

Spontaneous and Ion-Specific Formation of Inverted Bilayers at Air/Aqueous Interface

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KEYWORDS

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ABSTRACT

Developing better separation technologies for rare earth metals, an important aspect of a sustainable materials economy, is challenging due to their chemical similarities. Identifying molecular scale interactions that amplify the subtle differences between the rare earths can be useful in developing new separation technologies. Here, we describe ion-dependent monolayer to inverted bilayer transformation of extractant molecules at the air/aqueous interface. The inverted bilayers form with Lu^{3+} ions but not with Nd^{3+} . By introducing Lu^{3+} ions to preformed monolayers, we extract kinetic parameters corresponding to the monolayer to inverted bilayer conversion. Temperature-dependent studies show Arrhenius behavior with an energy barrier of 40 kcal/mol. The kinetics of monolayer to inverted bilayer conversion is also affected by the character of the background anion, although anions are expected to be repelled from the interface. Our results show the outsized importance of ion-specific effects on interfacial structure and kinetics, pointing to their role in chemical separation methods.

INTRODUCTION

Liquid-liquid extraction (LLE) is a chemical separation process widely used in hydrometallurgical processing of minerals, nuclear waste, and in recycling.¹ Despite being used for decades, molecular-scale details of LLE are not well-understood. A clear identification of free energy drivers in LLE will lead to more efficient separation technologies, a crucial task due to the increasing demand for rare earths (REs), platinum group metals, and other critical materials.

LLE is a two-phase free-energy driven process, involving complex ionic equilibria in both phases, interfacial effects, and solvent reorganization.²⁻³ The selective interfacial transport of metallic ions is thought to be mainly driven by the amphiphilic extractant molecules used in LLE.⁴ Dynamic structures forming at the liquid-liquid interface, such as water fingers, water ridges, and chemical “hinges” have been reported as some of the driving mechanisms for interfacial transport.⁵⁻⁹ Self-assembly of extractant-ion aggregates at the interface can also play a dynamic role in the interfacial ion transport.¹⁰ Thus, model systems focusing on the interfacial interactions of ions with amphiphilic molecules have been used to elucidate the processes in LLE.¹¹⁻²⁰ In the context of LLE, ion-surfactant interactions at the air/aqueous interface can elucidate both the dynamic ion transport across the interface and the equilibrium structures formed by the ion-extractant complexes in the organic phase. Langmuir monolayers at the air-water interface are convenient model systems for LLE and have been well studied to probe intermolecular forces.^{11, 21} Influence of dissolved chemical species on monolayers has been studied in order to understand the intermolecular interactions in various biological and physicochemical systems.²²⁻²⁵ Changes in the physical state of the interface are typically monitored by surface pressure isotherms, X-ray and neutron scattering techniques, vibrational spectroscopy, and light microscopy techniques.^{21, 25-28} However, a majority of these studies have been under static conditions, a drawback in understanding the kinetics of extractant ion interactions in ion-transport.

Dialkyl phosphoric acid extractants have been widely used in LLE of metals, particularly RE elements.²⁹ Bis(2-ethylhexyl) phosphoric acid (HDEHP) preferentially extracts the heavier lanthanides in a dimeric form such that there are six phosphate groups coordinating the extracted lanthanide in the organic phase.³⁰ Reverse micellar structures are formed in the organic phase after extraction of metals with HDEHP.³¹⁻³⁴ Interfacial studies using vibrational sum-frequency generation (VSFG) spectroscopy have shown the importance of hydrogen bonding interactions between the phosphate groups and water in stabilizing these micellar structures at the liquid-liquid interface.¹⁰ Peak shifts in VSFG in the phosphate region induced by different lanthanides have been attributed to increasing interaction strength between HDEHP and the lanthanides with increasing atomic number.³⁵ Interestingly, interfacial X-ray scattering and fluorescence results suggest a preference for lighter lanthanides at the Gibbs monolayers of HDEHP at the air/aqueous interface, due to the higher solubility of HDEHP complexes of heavier lanthanides.³⁶

Water-insoluble molecules, with longer alkyl tails, are limited to the interface and can plausibly provide more information on the ion-extractant interactions. Dihexadecylphosphate (DHDP) forms an insoluble monolayer on water, and it has been used as an analogue of HDEHP for this purpose.^{12, 20, 37} At the dodecane-water interface, “kinetically arrested” inverted bilayer of DHDP-Er(III) complexes has been observed.^{13, 37} This phenomena was proposed to underlie the micellization in the organic phases after LLE.¹³

Here, we show that the inverted bilayers of DHDP can be created at air/aqueous interface, allowing kinetic and temperature-dependent studies. Using synchrotron X-ray scattering techniques and VSFG, we first show that the inverted bilayers form with Lu³⁺ but not with Nd³⁺,

chemically very similar lanthanides, which shows that the charge density of the metal ion is the main driver behind the inverted bilayer formation (Figure 1). Bilayers can form regardless of the monolayer spreading procedure: a) when DHDP is spread on Lu^{3+} containing solutions, inverted bilayers form immediately, b) when DHDP monolayer is spread on pure water and Lu^{3+} ions are introduced later, the monolayer transforms into an inverted bilayer spontaneously. Temperature dependent studies determined that the monolayer to inverted bilayer transition follows first order kinetics with an Arrhenius behavior. Very interestingly, background anions, such as nitrate and thiocyanate, significantly affect the bilayer formation kinetics, although they are expected to be repelled from the interface due to electrostatic interactions. We discuss the static monolayer and bilayer structures in detail and investigate the kinetics of bilayer formation with multiple probes.

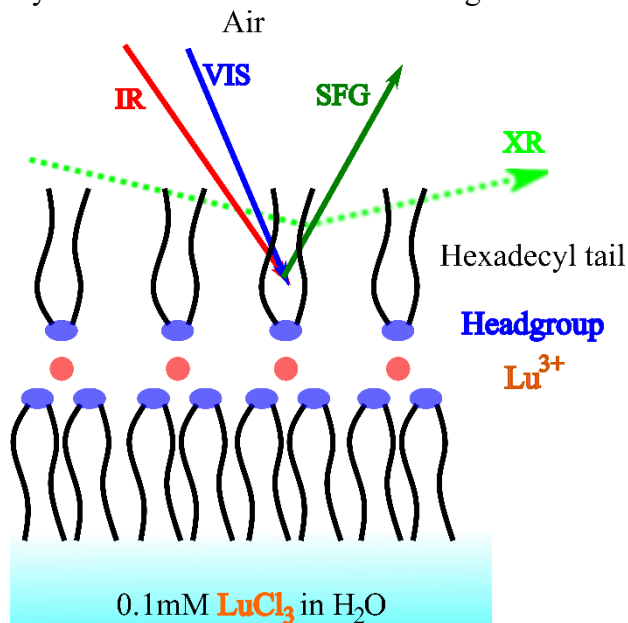


Figure 1. Schematic depiction of the experiments to probe interaction of DHDP molecules with Lu^{3+} ions at the air/aqueous interface. Samples are prepared by spreading DHDP on aqueous solutions of trivalent ions (See SI Methods). Specular XR and VSFG are complementary techniques that provide surface-specific structural information.

RESULTS AND DISCUSSIONS

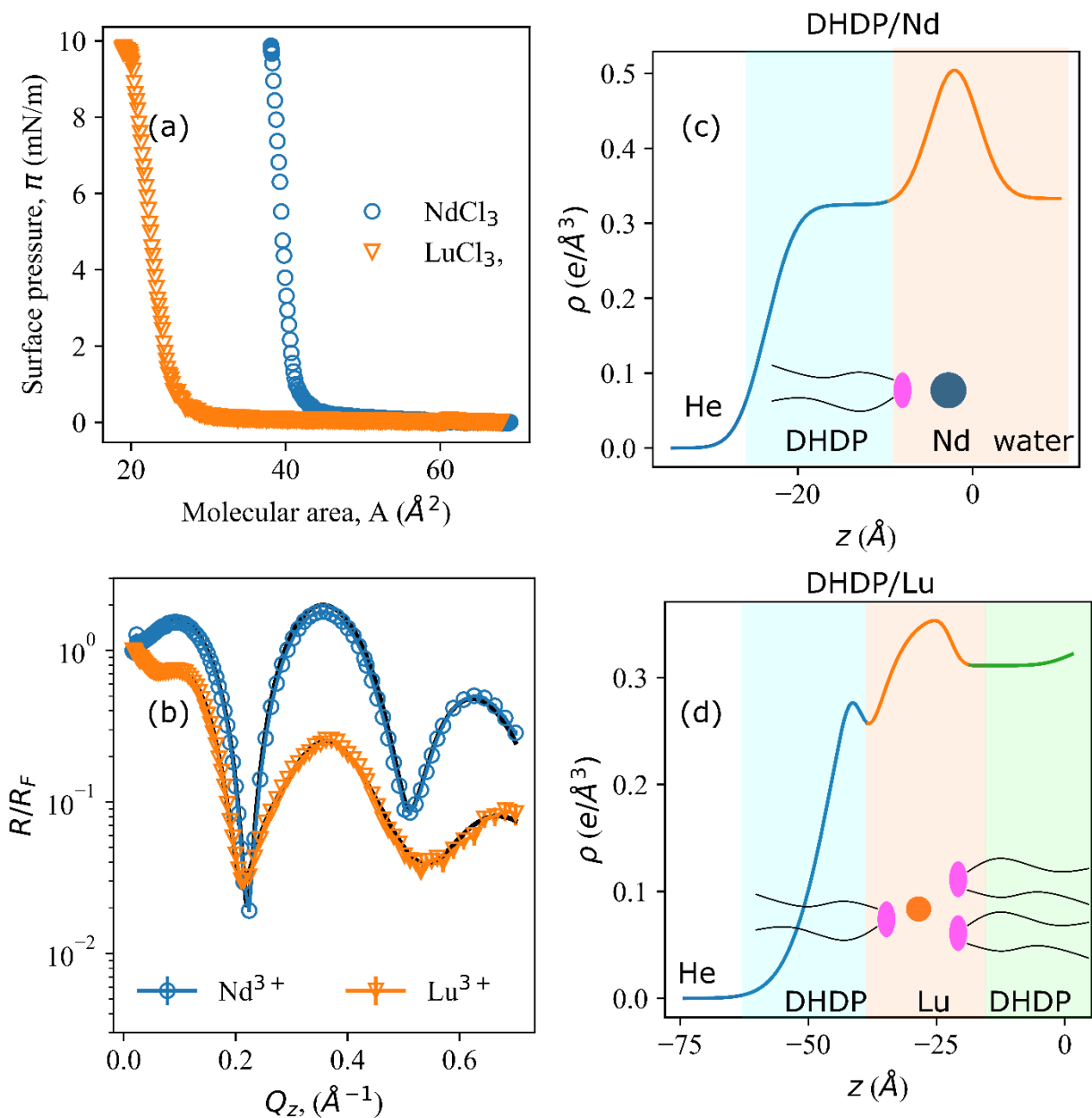


Figure 2. a) Langmuir isotherms showing the formation of a monolayer of DHDP on the surface of 0.1 mM NdCl_3 solution (blue circles), and an inverted bilayer on the surface of 0.1 mM LuCl_3 solution (orange triangles). b) X-ray reflectivity results for 0.1 mM NdCl_3 (blue circles) and 0.1 mM LuCl_3 in water (orange triangles) and the corresponding EDPs in (c) and (d). The fits for NdCl_3 were obtained using a 2-box model corresponding to the monolayer tail region and the headgroup region. The fits for LuCl_3 were obtained with a 3-box model and it shows the formation of an inverted bilayer at the air/aqueous interface. Schematics of the interfacial structure with Nd^{3+} and Lu^{3+} are also shown in (c) and (d).

Figure 2(a) shows the isotherms obtained by the compression of DHDP-covered surfaces, a common method to study Langmuir monolayers,²¹ in the presence of either of the lanthanide ions. In the presence of Nd^{3+} , the surface pressure increases rapidly as the surface area is compressed to $\sim 41 \text{ \AA}^2$ per DHDP. This is typical for a monolayer of double-chain molecule, considering that the molecular area for a single hydrocarbon tail is $\sim 20 \text{ \AA}^2$. In contrast, in the presence of Lu^{3+} in the subphase, the surface pressure begins to rise at much lower values of surface area per DHDP. The lower area per DHDP ($\sim 25 \text{ \AA}^2$) in the presence of Lu^{3+} suggests the formation of a bilayer or multilayer at the surface.

The interfacial structure can be resolved by specular X-ray reflectivity (XR) as it provides information on the electron density profile (EDP) normal to the surface.³⁸⁻³⁹ Figure 2(b) shows the Fresnel-normalized XR obtained for DHDP-covered surfaces in the presence of Nd^{3+} and Lu^{3+} . There are major qualitative differences in the reflectivity curves – with Nd^{3+} the normalized reflectivity rises at low Q_z whereas it decreases in the presence of Lu^{3+} . Further, the first extremum occurs at a smaller Q_z for Lu^{3+} surfaces. EDPs obtained from the box-model fits to the reflectivity curves are shown in Figure 2(c) and (d). The fit parameters are given in the Table S2 which provide information on the thickness of the layer (d), electron density (ρ), and roughness (σ). The interfacial region is wider in the case of Lu^{3+} compared to that of Nd^{3+} , which matches with the corresponding lower period of oscillations in the reflectivity curve. The EDP for Nd^{3+} sample precisely follows the expected profile for a monolayer, similar to those obtained with La^{3+} .⁴⁰ The boxes used in the fit correspond to the expected physical properties of the system – tail group region with a thickness of $\sim 20 \text{ \AA}$ and electron density $\sim 0.29 \text{ e/\AA}^3$ corresponding to a closely packed alkyl chain region. The integrated electron density of the headgroup region is $\sim 2.5 \text{ e/\AA}^2$ which includes contributions from the phosphate groups, adsorbed Nd^{3+} and water molecules. In the case of Lu^{3+} , the EDP suggests an inverted bilayer structure. However, the boxes do not appear to have one-to-one correspondence with the ideal molecular structure, which is expected due to possible interdigitation in the bilayer structure and the roughness of the interface. So, we perform an empirical analysis of the EDP as below.

We ascribe the peak in EDP (at $z \sim -30 \text{ \AA}$) to a layer of Lu^{3+} ions (Figure 2d, orange). For a regular bilayer, the electron density should uniformly decrease from this Lu^{3+} layer to the bulk aqueous region. The presence of a lower density region in the EDP between this Lu^{3+} layer and the aqueous bulk region ($\rho \sim 0.33$) suggests the presence of alkane chains, which in turn indicates that the surface is covered with an inverted bilayer. There can be two canonical conformations for the inverted bilayer – two DHDP molecules exposed to the air side and one towards the aqueous side, or vice versa. We can decompose the EDP shown in Figure 2(d) into three regions – top, middle, and bottom layers (Figure 2d, blue, orange, and green). We assume that the DHDP tail groups are fully extended in both top and bottom layers. This assumption is supported by the absence of any gauche defects (2850 cm^{-1} band) in the alkyl chains as shown by the VSFG spectra (Figure 3). Thus, we make the top and bottom layers to have approximately 20 \AA thickness which corresponds to the full length of all-trans hexadecyl chains. This gives us an integrated electron density of $\sim 3.1 \text{ e/\AA}^2$, 6.9 e/\AA^2 , and 6.7 e/\AA^2 for top, middle, and bottom layers, respectively. The higher electron density of the bottom layer than the top layer suggests that there are more DHDP molecules adjacent to the aqueous side. This conformation is favored possibly due to the higher shielding of water from the chains with a tightly packed alkyl chain layer compared to a loosely packed alkyl chain region.

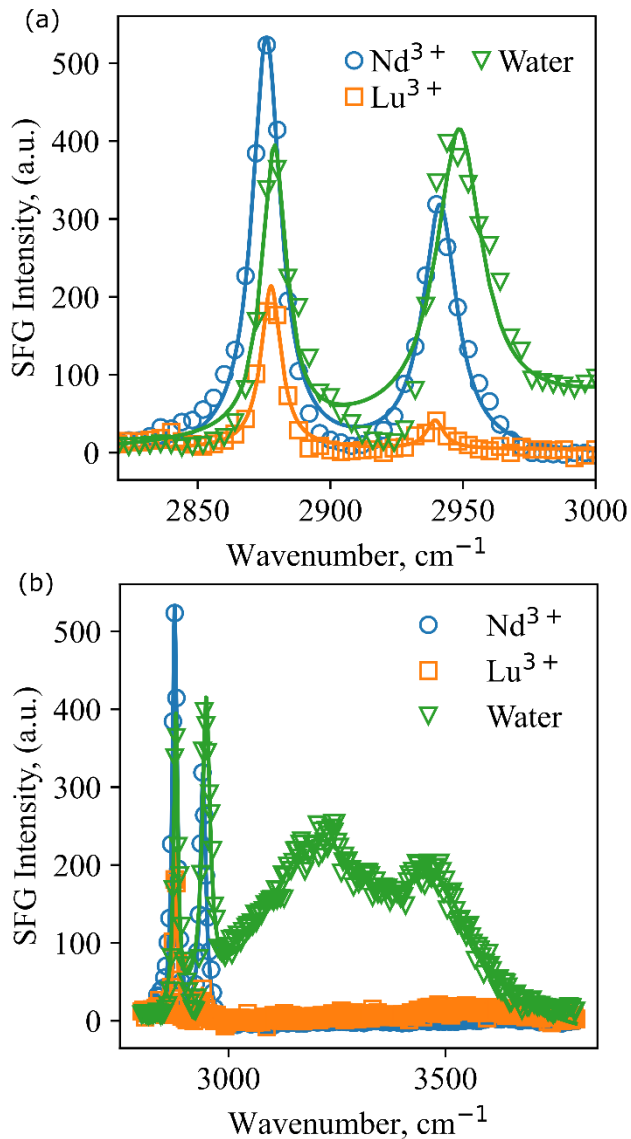


Figure 3. SFG spectra of DHDP/aqueous interface in the presence and absence of lanthanide ions showing (a) CH₂ and CH₃ stretch regions, and (b) CH₂, CH₃ and OH stretch region. The concentration of lanthanide ions in all the systems is 0.1 mM.

VSFG experiments provide further confirmation for the suggested bilayer structure. VSFG spectrum of the DHDP-Lu³⁺ system shows a decrease in CH₃ stretch peak intensity compared to DHDP-water case indicating lower asymmetry relative to a monolayer (Figure 3(a)). Since VSFG is a dipole forbidden process, molecules orienting opposite to each other either cancel or reduce the net dipole and lower the intensity. If the bilayer is symmetrical, having equal number of the DHDP molecules on top and bottom, the overall peak intensity would reduce to zero. Thus, our VSFG results support the XR results showing unequal distribution of DHDP between top and bottom layers. In the presence of Nd³⁺ ions there is no decrease in intensity confirming the monolayer structure. In fact, the signal slightly increases due to the better packing of the molecules as the headgroup charge is shielded by the adsorbed ions, reducing the repulsion. The

corresponding spectra in the OH region provides information on the interfacial water structure (Figure 3(b)). On pure water, the electric field of the headgroups orient the water molecules inducing a strong VSFG signal. In the case of Nd^{3+} , ions shield the charge of the headgroup diminishing the VSFG signal.^{14,41} In the case of Lu^{3+} , inverted bilayer forms and the tails touching the surface do not create any significant orientational ordering of water molecules.

We can directly detect the metal ions in monolayer and inverted bilayer structures by X-ray fluorescence near total reflection (XFNTR).^{15, 38} Figure S3 shows the variation of integrated fluorescence signal in the L_{α} region of Nd and Lu as a function of the vertical momentum transfer (Q_z). The fits to the data provide an estimate of the interfacial number density of the elements (Table S1). For Nd^{3+} we obtain an area of $\sim 110 \pm 5 \text{ \AA}^2$ per Nd. At $\sim 41 \text{ \AA}^2$ per DHDP molecule there is $\sim 0.36 \pm 0.02 \text{ Nd}^{3+}$ per DHDP which is close to the Nd^{3+} number density required for balancing the charge of the monolayer. With Lu^{3+} however, we obtain $37 \pm 4 \text{ \AA}^2$ per Lu, or approximately 0.68 Lu per DHDP molecule at 25 \AA^2 per DHDP. Assuming that the charge balance is satisfied only by DHDP and Lu^{3+} ions, the minimum surface area per Lu^{3+} when both the top and bottom DHDP layers are fully packed should be $120 \text{ \AA}^2 / 2 = 60 \text{ \AA}^2$. As the obtained surface area is significantly less than this minimum, the speciation of Lu is probably different from the trivalent species found in bulk solution, i.e. counterions may be present in the bilayer to compensate the charge. Presence of divalent hydroxyl-lanthanide species next to an anionic monolayer has been recently reported.⁴²

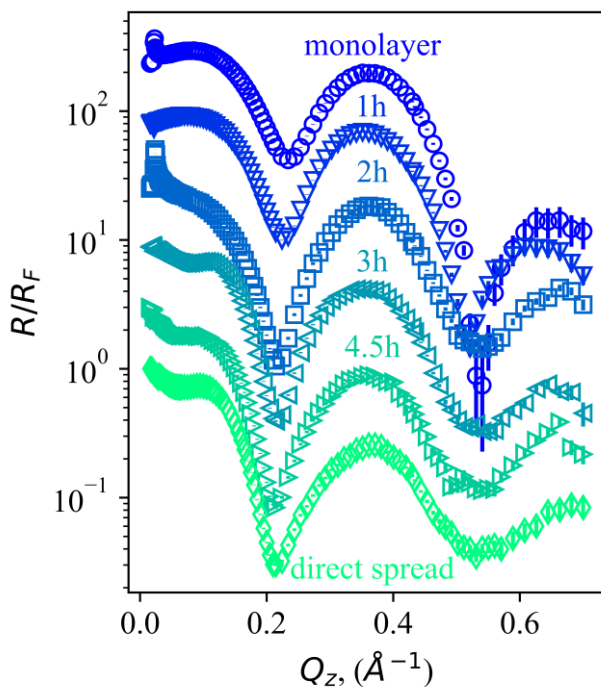


Figure 4. Time-dependent variation of the Fresnel-normalized XR profile of the DHDP-covered surface upon introduction of Lu^{3+} to the subphase. DHDP is spread on water and is compressed to form a monolayer at a surface pressure of 10 mN/m. At $t = 0$, a small volume of LuCl_3 solution is injected into the subphase, behind the trough barrier. The monolayer begins to shrink in area while

maintaining a constant surface pressure (see Figure 5(a) for the surface pressure isotherm). After ~ 4.5 hours, the XR profile of the surface resembles that of DHDP spread directly on LuCl_3 solution (Figure 2(b)). The XR curves at different time stamps have been shifted vertically for clarity.

In the absence of any Lu^{3+} ions, DHDP forms a monolayer on water, and this provides an opportunity to study the kinetics of the bilayer formation. XR of the interface after compressing DHDP on water to a surface pressure of 10 mN/m shows the formation of a monolayer (Figure 4, blue). Upon introduction of Lu^{3+} ions in the subphase, behind the trough barrier, the X-ray reflectivity shows a gradual change along with decrease in surface area for maintaining constant surface pressure. About 4.5 hours after the introduction of Lu^{3+} , the XR curve becomes very similar to the one shown in Figure 2(b) indicating that the interface has an inverted-bilayer structure similar to the one obtained by direct spreading of DHDP on Lu^{3+} -containing subphase (Figure 4, green).

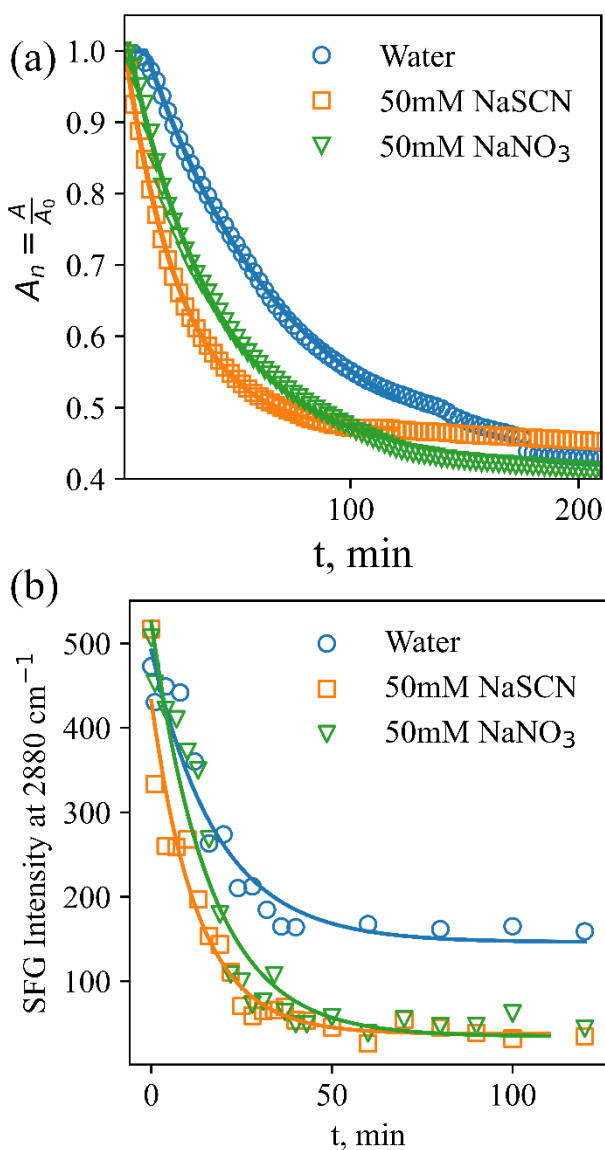


Figure 5. (a) The kinetics of the formation of inverted bilayer are dependent on the background anion present in the aqueous subphase. Thiocyanate (orange squares) leads to a faster formation of the bilayer compared to nitrate (green triangles), both faster than having no background salt (blue circles). The solid lines are fits to an empirical model based on nucleation growth theory shown in Eq. 1. (b) Decay rates of the amplitude of the CH₃ symmetric stretch peak from VSFG experiments also indicate that the monolayer to inverted bilayer transition is faster in the presence of NaSCN.

The effect of monovalent anions on the interfacial adsorption and transport of lanthanides has been reported earlier.^{14-15,43} We found no effect of background ions on the final static structure or XFNR results when spreading DHDP on the subphase containing lanthanides and background salts (Figure S3 and S4). However, there is an anion-dependence in the kinetics of monolayer to the inverted bilayer transition (Figure 5) upon addition of Lu³⁺. We spread DHDP monolayer on salt solutions (0.1 M of NaNO₃ or NaSCN) and introduced either Nd³⁺ or Lu³⁺ solution behind the barrier (Figure S2). The barrier position was allowed to move to maintain a constant surface pressure of 10 mN/m, same as the one used above. With the introduction of Nd³⁺, the surface area remains constant with time (Figure S5). Figure 5(a) shows the decay of trough area required to maintain the surface pressure constant upon injecting Lu³⁺ solution. We have modeled the decay as an exponential function of time according to Equation 1. This model has three parameters - t_0 (time offset after which the decay is exponential), k (rate constant for exponential decay), and a_∞ (the ratio of final to initial trough area). The fit parameters are listed in Table S3. The rate of decay roughly corresponds to the monolayer to inverted bilayer transition. Thus, there is an effect of background anion on the monolayer to inverted bilayer transition. Both nitrate and thiocyanate increase the rate of transition with thiocyanate having a stronger effect.

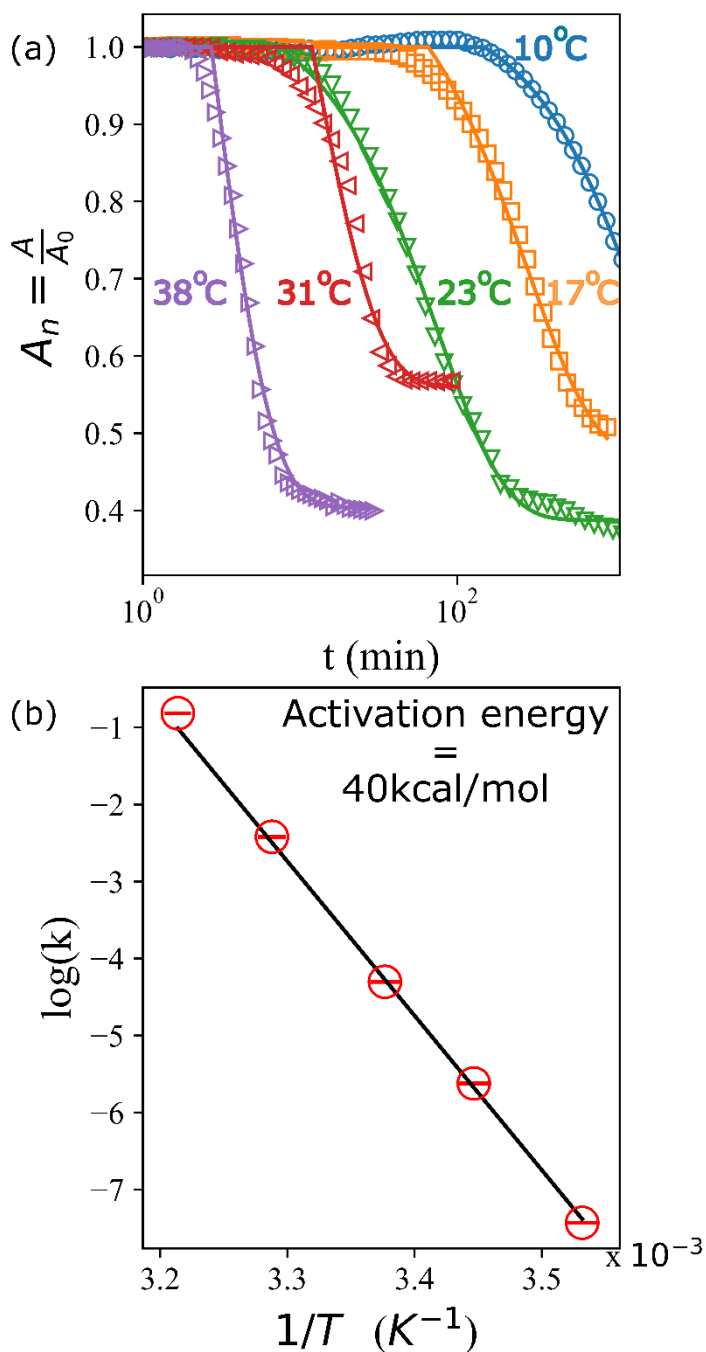


Figure 6. (a) Temperature dependence of the normalized area that is required to maintain a constant surface pressure of 10 mN/m as a function of time with injection of LuCl_3 to the subphase (final concentration of 0.1mM). While at a low temperature of 10 °C, the compression of the surface due to the formation of the bilayer occurs in the scale of hours, at 38 °C the transition occurs within minutes. Black solid lines show the fits obtained using an exponential decay, corresponding to first order kinetics of the transition (Eq. S1). (b) Variation of the first order rate constant (k) of monolayer–bilayer transition shows a classical Arrhenius type of behavior.

The intensity of CH₃ symmetric stretch peak in VSFG spectra, at 2875 cm⁻¹, provides a molecular scale description of monolayer to bilayer transition (Figure 3 and Figure S6). Figure 5b shows the decay of this peak upon introduction of Lu³⁺ to the subphases below DHDP monolayers. An exponential decay model was used to fit the data (solid lines in Figure 5(b)) and the parameters are listed in Table S4. The rate of monolayer to inverted bilayer conversion is increased by background ions; and thiocyanate has a stronger effect than nitrate. The rate of conversion obtained from VSFG appears to be faster than corresponding rates obtained by surface pressure isotherms. There may be a few reasons for the difference. First, VSFG probes the molecular scale structure directly, as opposed to the macroscopic surface area measurement. Also, a constant area setup used in VSFG versus the constant pressure setup in the isotherms can contribute to the differences (Figure S2). We note that the intensity of CH₃ symmetric stretch peak does not significantly change upon introducing Nd³⁺ ions to the subphase (Figure S7).

We investigated the temperature dependence of monolayer to bilayer transition to understand the energetics of the process (Figure 6a). The rate constant is derived from the fits to an empirical model based on the classical nucleation growth theory (Equation S1). Its variation as a function of the inverse temperature is shown in Figure 6b. The fit parameters are tabulated in Table S3. The linear relationship shows that the monolayer to inverted bilayer transition follows the Arrhenius equation. We obtain an activation energy of ~ 40 kcal/mol for the transition. Induction time for monolayer to inverted bilayer transition (t_0) decreases with increasing temperature.

Anion- and temperature-dependent studies are briefly described here, as a proof of concept, to demonstrate that we can elucidate the kinetics of amphiphile-ion interactions and obtain information that is not available in static measurements. More detailed studies utilizing these approaches will follow.

We have studied the differences in Lu³⁺ and Nd³⁺ adsorption onto DHDP-laden aqueous surfaces using X-ray scattering, VSFG, and surface pressure isotherms. Regardless of the surface preparation method, DHDP forms an inverted bilayer structure in the presence of Lu³⁺ ions and a monolayer in the presence of Nd³⁺ ions (Figure 7). The qualitative difference between the nanoscale structures induced by different charge densities of Nd³⁺ and Lu³⁺ directly affects the macroscopic system, a desirable feature in chemical separations. The ion-specific formation of inverted bilayer with Lu³⁺ indicates a difference in kinetics of ion transfer with lighter and heavier lanthanides even at longer time scales than that were investigated by simulations.

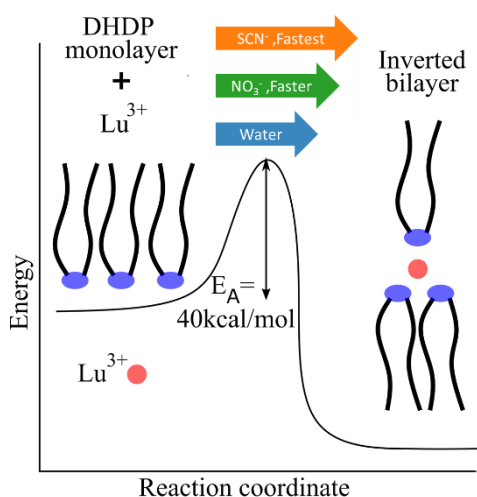


Figure 7. Schematic description of the monolayer to inverted bilayer transition of DHDP in the presence of Lu^{3+} ions based on Figures 5 and 6. The reaction follows first order kinetics with an energy barrier of 40 kcal/mol and is catalysed by background anions – SCN^- and NO_3^- .

All the RE ions are predominantly +3 charged and the main difference between them is in their ionic sizes, which decreases with atomic number for a given coordination number.⁴⁴⁻⁴⁵ The chemistry of REs is dominated by electrostatic interactions in solid state.⁴⁶⁻⁴⁷ In solutions, the mean-field theories developed for monovalent ions at dilute concentrations⁴⁸⁻⁵⁰ usually fail to describe experimental observations with RE ions which are multivalent. At surfaces, multivalent ions can induce “charge-reversal” or spontaneous collapse of monolayers, phenomena that are not observed with monovalent ions.⁵¹⁻⁵² In this context, effects of ion-ion, ion-surfactant correlations, and specific interactions between ions and surfactants, such as hydrogen bonds and coordination bonds have been described.^{11, 40, 53-54} Our results add a new dimension to these observations and show that the complex interactions of the trivalent ions can be fine-tuned to create qualitative differences in their interactions with amphiphiles, which directly affects the macroscopic behavior of the system.

Our results with DHDP at air-water interface and the prior results obtained with DHDP at water-dodecane interface show that an inverted bilayer of DHDP is formed with heavy, charge dense trivalent ions.^{13, 37} The dodecane-water interface experiments required lower temperatures to kinetically arrest the interfacial species formed during ion transfer. At the dodecane-water interface, Sr^{2+} adsorbs to a monolayer of DHDP at the interface.¹² This difference between trivalent and divalent ions was interpreted as different extraction mechanisms for them with dialkyl phosphoric acid extractants.¹³ Our results suggest that it is not necessarily a difference between divalent and trivalent ions, but possibly a difference in charge densities as DHDP forms a monolayer under both Nd^{3+} and Sr^{2+} .

We note that DHDP is used as an interfacial analogue to HDEHP in our study. It is important to consider the effects of tail structure. In LLE, the tail group plays a major role in extraction, organic phase structure and the phase behavior.⁵⁵⁻⁵⁸ Similarly, the tail structure plays a major role in the formation and structure of the Langmuir monolayers due to the Van der Waals interactions between the tails.^{21, 59-60} In contrast to the results obtained with DHDP, VSFG studies with HDEHP at the air-water interface suggest that HDEHP interacts with all the lanthanides in a monolayer-

like structure.^{35, 61} Similarly, XR of the HDEHP at the air-water interface is not qualitatively different for light and heavy lanthanides.³⁶ With a shorter chain analogue of HDEHP, namely dibutyl phosphate, a structure similar to inverted-bilayer is observed.⁶¹ Organic phase speciation of Er is also different when extracted with HDEHP (hexamer) or DHDP (trimer).³⁷ Regardless of these differences, it is evident that the small changes in ionic size of the lanthanides can have a major implications to the organic phase structure and thereby the extraction energetics.

Although there are several studies on the collapse of Langmuir monolayers due to compression⁶²⁻⁶⁵ there are fewer on the spontaneous collapse of monolayers induced by solutes. Recently, a spontaneous monolayer to inverted bilayer transformation of palmitic acid in the presence of calcium ions has been reported.⁵² Divalent cations have also been shown to reduce the surface pressure at which stearic acid films collapse.⁶⁶ Such interplay of ion-lipid interactions is especially important in the biophysics of cellular membranes where lipids affect selective ion transport and ions affect transbilayer lipid motions.⁶⁷⁻⁷² In this context, , a coordination-driven, ion-specific monolayer to inverted bilayer transition has been reported with calix[4]arene films on Cu(II) or Ni(II) solutions.⁷³ Unlike the lanthanide ions where ligands interact electrostatically, transition metals can show significant selectivities due to ligand-metal coordination bonds that are directional. Finally, a paper published while our manuscript was under review confirms the static inverted bilayer structure we propose for the lutetium system.⁷⁴

The kinetics of monolayer to inverted bilayer transition with Lu³⁺ in the subphase is strongly temperature dependent with an activation barrier of ~ 40 kcal/mol. This relatively large energy barrier is in correspondence with the low temperature required to arrest the heavy lanthanide species at the dodecane-water interface.³⁷ The onset of transition is also temperature dependent indicating a temperature dependent nucleation of inverted bilayer structure. The transformation of monolayer to inverted bilayer probably involves multiple steps with a first-order rate limiting step that is captured in our kinetic studies. DHDP forms stable monolayers with Nd³⁺ in the subphase at temperatures up to 37 °C. Whether inverted bilayers can form with lighter lanthanides at higher temperatures is an open question. It is not clear whether inverted bilayer formation with Nd³⁺ is kinetically limited or is thermodynamically unstable.

We have previously reported the anion-dependence in lanthanide adsorption at DHDP monolayers.¹⁵ These experiments were conducted with preformed monolayers and lanthanide injection behind the barrier. Under the impression that the surfaces were under equilibrium, we attributed the differences in fluorescence signals to anion-effect on number density of lanthanides adsorbing to the surface. We obtained an interfacial area per Lu that is lower than that for 1:3 Lu:DHDP complexes and interpreted that to be a result of excess background anions. This present report shows that the lower interfacial area per Lu is obtained even in the absence of background salts. Further, the reported difference in Lu adsorption with different background salts are due to the differences in kinetics of inverted bilayer formation in the presence of NO₃⁻ and SCN⁻.

CONCLUSIONS

We have demonstrated how monolayer to bilayer conversion can be used to identify important ion-specific effects in RE separations. Phosphoric acid based extractants are often used in the LLE of RE elements, but there are outstanding questions on the mechanisms that determine ion transport

and selectivity. Here we have shown that there is an ion-specific effect in the adsorption of trivalent ions to DHDP, an analogue of phosphoric acid based extractants: larger trivalent ion Nd^{3+} maintains the monolayer structure of DHDP while smaller Lu^{3+} ion induces the formation of an inverted bilayer. This shows that the air/aqueous interface models can be used to reproduce important aspects of oil/water interfaces. Further, the monolayer of DHDP collapses to an inverted bilayer upon the introduction of Lu^{3+} ions where the rate of collapse is temperature dependent. These results show that the minor differences in ionic sizes of the RE elements have major impacts on the interfacial structure. Elucidating these effects at the air-water interface, can show the drivers of ion-transport and selectivity in LLE. The kinetics of ion-dependent monolayer to inverted bilayer transition provide a route to investigate ion transport and lipid structure in various physicochemical processes.

EXPERIMENTAL METHODS

Materials: Dihexadecyl phosphate (DHDP) was purchased from Avanti Polar Lipids Inc. Neodymium (III) chloride hexahydrate, lutetium (III) chloride hexahydrate, sodium chloride, sodium nitrate, and sodium thiocyanate were purchased from Sigma Aldrich Inc., and used as received without any further purification. Aqueous solutions of lanthanides and sodium salts were prepared in volumetric flasks. DHDP was dissolved in chloroform to prepare a 0.25mM solution. The pH of the solutions was 5.8 ± 0.1

Sample preparation for static studies: X-ray scattering studies were conducted at sector 15-ID-C of Advanced Photon Source, Argonne National Laboratory. In a typical experiment the aqueous subphase containing lanthanides was poured into the Langmuir trough placed in a sealable chamber. The liquid surface was compressed and aspirated as a surface preparation step. With the barrier in the “open” position, a measured volume of DHDP solution was spread on the surface, dropwise, with a 100 μL glass Hamilton syringe. The surface was then compressed by moving the motorized barrier at 8 cm^2/min to reach a surface pressure of 10 mN/m . The surface is kept under this constant pressure by barrier motion controlled with a NIMA IU4 controller. The chamber was then sealed and purged with water-saturated He gas.

The VSFG studies were conducted in a fixed area mode. Approximately 40 mL of the aqueous subphase is poured into a shallow PTFE dish with circular cross-section (diameter = 10 cm). Droplets of DHDP solution were spread on the surface of the liquid slowly using 10 μL Hamilton syringe while monitoring the surface pressure. Enough droplets were added to achieve a surface pressure of 10 mN/m .

Sample preparation for kinetic studies: For X-ray scattering experiments 198 mL of lanthanide-free aqueous subphase (water or a salt solution) was poured into the trough and DHDP was spread on the liquid surface. The monolayer was compressed to a surface pressure of 10 mN/m . After the formation of a stable monolayer 2 mL of the lanthanide solution at an appropriate concentration was added to the subphase by injecting the solution behind the trough barrier using a plastic syringe. The subphase was then mixed by pumping the solution in and out of the syringe for 10 minutes at the rate of $\sim 45 \text{ mL/min}$

For temperature dependent kinetic studies the trough temperature was controlled by pumping an ethylene glycol solution (~5wt%) that was cooled or heated with a NESLAB RTE 111 chiller. The temperature of the subphase was measured using a thermocouple.

We used the following empirical model based on the classical nucleation-growth theory⁷⁵ to fit the decay of trough area required to hold a constant surface pressure in the presence of Lu³⁺ ions as follows:

$$\frac{a(t)-a_{\infty}}{1-a_{\infty}} = u(t-t_0)(e^{-k(t-t_0)}) + u(t_0-t) \quad \text{Eq.1}$$

Where a(t) is the ratio of area at a given time to the initial monolayer area, k is the exponential decay rate constant, t₀ is the time delay between the introduction of Lu³⁺ and the onset of exponential decay, and a_∞ is the area ratio at steady state, and u(x) is the Heaviside function.

Synchrotron X-ray studies: XR and XFNR studies were conducted at sector 15-ID-C of Advanced Photon Source, Argonne National Laboratory as described in our previous papers.^{14, 41} X-ray energy was set to 18.3 keV, above the L3 absorption edges of Lu and Nd. Dectris PILATUS 100 detector was used for obtaining reflected X-ray intensity. At each incident angle, a background signal was subtracted from the reflection. The XR data was fit using Stochfit.⁷⁶ XFNR data was collected using an energy dispersive Vortex detector setup normal to the surface with a collection snout placed ~ 10.6 mm from the surface. At each incidence angle, Gaussian curves were fit to the fluorescence spectra corresponding to the element of interest. Integrals of the peaks are used in the XFNR figures.

VSFG Experiments: The VSFG measurements are acquired using an EKSPLA system, which has been described previously.^{14, 16-17, 41} Briefly, an amplified Nd:YAG laser system produces 29 ps pulses having 28 mJ energy centered at 1064 nm with a repetition rate of 50 Hz. The harmonic unit splits the 1064 nm laser and generates two beams of 532 nm. Fundamental laser beam 1064 nm and second harmonic beam 532 nm are used to generate a narrowband IR pulse tunable from 1000-4000 cm⁻¹ via optical parametric generator and difference frequency generation. The other 532 nm laser beam is used as a visible source to generate VSFG signal. The SFG signal is passed through a monochromator and collected using a photomultiplier tube.

The VSFG measurement is carried out using a reflection geometry where the incident angles of the visible and IR beams are 60° and 55°, respectively, to the surface normal. The visible light is attenuated to an average energy of 600 μJ and the IR energy is maintained at 100 μJ for all measurements. A motorized piezoelectric rotation stage is used to rotate the sample to avoid beam damage. Each spectrum is collected with a 4 cm⁻¹ increment over the range of 2800-3800 cm⁻¹ and averaged over 300 laser shots per point. The spectra are collected under various polarization combinations and are normalized against the SFG spectrum of a z-cut quartz.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

Authors declare no competing financial interest.

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ABBREVIATIONS

XFNTR, X-ray fluorescence near total reflection; VSF, vibrational sum frequency generation; LLE, liquid-liquid extraction; XR, X-ray reflectivity; DHDP, Dihexadecylphosphate;

ASSOCIATED CONTENT

SUPPORTING INFORMATION.

The supporting information document has the following: a) VSF spectra showing the OH region, b) results from X-ray fluorescence near total reflection, c) X-ray reflectivity curves in the presence of salts, d) Surface pressure isotherm of DHDP on Nd³⁺ solution showing its stability, and e) Fit parameters for the empirical model describing the kinetics of monolayer to inverted bilayer transition.

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TOC Figure

