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Project Title: **Synthesis and Characterization of Templated Ion Exchange Resins for the Selective Complexation of Actinide Ions**

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Progress Report

RESEARCH OBJECTIVE

The purpose of this research is to develop polymeric extractants for the selective complexation of uranyl ions (and subsequently other actinyl and actinide ions) from aqueous solutions. Selectivity for a specific actinide ion will be obtained by providing the polymers with cavities lined with complexing ligands so arranged as to match the charge, coordination number, coordination geometry, and size of the actinide ion. These cavity-containing polymers will be produced by using a specific actinide ion (or surrogate) as a template around which monomeric complexing ligands will be polymerized. The polymers will provide useful sequestering agents for removing actinide ions from wastes and will form the basis for a variety of analytical techniques for actinide determination.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes progress from month ten to month nineteen of a three-year project. During this period polymeric reagents have been synthesized and tested to refine the formula of a uranium sequestering polymer. It has been determined that a sharp increase in selectivity occurs while the amount of crosslinking is being increased over a narrow range. This abruptness of the change in selectivity is much greater than the change observed in previous work on Pb(II) selective polymers. This may be due to the more complex geometry of uranyl ion as compared to other soluble metal ion species.

The formula used to make uranyl ion selective electrodes has been modified to extend the operational lifetime from weeks to months. The variables in the optimization of the electrode performance include: 1) adjusting polymer formulations, 2) varying the plasticizers and their relative amounts in the formulations, and 3) changing membrane compositions. The copolymers made with vinyl salcylaldoxime exhibit better selectivity than those prepared with vinyl benzoic acid. The calibration plots show that the response of the vinyl sacylaldoxime membranes to high levels of interfering ions is less than the response to uranyl ion at the detection limit. Attempts to make a composite membrane for the electrode has met limited success. The response of the composite membrane gave a lesser calibration slope and was erratic. The problems with the composite membrane stem from too great a thickness for conductivity. This is a fabrication issue that we will address in the coming year.

The molecular imprinting process has been applied to the production of membranes for the selective permeation of uranyl ion. While working on a composite ion selective electrode membrane, it was determined that a robust membrane could be fabricated but the thickness precluded its use in an electrode. The membranes swelled in aqueous solution and seemed to have a good loading capacity. The commonly used porogens were rejected as being too small to form channels to span the membrane. Thus a linear polymeric porogen was used that was removed during the final phase of membrane preparation. This polymer has polar functional groups that may be interacting with the polymerizable metal ion complexes to impart regularity to their dispersion in the film. The resultant polymer membranes appear to allow selective permeation of uranyl ion in the presence of several interferences. These findings will require further experiments to verify the preliminary results and to determine the selectivity and kinetics of membrane transfer.

Ionic templating was also an approach of choice in preparing a luminescent sensor for determination of uranyl in aqueous solutions. It was reconfirmed that 2,6-pyridinedicarboxylic acid (DPA) forms complexes with uranyl that are strongly luminescent. The luminescence of these complexes is significantly stronger than that of the ones formed with alternative ligands, such as benzoate and salicylaldoxime, and therefore provides for a better luminescence-based sensor. A chemical modification of the ligand is necessary, however, to provide it with polymerizability. Thus, a diamide derivative of DPA was synthesized, using 2,6-pyridinedicarbonyl dichloride and methacrylamide, which preserves the essential configuration of the chelating moiety and adds two vinyl-terminated polymerizable side chains. The uranyl complex with the modified ligand exhibited luminescent properties similar to those of DPA uranyl chelates. Unfortunately, low solubility of the complex in the regularly employed matrix monomers limits its usefulness in the styrene-based polymer systems, and currently new host polymers are being investigated along with other means of enhancing the solubility of the polymerizable complex.

PLANNED ACTIVITIES

The uranyl ion sequestering agent will be optimized and tested against a broader range of interferences. Levels of crosslinking will be carefully evaluated in order to better understand the abrupt changes in selectivity. The ion selective electrode work will continue with the goal of fabricating membranes without using a PVC matrix. Plasticizer and ionophore will be added directly to the mixture of metal-ligand complex and spincoated after the polymerization has been initiated in order to achieve appropriate thicknesses. The selective ion permeating membrane will also be fabricated by the spin coating method to effect a higher uranyl throughput. The luminescent uranyl compounds will be used to construct optical sensors.

INFORMATION ACCESS

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3. Kimaro, A. and Murray, G. M. “Synthesis and Characterization of Templated Ion Exchange Resins for the Selective Complexation of Actinide Ions,” Abstract No. 2315P, Pittsburgh Conference, March 7-12, 1998, Orlando, Florida.