The Organization of Complex Anions at Aqueous Interfaces: Sum Frequency Generation Spectroscopy and Synchrotron X-ray Scattering Studies

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ABSTRACT

Highly selective and efficient techniques are required for the separation of chemically similar rare earth elements (REEs) to fulfill their increasing demand for technological applications. Liquid-liquid extraction (LLE) is a relatively less energy-intensive technique, widely used in industry for the separation of lanthanides and actinides. The interface between the two immiscible liquids plays a vital role during the process where the formation of metal-ligand complexes and the subsequent transfer of metal from the aqueous to organic phase takes place. The nature of the extractant and counterion present in the subphase including the interactions between them has a significant impact on the extraction process. However, the molecular scale detail of the mechanism is little-known. Here, we combine vibrational sum frequency generation (VSFG) spectroscopy and surface-sensitive synchrotron X-ray measurements to investigate the fundamental chemical and physical processes at the aqueous interface. We study the effect of the background ions such as nitrate (NO\textsubscript{3}\textsuperscript{-}), thiocyanate (SCN\textsuperscript{-}), and selenocyanate (SeCN\textsuperscript{-}) in the presence of the extractant monolayer to better understand the ion-specific effects. A comparison to X-ray fluorescence experiments of Se K-edge and VSFG studies of -OH stretch shows that SeCN\textsuperscript{-} interfacial coverage saturates at very low bulk concentrations, but their orientational organization and effects on the hydrogen bonding network of the interfacial water continue with the increasing bulk SeCN\textsuperscript{-} concentration. These results show that the increasing chemical potential may lead to further reorganization of the adsorbed ions even though the interfacial ion population does not change. The reorganization of the interfacial ions and the water are very important in chemical separations of heavy metals, where metal-anion complexes drive the selective ion transfer.