er interfaces. Lines are the best fits to the model described in the text. (B) Electron density profiles determined by the fits in A, where the right three curves were

near Total Reflection Analysis of Y Samples, which yields the interfacial area per Y, $A_Y = 68 \pm 3 \text{ \AA}^2$. Previously published values include $81 \pm 5 \text{ \AA}^2$ for the low-density Er_{LD} inverted bilayer and $90 \pm 9 \text{ \AA}^2$ for the Sr monolayer (at pH 5.3) (19, 20). By combining XFNT measurements of the area per ion with X-ray reflectivity results, the analysis described in *Composition of the Head Group Region in the Inverted Bilayer*, shows that the head group region of the inverted bilayer contains enough electrons to account for three DHDP head groups for each metal ion (Y or Er) plus roughly 0 to three water molecules.

A molecular interpretation of the Y inverted bilayer is the result of modeling that is constrained by the measured values of electron density and thickness of each slab (from X-ray reflectivity), the measured area per Y ion (from X-ray fluorescence), and the constraint that the upper and lower leaflets must occupy equivalent interfacial areas. An earlier analysis, subject to similar constraints, of the low-density inverted bilayer of Er showed that it is equivalent to a condensed state of charge-neutral ion-extractant complexes $\text{Er}(\text{DHDP})_3(\text{H}_2\text{O})_m$ (19), where the structure of the complex is shown in the blue box in Fig. 1F. Here, we assume that the Y inverted bilayer comprises charge-neutral ion-extractant complexes $\text{Y}(\text{DHDP})_3(\text{H}_2\text{O})_m$. If all complexes were oriented down (blue boxes in Fig. 1E and F) as in the low-density Er bilayer (Fig. 1F), then the area per Y would be twice the area per close-packed DHDP, $A_Y \approx 79 \text{ \AA}^2$ (*Analysis of Y Inverted Bilayer Structure*). If complexes alternate their orientation (with the same number of up and down orientations, as illustrated in Fig. 1E), then the area per Y would be 1.5 times the area per DHDP, $A_Y \approx 59 \text{ \AA}^2$. The intermediate value measured by

XFNT for the Y inverted bilayer, $A_Y = 68 \pm 3 \text{ \AA}^2$, suggests an intermediate arrangement. Proceeding beyond this point in the analysis requires an assumption about the mixing of dodecane and DHDP tail groups because our X-ray techniques do not distinguish between them. If we assume that the lower leaflet consists of only DHDP tail groups, but that dodecane can mix into the upper leaflet, then the analysis presented in *Analysis of Y Inverted Bilayer Structure*, shows that there are 1.5(5) dodecane molecules for each DHDP molecule in slabs 3 and 4 that model the upper leaflet and the fraction of complexes pointing down is 0.3(1). Although other assumptions about the location of dodecane within the inverted bilayer lead to different numerical values, the analysis shows that the structure of the Y inverted bilayer can be described as a condensed phase of ion-extractant complexes at the interface. Although the lack of XFNT data for the observation of the high-density Er inverted bilayer does not allow for this type of analysis, the similarity of its electron density profile to the Y system suggests that it too can be described as a condensed phase of interfacial ion-extractant complexes.

We performed classical MD simulations to investigate the stability of the inverted bilayer structure. Fig. 2A shows the last frame of this simulation, and Fig. 2B shows the time-averaged

shifted for clarity, although $\rho_{\text{water}} \rightarrow 0.333 \text{ e}^{-}\text{\AA}^{-3}$ as $z \rightarrow -20 \text{ \AA}$ for all curves before shifting. The profiles are rounded as the result of capillary wave roughness of the interface; the dashed line for Y shows an example of the underlying zero-roughness profile. (C) X-ray fluorescence near total internal reflection (XFNT) data (dots) and analysis (line) from an interface between 10^{-4} M DHDP in dodecane and 3×10^{-7} M YCl_3 in water (pH 2.5) at 28 °C. Error bars (± 1 SD) are generally smaller than or similar to the size of the dots in A and C. (D–F) Molecular representations of the interfacial structures with zero interfacial roughness. (D) Cartoon of the measured monolayer with Sr(II). (E) Cartoon of a hypothetical maximum density inverted bilayer. (F) Cartoon of the measured low-density (LD) inverted bilayer of DHDP with Er(III). High-density (HD) inverted bilayers containing Y(III) or Er(III) consist of an intermediate configuration of ion-extractant complexes to those shown in D and E, as described in the text. Red and blue boxes identify the ion-extractant complexes; red indicates the “up” orientation, and blue is the “down” orientation. Panels E and F are modified and reprinted with permission from ref. 19 (Copyright 2014, American Chemical Society).

Table 1. Best-fit parameters to the X-ray reflectivity data

Ion	σ , Å	d_1 , Å	ρ_1 , e ⁻ ·Å ⁻³	d_2 , Å	ρ_2 , e ⁻ ·Å ⁻³	d_3 , Å	ρ_3 , e ⁻ ·Å ⁻³	d_4 , Å	ρ_4 , e ⁻ ·Å ⁻³
Y	3.1(2)	21.5(2)	0.303(1)	6(1)	0.42(1)	16(1)	0.332(1)	9(1)	0.265(2)
Er _{HD}	3.4(3)	20.6(1)	0.318(1)	8(2)	0.40(2)	15(2)	0.319(5)	5(2)	0.25(1)
Er _{LD}	3.6(3)	18.9(7)	0.279(3)	9(3)	0.33(1)	18(3)	0.324(3)	—	—
Sr	4.3(2)	4(2)	0.6(1)	17(1)	0.333(2)	3(1)	0.21(3)	—	—

Fits to data from interfaces between 10⁻⁴ M DHDP in dodecane and (line 1) 3 × 10⁻⁷ M YCl₃ in water (pH 2.5) at 28 °C; (line 2) 10⁻⁷ M ErCl₃ in water (pH 2.5) at 28 °C with a high density of Er ions; (line 3) 5 × 10⁻⁷ M ErBr₃ in water (pH 2.5, adjusted with HBr) at 28 °C (19) with a low density of Er ions; (line 4) 10⁻⁵ M SrCl₂ in water (pH 5.3, adjusted with acetate buffer) at 36.7 °C (20). The electron densities of the bulk aqueous and organic phases are 0.333 e⁻·Å⁻³ (28 °C) and 0.2574 e⁻·Å⁻³, respectively. The thicknesses of the four slabs (d_1 , d_2 , d_3 , and d_4), the electron densities of the slabs (ρ_1 , ρ_2 , ρ_3 , and ρ_4), and the interfacial roughness σ are fitting parameters. For the Y and Er samples: slab 1 represents the DHDP tail groups of the lower leaflet (in contact with water) of the inverted bilayer, slab 2 represents the DHDP head group region that includes metal ions and possibly water, and slabs 3 and 4 represent the tail groups of the upper leaflet (in contact with dodecane). For the Sr sample: slab 1 represents the DHDP head group and Sr ions, and slabs 2 and 3 represent the DHDP tail group. Parenthetical numbers represent 1 SD in the last significant digit.

electron density profile. Both illustrate the qualitative features of the measured electron density profiles of the high-density inverted bilayers containing Y and Er (Fig. 1*B*), namely, a high-density peak from the head groups and metal ions, with shoulders from the DHDP tail groups in the upper and lower leaflets of the bilayer. The experimental electron density profiles appear more disordered because they are roughened by capillary wave fluctuations of the interface (σ in Table 1), which have a much smaller effect on profiles calculated from small simulation boxes. This roughening will smear the dips in electron density at the bottom and top of the bilayer observed in the simulations, but not observed in the experiments.

These simulations were designed to test the stability, but not the formation, of the low-density Er inverted bilayer. The initial state of the simulation placed one-half the number of DHDP molecules in the lower leaflet than in the upper leaflet; the extra space in the lower leaflet was filled with dodecane. This led to a higher electron density in the lower leaflet than observed in experiments of the low-density Er inverted bilayer, but similar to the electron density measured in the high-density inverted bilayer. The simulations demonstrated that the structure of the inverted bilayer is stable at the interface for the 100-ns span of the simulation, with occasional motion of dodecane molecules between the two leaflets.

Fig. 2*C* shows a mesh-like coordination of Er with water molecules and DHDP head groups. The low density of Er ions used for the simulation (86 Å² per Er) produces blank regions in Fig. 2*C*. The geometry of Er–O coordination is octahedral (Figs. S2 and S3) with coordination to six oxygen atoms, as observed in Er–DHDP complexes that have been extracted into the bulk dodecane (19). Radial distribution functions from the Er ion (Figs. S4 and S5) demonstrate that bond lengths are different in the inverted bilayer and in bulk extracted Er–DHDP complexes (19), most likely as the result of constraints placed upon the geometrical arrangement of the DHDP tail groups in the inverted bilayer.

Discussion

Static Interfacial Structures. The measurements reported here characterized the static structure of interfacial states formed in the midst of solvent extraction, as ions are transported across the water–dodecane interface. They show that small rare earth ions with oxidation state +3, Y(III) and Er(III), form inverted bilayers at the liquid–liquid interface upon thermally retarding the extraction process. Although we have observed different variations of the inverted bilayer, all have a single layer of ions sandwiched between back-to-back layers of DHDP extractants. The X-ray measurements are consistent with a model of the inverted bilayer as an interfacial condensed state of supramolecular ion–extractant complexes of the form M(DHDP)₃(H₂O)_{*m*}, where M is Er or Y and *m* varies roughly from 0 to 3. Although the inverted bilayer is not expected to be an equilibrium state, since it was formed under nonequilibrium conditions, MD simulations confirmed the short-term stability of this structure.

Studies of Sr(II) extraction with DHDP under similar conditions exhibited a different intermediate state, in which Sr(II) ions remained in the water phase and were bound (or located adjacent) to the head groups of an interfacial monolayer of DHDP. Comparison of the intermediate states of these three ions, Y(III), Er(III), and Sr(II), suggests that the oxidation state of the ion, or possibly just ionic charge, is the primary factor that determines the form of the intermediate state. These studies also allow for a comparison of the effect of electronic configuration on the intermediate state. We note that Sr(II) and Y(III) have the same closed-shell electronic configuration (4p⁶) of the unreactive noble gas Kr, whereas Er(III) has a more complex 4f¹¹ electronic configuration. It appears that the electronic configurations of these ions are not the determining factor in the structure of the intermediate state, in contrast to previous suggestions from kinetic studies of divalent ion extraction (17). Further studies are required to explore other effects. For example, since the ionic radius of Sr(II) (118 pm) is substantially larger than that of either Er(III) (89 pm) or Y(III) (90 pm), which are roughly equal, future studies will explore the role of ion size (27).

Consequences for the Mechanism of Extraction. Our results demonstrate that Y(III) and Er(III) are more effective at coordinating with DHDP than Sr(II). For instance, the formation of inverted bilayers containing Y(III) and Er(III), as well as their extraction at temperatures above the adsorption transition *T*₀, were observed with pH 2.5 water for which 94% of the phosphoric acid head

Fig. 2. MD simulation results. (A) Snapshot of inverted bilayer from the last frame of the simulation—water (Bottom, red and white), dodecane (Top, green), inverted bilayer: ions in blue, dodecane that started in the top leaflet is shown in green, dodecane that started in the bottom leaflet is colored cyan, DHDP molecules that started in the top leaflet are colored gold, and DHDP that started in the bottom leaflet is colored black. Topmost layer of dodecane is ordered at the vapor interface, which is not relevant for comparison with the results of X-ray measurements. A smaller, disordered layer of dodecane exists immediately adjacent to the inverted bilayer. (B) MD electron density profile averaged over the final 100 ns of the simulation: total density profile in solid green, water in black, dodecane in red, Er ions in blue, and DHDP in dashed green. (C) Er coordination showing only DHDP head groups and water molecules.

Fig. 3. Domain budding mechanism. (A) A flat region of bare interface (dodecane above, water below) becomes (B) spontaneously curved due to the adsorption of extractants and their interactions with ions (not shown) at the interface. (C) The reduction in length of the domain edge (dashed line) reduces the line tension energy, which balances the bending energy required to form a spherical reverse micelle. (D) Separation of the micelle from the interface extracts the ions (not shown) in the interior of the reverse micelle into the bulk organic phase.

groups would have been protonated and uncharged in the absence of metal ions (*Fraction of Protonated Head Groups in DHDP Monolayer*). However, Sr(II) binding to the charge-neutral DHDP monolayer under similar low-pH conditions was not observed (20). Instead, Sr(II) binding was observed only at higher pH, with one Sr(II) for every two DHDP measured at pH 5.3 and higher pH values. Even under these conditions of Sr saturation of the interface, combined X-ray reflectivity and XFTR results show that approximately one-third of the interfacial Sr(II) ions are not closely bound to the DHDP head groups, but exist only in a diffuse electrical double layer near the interface (20).

Y(III) and Er(III) are also more efficiently extracted from the aqueous phase than Sr(II). Analysis of the metal content in the aqueous phase before and after extraction by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and ICP mass spectroscopy showed that 87 (3)% of the Y(III) was extracted at 50 °C, more than 80% of the Er(III) was extracted at 55 °C (19), but only 45% of Sr(II) was extracted at 50 °C (pH 5.3) (20).

The interfacial state of Y(III) and Er(III) sandwiched between layers of DHDP extractants suggests the prompt transfer of these cations from the aqueous side of the liquid–liquid interface to a coordinated ion–extractant environment on the organic side. These ion–extractant complexes represent an intermediate state in which ions have been transported across the aqueous–organic interface, but have not yet been dispersed in the organic phase. In contrast to this, the observation of a conventional monolayer of DHDP extractants with Sr(II) bound to DHDP head groups, but remaining in contact with the water phase, suggests a slower kinetics of transfer of Sr(II) from water to dodecane, whose mechanism involves at least one additional step to transport the ion across the aqueous–organic interface.

Insight into this additional step may be provided by small angle neutron scattering measurements by Steytler et al. (6) of the metal salts $M^{n+}(\text{DEHP})_n$ dissolved in cyclohexane. The extractant bis(2-ethylhexyl) phosphoric acid (DEHP) has shorter, branched chains, but the same head group as DHDP. Steytler et al. studied the trivalent ion Al(III) and several divalent ions, including Ca(II) that is similar to the Sr(II) studied here. Although they observed small spherical complexes of Al-DEHP that were similar in size to Er-DHDP complexes that had been fully extracted into bulk dodecane (19), they observed larger rod-like reverse micelles of several different divalent ions, including Ca(II).

If reverse micelles form in our Sr(II)–DHDP extraction system, then budding of the micelle at the interface could be the additional, unobserved step in the ion transport across the aqueous–organic interface (17). A plausible mechanism for this process consists of three stages: (i) DHDP adsorption onto the interface and binding to Sr(II) ions, (ii) formation of interfacial domains of $\text{Sr}(\text{DHDP})_2$ complexes, and (iii) domain budding of reverse micelles into the organic phase. To explore the plausibility of budding of reverse micelles at the interface, we consider circular domain budding into a spherical reverse micelle (Fig. 3), as described in the following equation introduced by Lipowsky to model the energy E of bud formation in biomembranes (28):

$$E = E_{\text{bend}} + E_{\text{edge}} = 2\pi\kappa(LC - LC_{\text{sp}})^2 + 2\pi\lambda L\sqrt{1 - (LC/2)^2}. \quad [1]$$

The first term in Eq. 1 is the energy E_{bend} required to bend the domain into a spherical cap, or full sphere, of curvature C different from its spontaneous curvature C_{sp} . The domain is further characterized by its bending rigidity κ and domain area πL^2 (Fig. 3). Spontaneous curvature of the domain can arise from the asymmetry of the monolayer-containing interface, which has ions on one side interacting with extractants on the other. The second term in Eq. 1 expresses the energy E_{edge} of the domain edge in terms of its line tension λ , where dashed lines in Fig. 3 illustrate the domain edge. Formation of a complete spherical bud leads to the extraction of enclosed ions when the bud separates from the interface and goes into the organic phase (Fig. 3D).

A minimum size L^0 is required for the domain to form a complete bud. A domain can increase its size to this value by the aggregation of interfacial $\text{Sr}(\text{DHDP})_2$ complexes. The larger domain size that results from this aggregation has a longer domain edge and, consequently, larger edge energy. This larger edge energy can be recovered: as the domain bends to form a more complete sphere, illustrated by progressing from Fig. 3B to Fig. 3C, the reduction in edge length reduces the edge energy. This reduction balances the cost in bending energy required to form a spherical bud.

Lipowsky showed that complete budding is energetically favorable for domain sizes $L \geq L^0$, where $L^0 = 8\kappa/\lambda[1 + (4\kappa|C_{\text{sp}}|/\lambda)^{2/3}]^{3/2}$ (28). Literature values for κ , λ , and C_{sp} for compounds similar to our extractant DHDP are discussed in *Literature Values for κ , λ , and C_{sp}* , and yield a range of values for the ratio κ/λ , given by $4 \text{ nm} \leq \kappa/\lambda \leq 20 \text{ nm}$, and for C_{sp} , given by $0.1 \text{ nm}^{-1} \leq C_{\text{sp}} \leq 0.3 \text{ nm}^{-1}$. These values produce a range of limiting lengths, $4 \text{ nm} \leq L^0 \leq 14 \text{ nm}$, whose lower value of 4 nm describes a bud that contains the same number of extractants as the aggregation number of the reverse micelles measured by Steytler et al. (6). Note that the DEHP studied by Steytler et al. will have values of C_{sp} at the higher end of the stated range, thereby leading to values of L^0 at the lower end of our prediction. These calculations suggest that Sr–DHDP reverse micelles can be formed at the interface by spontaneous budding, although additional experiments are required to confirm this result.

Eq. 1 indicates that interfacial ion–extractant complexes that produce larger values of spontaneous curvature C_{sp} will require

Fig. 4. Cartoon of the interaction of a bulky branched-chain extractant DEHP with (A) a divalent ion (and two DEHP molecules) and (B) a trivalent ion (and three DEHP molecules) at the liquid–liquid interface (represented by the line), which illustrates how the interaction with the ion produces a spontaneous curvature of the interface.

Scheme 1. Bis(hexadecyl) phosphoric acid (DHDP).

less bending energy to make a complete bud. Larger values of C_{sp} may result from the interaction of bulky extractants with ions at the interface—these include extractants that are commonly used in solvent extraction processes, like DEHP that has branched alkyl tail groups (Fig. 4A), or malonamides and diglycolamides (29) that have bulky head groups. Bulky extractants form smaller complete buds since the spontaneous curvature is closer to the value of curvature $C = 2/L$ required to make a complete spherical bud. Higher oxidation state ions that coordinate a larger number of extractants are expected to produce an even larger spontaneous curvature (Fig. 4B). This physical picture suggests the formation of small supramolecular complexes relevant to the extraction of Y(III) and Er(III). Further research is required to establish a quantitative relationship between the shape and chemical properties of the extractant molecule, the interfacial elastic properties— κ , λ , and C_{sp} —and the extraction kinetics.

Materials and Methods

Materials and Sample Cell. *N*-Dodecane [$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$] (>99%; Sigma-Aldrich) and bis(hexadecyl) phosphoric acid (DHDP) [$\text{CH}_3(\text{CH}_2)_{15}\text{O}_2\text{POOH}$] (>98%; Sigma-Aldrich) (Scheme 1) were purified as described previously (19). Aqueous solutions of yttrium chloride hexahydrate ($\text{YCl}_3 \cdot 6\text{H}_2\text{O}$) (>99.99%; Sigma-Aldrich) were purified as described previously for ErBr_3 (19). Water was produced by a Nanopure UV Barnstead system. Hydrochloric acid (Optima grade; Fisher Scientific) was used to adjust the pH values of YCl_3 solutions. Dodecane–water interfaces (2.2:1 volume ratio) were temperature controlled ($\pm 0.03^\circ\text{C}$) (20).

Fraction Extracted. Aqueous and organic phases were heated to 50 or 55 $^\circ\text{C}$, placed into contact in a glass dish, and sat for periods varying from 1/2 to 24 h. A portion of the aqueous phase was extracted and analyzed by ICP-MS (Galbraith Laboratories) for Y or by ICP-AES for Er and Sr.

X-Ray Reflectivity and XFTR. X-ray measurements from liquid–liquid interfaces were made at ChemMatCARS Sector 15 of the Advanced Photon Source at an X-ray energy of 20 keV. X-ray reflectivity $R(Q_z)$ was measured as a function of wave vector transfer normal to the interface $Q_z = (4\pi/\lambda_x)\sin\alpha$, where λ_x is the X-ray wavelength and α is the angle of incidence. The reflected intensity (with background subtracted) was normalized to the incident intensity. The $R(Q_z)/R_F(Q_z)$ data in Fig. 1A represent the measured reflectivity normalized to the calculated Fresnel reflectivity (30). Data are analyzed with a slab model described previously (19, 30). XFTR data consisted of measurements of fluorescence spectra for values of Q_z slightly below and above the condition for total reflection (Fig. 1C). Measurement and analysis methods were published previously (20).

MD Simulations. Classical MD simulations were performed with Schrodinger Desmond (academic release) using the OPLS-2015 force field (31). The inverted bilayer system was built from two back-to-back monolayers on a $65.6 \times 65.6\text{-}\text{\AA}^2$ rectangular grid (x – y) of 100 DHDP (initial all-*trans* state) with phosphate head groups in the x – y plane and tail groups oriented along the z axis. Fifty DHDP molecules were removed from the lower leaflet, and dodecane added into the intervening spaces. Monolayer leaflets were separated by 8 $\text{\AA}$, which was filled with 50 Er(III) ions and 150 water molecules to mimic the low-density Er inverted bilayer. A preequilibrated slab of SPC-E water molecules was placed in proximity to the tail groups of the lower leaflet and a preequilibrated slab of dodecane molecules was placed in proximity to the tail groups of the upper leaflet. The box dimension in the z direction was set to 200 $\text{\AA}$, allowing for two liquid–vapor interfaces at the top and bottom of the periodic box. Equilibration occurred in stages, first by restraining the ions and head groups of the surfactant with a harmonic potential and allowing the water and dodecane to equilibrate. Harmonic restraints were then removed and further equilibration was performed for 50 ns before data production for 100 ns commenced.

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