

Molecular Recognition through Ionic Liquids

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The discovery of crown ethers has led to a new class of ligands for alkaline and alkaline earth metal cations.¹ Crown ethers and related macrocycles have found wide application in the design of novel solvent extraction systems that are *selective* for fission products, such as Cs⁺ and Sr²⁺, based on the sizes of the crown-ether rings.² For example, a separation factor of 10⁶ for Sr²⁺ has been achieved using crown ethers, when extracted from a solution of strontium and actinide nitrates. These systems utilize organic phases containing crown ethers to extract target metal ions from aqueous solutions through the complexation of the targeted radionuclides and the specific crown ethers. The distribution ratios (D_M) for the extraction process depend on two major factors: (a) the thermodynamic driving force for cation complexation by a crown ether and (b) the solvation of the cation and counter anion by the organic solvent.^{1, 3} The former factor is usually thermodynamically favored. For example, the stability constant (K) of Li⁺ with 15-crown-5 is more than 10⁴. Difficulties in increasing the solvent extraction efficiency of conventional solvent extraction systems using crown ethers as extractants lie in the unfavorable transport of the cation and counter anions from aqueous phases to organic phases. Limited solubilities of ionic species in non-ionic organic solvents are the main problem associated with conventional solvent extractions. The inability of organic solvents to solubilize ionic crown-ether complexes and their counter anions is one of the main obstacles in improving the separation efficiency of fission products based on conventional solvent extractions. Because the solvation of ion-pair species is more favorable than the solvation of individual ions in organic solvents, the crown-ether complexes and counter anions are compelled to form ion pairs, despite the entropic cost. Fundamentally, conventional organic solvent extractions using crown ethers involve the transport of ion pairs from the aqueous phase to the organic phase. Although the formation of ion pairs helps to reduce the total thermodynamic cost of transporting ionic species into the organic phase, the free-energy gain in this process is *not* enough to make up its loss in solubilizing individual ions in the organic phase. Accordingly, this leads generally to a very small distribution ratio for the total extraction process. For example, the distribution ratio for the extraction of strontium nitrate into non-polar organic phases from aqueous solutions by crown ethers is generally less than one, even though the thermodynamic driving force for the complexation of Sr²⁺ with a number of crown ethers is very favorable. This distribution ratio is low because the solvation free energies for simple inorganic anions such as nitrate by organic solvents are *extremely* unfavorable, thermodynamically. A number of strategies have been proposed to address this problem, including the addition of hydrophobic anions to the aqueous solution or the addition of hydrophilic solvents to the organic phase. For example, McDowell *et al.*³ made use of lipophilic carboxylic acids to enhance the distribution ratio of Sr²⁺. The solvation of the carboxylic anion in organic phases is more favorable than those of simple inorganic anions. The obvious drawback to these approaches is that more

chemicals would have to be added to the system thereby increasing both toxicity and the complexity of the original aqueous solution. Another drawback to this approach is the loss of some selectivity due to the non-selectivity of the ion-exchange capability of the ion-exchanger (carboxylate anion).

These key deficiencies associated with current extraction processes based on crown ethers prompted us to search for alternative extraction media that could convert the solvation of ionic species into a *more favorable* thermodynamically process. Here, we summarized our recent work on the use of *room-temperature ionic liquids* (also called as room-temperature molten salts or melts) containing macrocyclic ligands as extraction solvents to selectively remove the fission products strontium-90 (Sr²⁺) and cesium-137 (Cs⁺).⁴ Ionic systems consisting of salts that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species.⁵ These ionic liquids are attracting increased attention world-wide because they promise significant environmental benefits. Unlike the conventional solvents currently in use, they are nonvolatile and therefore do not emit noxious vapors, which can contribute to air pollution and health problems for process workers. The very unusual intrinsic property of these melts is that they consist *only of ions* and that they can be made *hydrophobic* ! The novel dual properties of these new ionic liquids make them efficient solvents for the extraction of *ionic species* from aqueous solutions. From a thermodynamic perspective, the solvation of ionic specie, such as crown-ether complexes, in the ionic liquids, should be much more favored thermodynamically than those of conventional solvent extractions. This is one of the key advantages of using ionic liquids in separations involving ionic species. In this case, cationic crown-ether complexes and their counter anions are *not* expected to form ion pairs, but to be solvated separately by ionic species from the ionic liquids. Therefore, the extraction process using crown ethers in ionic liquids may *not* be an ion-pair extraction process.

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