

Application of the Tri-1-butylmethylammonium Bis((trifluoromethyl)sulfonyl)imide Ionic Liquid to the Removal of Cs⁺ and Sr²⁺ from Nuclear Waste

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Ions of the long-lived radioactive nuclides, ¹³⁷Cs and ⁹⁰Sr are among the many radioactive species found in the aqueous tank waste resulting from the reprocessing of nuclear fuel. Considerable research has been devoted world-wide to the discovery of efficient methods for the extraction and concentration of these ions. Studies carried out at ORNL have determined that hydrophobic ionic liquids, such as those based on dialkylimidazolium cations and hexafluorophosphate (PF₆⁻) or bis((trifluoromethyl)sulfonyl)imide (Tf₂N⁻) anions containing the macrocyclic ligands calix[4]arene bis(*tert*-octylbenzocrown-6) (BOBcalixC6)¹ and dicyclohexano-18-crown-6² are efficient, selective solvents for the extraction of Cs⁺ and Sr²⁺, respectively, from simulated tank waste.^{3,4} However, one problem that must be addressed before these ionic solvents can be used to treat tank waste is the identification of a method for recycling the extraction solvent wherein the Cs⁺ and Sr²⁺ are removed without damage to the ionic liquid or macrocyclic ligands.

The electrodeposition of Cs⁺ and Sr²⁺ at mercury electrodes may be a direct and useful technique for this purpose. However, it is not possible to reduce these ions within the electrochemical window of the imidazolium-based ionic liquids such as BuMeIm⁺Tf₂N⁻ after they have been coordinated by the ionophores described above. Therefore, a relatively new ionic solvent, tri-1-butylmethylammonium bis((trifluoromethyl)sulfonyl)imide or Bu₃MeN⁺Tf₂N⁻,⁵ which has a more negative cathodic potential limit than the imidazolium-based systems, was investigated. The cathodic electrochemical window of this ionic liquid is compared to that for BuMeIm⁺Tf₂N⁻ in Fig. 1. Figure 2 shows that it is possible to reduce coordinated Cs⁺ and Sr²⁺ ions at a mercury film electrode without electrolyzing the ionic liquid or macrocyclic ligands.

In addition, studies in our laboratory show that Bu₃MeN⁺Tf₂N⁻ possess greater hydrophobicity than BuMeIm⁺Tf₂N⁻. This is an important factor because trace water in the ionic liquid will interfere with the electrodeposition of Cs and Sr at Hg. Although recent research⁶ suggests that the extraction of Sr²⁺ with hydrophobic ionic liquid solvents does not involve transfer of the counter ions as is found in conventional organic solvents, we find that trace water in the ionic liquid can facilitate the transfer of small amounts of undesirable counter ions such as NO₃⁻ that can complicate the reduction of the coordinated Sr²⁺. This is illustrated in Fig. 3 where the electrochemical reduction of coordinated Sr²⁺ is improved after the addition of a Cl⁻ ion exchange resin to the aqueous phase before extraction. Similar investigations are in progress with Cs⁺.

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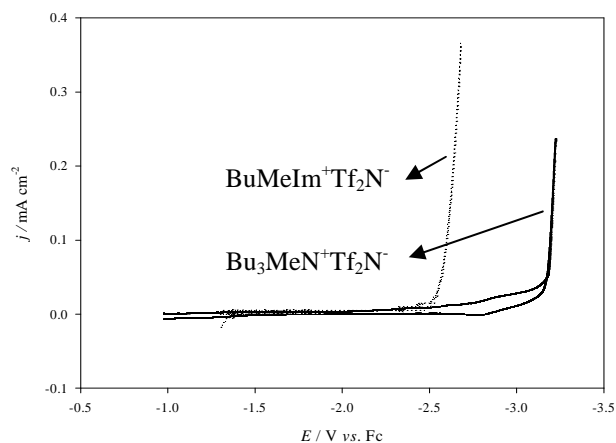


Figure 1. Voltammograms recorded at a Hg film electrode.

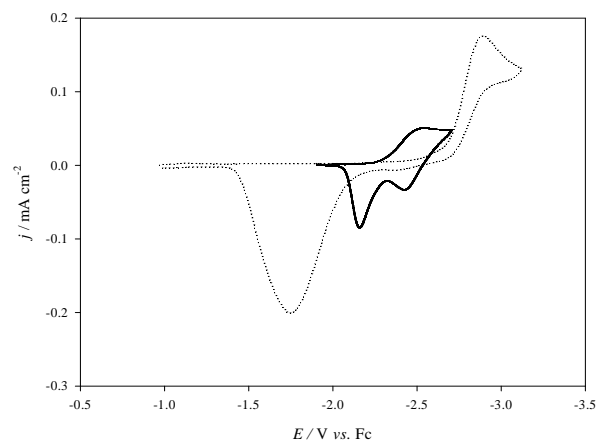


Figure 2. Voltammograms of Cs⁺ coordinated by BOBcalixC6 (—) and Sr²⁺ coordinated by dicyclohexano-18-crown-6 (---) at a Hg film electrode.

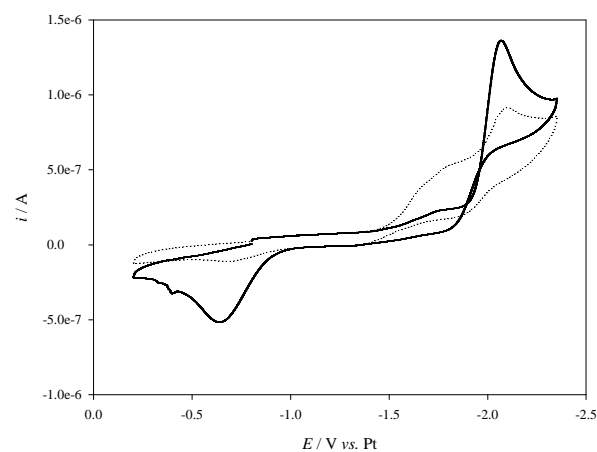


Figure 3. Voltammograms of Sr²⁺ extracted from an aqueous solution containing Sr(NO₃)₂ before (---) and after (—) the addition of a Cl⁻ ion exchange resin to the aqueous phase.