Lanthanide Binding Tag Peptides for the Foam Fractionation of Rare Earth Elements

Luis Ortuno-Macias[(a)], Stephen Crane[(b)], Jason Marmorstein[(c)], James Petersson[(c)], Kathleen Stebe[(b)], Raymond Tu[(a)], Charles Maldarelli[(a)].

(a) Department of Chemical Engineering, The City College of New York, New York, United States.
(b) Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Pennsylvania, United States.
(c) Department of Chemistry, University of Pennsylvania, Pennsylvania, United States.

Solvent extraction is widely used for separation of rare earth elements trivalent cations (REEs or Ln^{3+}) from an aqueous phase into an organic solvent. This process is energy intensive and environmentally unfriendly, requiring large volume of organic solvent and organo-phosphate surfactants. Here, we exploit the high affinity of a surface-active Lanthanide Binding Tag (LBT) peptide (LBT1, YIDTNNDGWYEGDELLA), that coordinates selectively with Ln^{3+} ions for its use in bioinspired/eco-friendly extraction processes in which the complexed LBT-Ln^{3+} peptide adsorbs to the air/aqueous interfaces of bubbles for foam recovery. To understand the surface activity and identify the bound cationic species at the air-water interface, we characterized the surface molecular adsorption and arrangement of LBT1, the more surface active LBT1-LLA (YIDTNNDGWYEGDELLALLA), and the less negatively charged LBT1-3 (YIDTNNDGWYEGNELLA). Furthermore, we exploit the high affinity of glutaraldehyde with proteins and peptide to promote the extraction of REEs and to control the foam stabilization of Lanthanide-bound peptides.

X-ray reflectivity (XRR) and x-ray fluorescence near total reflection (XFNTR) measurements on the adsorbed layer were used to compute the surface concentration of the peptide and the Ln^{3+} cation, and electron density profile (EDP) of the interfacial layers. The addition of three hydrophobic residues to LBT1 increased the adsorption of Tb^{3+} ions to the air-aqueous interface up to approximately 30%. We demonstrated that this cation adsorption enhancement was also promoted by electrostatic interactions between the charged LBT1LLA-Tb^{3+} complexes and free trivalent ions in solution. Moreover, we showed that bridging of complexes via O-Tb-O association can be eradicated by substituting negatively charged groups that do not participate in the selective coordination with neutral amino acids. The ability to tune the amino acid sequence of these surface-active molecules to either improve their adsorption and/or selectivity with REEs could be advantageous for a green, eco-friendly, selective separation method of REEs. Moreover, the foam stabilization and REEs extraction enhancement by the LBT peptides presented in this work provide an approach to use peptide-glutaraldehyde conjugates for the recovery of rare earth elements.