Interrogating the role of water in metal ion extraction into room temperature ionic liquids

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The fission product ⁹⁰Sr has a number of important practical applications, however, its release to the environment poses substantial risks to human health. Accordingly, there has long been interest in methods for its separation and preconcentration from biological and environmental samples for subsequent determination. Classical approaches to accomplish this involve complex and tedious sample treatment steps, resulting in low sample throughput. Although extraction chromatography has reduced the time and tedium associated with this separation, certain aspects of the method remain problematic. Ionic liquids (ILs) have shown promise as the basis of new systems for the separation and preconcentration of ⁹⁰Sr, displaying unique selectivity for strontium over other metal ions inherent to biological samples. The mechanisms by which metal ions partition between an aqueous and IL phase are more complex than those observed in molecular solvents, however, and the equilibria remain incompletely understood. This can render an IL-based separation difficult to control. In an effort to better define the equilibrium processes involved in Sr(II) extraction by a crown ether (e.g., dicyclohexano-18-crown-6; DCH18C6) into hydrophobic ILs, we have been evaluating a three-pathway model that is dependent on, among other factors, the aqueous acidity. In a recent study, we observed a linear correlation between the extent of extraction of Sr(II) and the equilibrium concentration of water in the ionic liquid phase. Under the conditions of extraction, metal ion transfer is thought to be limited to two of the three pathways, through which the hydration of co-extracted nitrate ions and the exchange via a hydronium ion-DCH18C6 complex would predominate. Our goal has been to verify and quantify these mechanisms. To this end, two hydrophobic imidazolium-based ILs, one of them containing an alcohol functionality to encourage water dissolution, have been synthesized as their bis[(trifluoro- methyl)sulfonyl]imide salts. Vibrational and NMR spectroscopy have been employed to interrogate the states of water in these ILs and to explore the competition between acid, water, and metal ions for DCH18C6 dissolved in them. By quantifying the partitioning of various species in the titration of acid and metal ion, it is expected that a more complete, thermodynamics-based understanding of these systems will emerge.