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**SEPARATION OF FISSION PRODUCTS BASED ON IONIC LIQUIDS:
ANION EFFECT**

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INTRODUCTION

The applications of ionic liquids (ILs) as new separation media have been actively investigated recently.¹⁻¹³ The most commonly studied class of ILs for such applications is based on dialkyl imidazolium cations. In comparison with conventional molecular solvents, ILs exhibit enhanced distribution coefficients (D_M 's) for a number of complexing neutral ligands in extraction of metal ions from aqueous solutions.^{5,6,8,12} Such enhancements were initially attributed to two major fundamental factors: (1) ion-recognition capabilities of complexing ligands and (2) unique ionic solvation environments provided by ILs for ionic species.⁵

The effect of the alkyl chain length of imidazolium cations on the distribution coefficients of solvent extraction using crown ethers was the subject of a number of investigations.^{5,7,8} The distribution coefficients have been found to decrease with the alkyl chain length of the IL cations. This observation led Dietz *et al.*⁸ and Visser *et al.*⁶ to propose that the extraction process also involves the exchange of the IL cations with metal ions. The longer the alkyl chain lengths of the IL cations are, the more hydrophobic are the IL cations and more difficult to be transported into aqueous phases *via* ion exchange. Accordingly, the ion-exchange process is another unique property of IL-based extractions involving charged species. Here, we report the investigation about the effect of the variation of IL anions on the solvent extraction of metal ions using

crown ethers as extractants. The elucidation of different solvation effects involved in ionic liquids could lead to optimized separation media for these novel solvents.

RESULTS AND DISCUSSION

The cations of the ILs (see below) used in this work were 1-R-3-methylimidazolium ($C_n\text{mim}^+$), where R = C_2 (ethyl) or C_4 (butyl). The anions are hexafluorophosphate (PF_6^-), bis[(trifluoromethyl)sulfonyl]imide (Tf_2N^-) and bis(perfluoroethanesulfonyl)imide (BETI^-). The connolly solvent-excluded volumes of PF_6^- , Tf_2N^- and BETI^- are 133.4 \AA^3 , 136.6 \AA^3 and 187.9 \AA^3 , respectively. These ionic liquids were synthesized *via* metathesis reactions as described in the literature and *are known to be immiscible in water*.^{14,15} The order of hydrophobicity is $\text{BETI}^- > \text{Tf}_2\text{N}^- > \text{PF}_6^-$. The metal compounds used in this work were strontium chloride and cesium chloride, because both ^{90}Sr and ^{137}Cs are fission products and development of efficient extraction methodologies for their removal from radioactive waste sites is a very important waste minimization issue. The crown ether chosen was dicyclohexyl-18-crown-6 (DCH18C6), which is known to form a strong complex with Sr^{2+} .¹⁶

The extraction results indicated that the distribution coefficients for both Sr^{2+} and Cs^+ increase with the hydrophobicity of the IL anions for the same IL cations. A very large change of over 2 orders of magnitude in the D_{Sr} value can be induced by changing the anions of IL from PF_6^- to BETI^- . The increase of D_{Sr} with the hydrophobicity of the counter anions is in sharp contrast to the observation with the cation effect of ILs. In the latter case, D_{Sr} decreases with the hydrophobicity of the IL cations.

One of the drawbacks associated with solvent extraction based on ionic liquids is the loss of ILs induced by the direct equilibrium partition of ILs into aqueous phases and the ion-exchange process. The former is a dominant factor for the loss of ILs. The loss of ILs as function of the IL anions was investigated by determining the concentration of the leached IL cations in aqueous solution *via* UV spectroscopy.¹⁷ The loss of the ILs was found to be strongly correlated to the conjugate anions. The more hydrophobic the anions are, the less are the losses of the ILs. The loss of $C_4\text{min-BETI}$ is about 25 fold less than that of $C_4\text{min-PF}_6$. Accordingly, the more hydrophobic anions give rise to not only greater distribution coefficients but also the less losses of ILs.

CONCLUSION

In conclusion, the investigation of the effect of the IL anions on the solvent extraction of Sr^{2+} using DCH18C6 revealed that the large and hydrophobic anions favor the extraction. Accordingly, the highest extraction efficiency was observed with the ILs with BETI^- as counter anions. Another key advantage of using hydrophobic anions in such solvent extractions is the less loss of the corresponding ILs.

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