### Supplementary Information

# Interfacial Structure in the Liquid-Liquid Extraction of Rare Earth Elements by Phosphoric Acid Ligands: A Molecular Dynamics Study

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#### 1. Gibbs Dividing Surface, Interfacial Thickness and Interfacial Tension

Firstly, the water molecules that drifted to the other end due to periodic boundary conditions were reconstructed to get a single block of water. The simulation box was then divided into bins of 1Å along the normal to the interface to calculate the mass density of water. Gibbs Dividing surface is taken at the position where the mass density of water becomes 50% of its bulk density. Periodic boundary conditions resulted in formation of two interfaces; one near the middle of the simulation box and other on the edge of the periodic boundary. Thus, we have two positions of Gibbs Dividing Surface. All the properties were calculated at both the interfaces and the average values are reported. Similarly, the position of the Gibbs Dividing Surface for the n-heptane block was calculated. A difference between the values of Gibbs Dividing Surface of water and n-heptane is considered as the intrinsic interfacial thickness of the system.

The density profile of water along the normal to the interface was fit to the following equation to obtain the capillary wave width due to thermal fluctuations.

$$\rho_W(z) = 0.5\rho_{WB} + 0.5\rho_{WB}erf\left[\frac{z - \langle z_W \rangle}{\sqrt{2}t_C}\right]$$
(S1)

where,  $\rho_W(z)$  is the density of water at a given z coordinate,  $\rho_{WB}$  is the density of water in bulk aqueous phase,  $\langle z_W \rangle$  is the average position of the Gibbs Dividing Surface on the aqueous phase and  $t_c$  is the capillary wave width.

Table S1 gives the intrinsic interfacial width (obtained as a difference between position of Gibbs dividing surface on organic and aqueous sides) and the capillary wave width (obtained by fitting density profile of water to equation S1). Both the intrinsic interfacial width and the capillary width increase with increase in aqueous phase ionic strength.

System	Intrinsic Width (Å)	Capillary wave width (Å)
N1	0.68 (0.29)	1.55 (0.02)
N2	4.63 (0.76)	1.60 (0.02)

Table S1 Intrinsic interfacial width and capillary wave width for different systems

AF1	4.92 (0.71)	1.57 (0.02)
AF2	4.53 (0.74)	1.61 (0.02)
AF3	5.70 (0.83)	1.94 (0.03)
AH1	4.98 (0.64)	1.66 (0.02)
AH2	6.18 (0.56)	1.64 (0.02)
AH3	6.08 (0.66)	1.90 (0.02)
NF1	4.85 (0.65)	1.58 (0.02)
NF2	5.52 (0.73)	1.64 (0.03)
NF3	5.85 (0.76)	1.98 (0.03)
NH1	4.84 (0.63)	1.60 (0.01)
NH2	5.32 (0.62)	1.64 (0.03)
NH3	5.79 (0.70)	2.00 (0.05)
DF1	5.43 (0.68)	1.61 (0.02)
DF2	4.09 (0.74)	1.56 (0.02)
DF3	5.70 (0.85)	1.91 (0.03)
DH1	4.90 (0.68)	1.61 (0.02)
DH2	5.17 (0.61)	1.65 (0.02)
DH3	5.34 (0.67)	1.65 (0.02)

Interfacial tension of the systems was calculated using components of pressure using the following equation.

$$\gamma = \frac{L_z}{2} \left[ \langle p_{zz} \rangle - \left( \frac{\langle p_{xx} \rangle + \langle p_{yy} \rangle}{2} \right) \right]$$
(S2)

where,  $\gamma$  is the interfacial tension,  $L_z$  is the length of the simulation box in z dimension,  $\langle p_{xx} \rangle$ ,  $\langle p_{yy} \rangle$ ,  $\langle p_{zz} \rangle$  and are the average components of pressure in x, y and z directions respectively. Table S2 gives the values of Interfacial tension obtained by using equation S2. Our value of 52.84 mN/m is in excellent agreement with the experimental value of 51.7 mN/m [1] for the neat water: n-heptane interface.

Table S2 Interfacial Tension for different systems

System	Interfacial Tension (mN/m)
N1	52.84 (0.02)
N2	46.70 (0.03)

AF1	46.42 (0.05)
AF2	45.91 (0.04)
AF3	42.84 (0.05)
AH1	46.37 (0.03)
AH2	46.07 (0.04)
AH3	40.60 (0.03)
NF1	46.29 (0.03)
NF2	47.08 (0.06)
NF3	42.08 (0.02)
NH1	46.28 (0.01)
NH2	45.63 (0.0.01)
NH3	40.52 (0.0.04)
DF1	46.88 (0.04)
DF2	46.56 (0.03)
DF3	42.03 (0.0.03)
DH1	46.47 (0.02)
DH2	45.98 (0.03)
DH3	41.08 (0.06)

The 3D coordinates of the interface was used to fit a wave-like equation of the form

$$\overline{d} = \frac{a\xi l}{a+\xi l}$$

where,  $\overline{d}$  is the average normal distance between two surface points and *l* is the lateral distance between these points while  $\xi$  and *a* are frequency and amplitude like parameters of the rough interfacial surface, respectively. The values of  $\xi$  and *a* for various systems are given in table S3.

a	ىئ
2.417	0.834
2.412	0.870
2.645	0.802
	a 2.417 2.412 2.645

Table S3 Values of the constants used to characterize interfacial roughness

AF2	2.800	0.755
AF3	2.872	0.985
AH1	2.472	0.851
AH2	2.381	0.994
AH3	2.644	1.096
NF1	2.531	0.792
NF2	2.324	0.949
NF3	2.674	1.285
NH1	2.378	0.915
NH2	2.514	0.928
NH3	3.039	0.999
DF1	2.386	0.797
DF2	2.666	0.827
DF3	2.947	0.954
DH1	2.350	0.933
DH2	2.525	0.860
DH3	2.503	1.168

2. Number of hydrogen bonds per water molecule



**Figure S1:** Number of Hydrogen bonds per water molecule as a function of distance from Gibbs Dividing Surface for neutral systems N1 and N2. Positive distances with respect to the Gibbs dividing surface correspond to aqueous phase.



**Figure S2:** Number of Hydrogen bonds per water molecule as a function of *distance* from Gibbs Dividing Surface for Acidic systems in absence of REE Ions with (a) HA molecules at the interface and (b) HA molecules and A<sup>-</sup> ions at the interface. Positive distances with respect to the Gibbs dividing surface correspond to aqueous phase.

**3.** Radial distribution function between the donor oxygen of D2EHPA anion at the interface with water molecules and hydronium ions



**Figure S3:** Radial distribution function between the donor oxygen atoms of the D2EHPA anion (A<sup>-</sup>) with (a) oxygen atom of the water molecules and (b) oxygen atom of the hydronium ions.



4. Orientation of the water dipole moment with respect to the interface normal in various systems

**Figure S4:** Distribution of water dipole near the interface for pure heptane – water system (N1) and heptane – water system with 0.5M HA molecules in the organic phase (N2). The legend indicates the distance from the Gibbs Dividing Surface. Positive distances correspond to aqueous phase.



**Figure S5:** Distribution of water dipole near the interface for Acidic systems without Nd and Dy ions. The legend indicates the distance from the Gibbs Dividing Surface. Positive distances correspond to aqueous phase.



**Figure S6:** Distribution of water dipole near the interface for Nd and Dy Systems with neutral HA molecules in the organic phase at various acidities. The legend indicates the distance from the Gibbs Dividing Surface. Positive distances correspond to aqueous phase.

## **5.** Radial Distribution Functions between extractant molecules adsorbed at the liquid-liquid interface



**Figure S7:** P-P radial distribution function of HA molecules at various acidities in (a) systems with no REE ions in the aqueous phase, (b) systems with Nd ions and all the extractant molecules in their neutral (HA) form, (c) systems with Dy ions and all the extractant molecules in their neutral (HA) form, (d) systems with no REE ions and 50% extractant molecules in their deprotonated (A<sup>-</sup>) form, (e) systems with Nd ions and 50% extractant molecules in their deprotonated (A<sup>-</sup>) form and (f) systems with Dy ions and 50% extractant molecules in their deprotonated (A<sup>-</sup>) form.



**Figure S8:** P-P radial distribution function between HA molecules and A<sup>-</sup> ions at various acidities in (a) systems with no REE ions and 50% extractant molecules in their deprotonated (A<sup>-</sup>) form, (b) systems with Nd ions and 50% extractant molecules in their deprotonated (A<sup>-</sup>) form , (c) systems with Dy ions and 50% extractant molecules in their deprotonated (A<sup>-</sup>) form.



**Figure S9:** P-P radial distribution function between  $A^-$  ions at various acidities in (a) systems with no REE ions, (b) systems with Nd ions and (c) systems with Dy ions.

### 6. Spatial Distribution of Hydronium and Chloride ions



**Figure S10** Distribution of hydronium and chloride ions as a function of distance from Gibbs Dividing Surface for (a,b) Nd and (c,d) Dy systems, respectively.

7. Radial distribution functions between the rare earth ions and various donor atoms



**Figure S11:** Radial Distribution functions and corresponding Coordination numbers of (a) chloride ion with unbound Nd ions, (b) oxygen of water with bound Nd ions, (c) oxygen of water with unbound Nd ions, (d) double bonded oxygen of deprotonated D2EHPA with bound Nd ion and (e) deprotonated oxygen of deprotonated D2EHPA with bound Nd ion in Nd containing systems.



**Figure S12:** Radial Distribution functions and corresponding Coordination numbers of (a) chloride ion with unbound Dy ions, (b) oxygen of water with bound Dy ions, (c) oxygen of water with unbound Dy ions, (d) double bonded oxygen of deprotonated D2EHPA with bound Dy ion and (e) deprotonated oxygen of deprotonated D2EHPA with bound Dy Ion in Dy containing systems. In panel (a), no chloride ions were present within a distance of 3.5A at 1M acidity (i.e., DH1 system). Hence curves for DH2 and DH3 systems are alone plotted.

### 8. Percentages of various complexes formed at the interface by the rare earth ions with the extractant and water molecules.

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S No.	#HA	#A-	#H <sub>2</sub> O	NH1	NH2	NH3	DH1	DH2	DH3
1	0	2	9	0.03	0	0	0	0.02	0
2	0	1	9	0.13	0.06	0.10	0.06	0	0
3	1	2	8	0.01	0.02	0	0	0	0
4	0	1	8	15.15	18.33	99.20	31.67	8.20	29.85
5	0	2	8	2.46	0.26	0.20	2.97	1.10	1.05
6	1	1	8	0.24	0.16	0	0.09	0.02	0.15
7	0	3	7	1.24	1.98	0	0.34	0.32	0
8	1	2	7	0.10	0.24	0	0.14	0.26	0
9	0	2	7	77.48	76.32	0	8.61	24.54	1.79
10	1	1	7	0.84	0	0	0.51	0.54	0.95

**Table S4** Percentages of different complexes formed at the interface by Nd and Dy ions at various acidities.

11	0	1	7	0.09	0.10	0.50	15.07	8.06	15.50
12	1	3	6	0	0	0	0.01	0.64	0.45
13	2	2	6	0.06	0	0	0	0	0
14	0	3	6	0.03	0.02	0	0.64	1.62	0.11
15	1	2	6	0.21	0.08	0	0.60	4.08	0.90
16	0	2	6	1.93	2.44	0	10.94	43.94	32.15
17	1	2	5	0	0	0	6.50	4.26	0
18	0	2	5	0	0	0	0	2.40	0
19	0	3	5	0	0	0	5.97	0	0
20	1	3	5	0	0	0	0.70	0	0
21	0	3	4	0	0	0	7.47	0	0
22	1	3	4	0	0	0	0.53	0	0
23	1	2	4	0	0	0	7.13	0	0
24	2	2	4	0	0	0	0.03	0	0



9. Sequence of events in the transport of an interfacial complex into the bulk organic phase



**Figure S13:** Sequence of events in the transport of a Dy complex from the interface into the bulk organic phase. The interfacial complex contained 3 D2EHPA anions bound to the Dy cation. These anions are represented by cyan sticks. The Dy cation is shown as a green sphere. The 3 D2EHPA molecules that eventually became a part of the extracted complex are shown as orange, green and blue sticks.

#### References

1. Mitrinović, D.M., Tikhonov, A.M., Li, M., Huang, Z. and Schlossman, M.L., 2000. Noncapillary-wave structure at the water-alkane interface. Physical review letters, 85(3), p.582.