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Synthesis and Characterization of Templated Ion Exchange Resins for the Selective Complexation of Actinide Ions

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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 (lakes, streams, waste tanks and body fluids). Selectivity for a specific actinide ion is obtained by providing polymers with cavities lined with complexing ligands so arranged as to match the charge, coordination number, coordination geometry, and size of the actinide metal ion. These cavity-containing polymers will be produced 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 determinations.

Research Progress and Implications

This report summarizes the first nine months of a three year project. During this period polymers have been synthesized using each of the three coordinating ligand monomers: vinyl benzoic acid, vinyl salcylaldehyde and vinyl salcylaldoxime. Uranyl compounds for each of these ligands were synthesized in the mole ratio of one uranyl to two moles ligand and the stoichiometry verified by elemental analysis. Copolymers were synthesized in sets of analogous composition to ascertain optimal uranyl binding ability. For example, nickel vinylbenzoate salt, uranyl vinylbenzoate salt and a vinylbenzoic acid blank were reacted with varying amounts of divinyl benzene (DVB), azobisisobutyronitrile (AIBN), pyridine (solvent), and styrene. The salt and blank concentrations remained constant at 5 weight percent while DVB concentrations varied by 2-4 percent of total reactant weight with AIBN remaining constantly at 1 weight percent. Polymerization was performed in scintillation vials by two different methods. Half of the reactions were performed at 60ºC for 024 hours under an N_2 atmosphere in a mineral oil bath, while the remaining half were performed under similar conditions except an ultrasonic bath was substituted for the mineral bath. The resulting polymers ranged from bubbly yellow-brown (uranyl salts) solids to bubbly dark green (nickel salts) solids.

The copolymers made with vinyl benzoic acid and vinyl salcylaldoxime have been examined using uranyl ion luminescence spectroscopy and compared to the luminescence spectra of the isolated analogous compounds. For example, the compounds of uranyl benzoate (UO_2 benzoate2), uranyl vinylbenzoate and the uranyl vinylbenzoate copolymer were investigated by low temperature (77 K) luminescence spectroscopy. The appearance of the spectra show that the structural integrity of the complex is not compromised by the copolymerization process.

The resins were ground into a powder with a cryogenic ball mill and a fraction of uniform size was obtained using sieves. The ground resins were swollen, washed with acetone to remove unreacted monomer and eluted with acid to remove accessible metal ions. After drying, weighed quantities of resin were tested for their exchange capacity by batch loading and extraction. Uranyl ion and competing metal ions were measured using Inductively Coupled Plasma Atomic Emission spectroscopy (ICP-AES) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Preliminary data suggested that for 5 weight percent benzoate complex, 4 weight percent crosslinking and sonication produced the highest capacity polymer. Sonication seems to have a greater positive effect on the polymers made with vinyl salcylaldoxime than those using vinyl benzoic acid. A quantity of the above polymer composition has been applied to sequestration and preconcentration of uranyl from a complex matrix (seawater). The experiment was performed to see if the resin was capable of removing and preconcentrating small amounts of uranium in a mixture of a wide variety of other metals ions prior to their determination by UV-VIS spectrophotometry. The combination of resin extraction and UV-VIS spectrometry yields a simple and inexpensive yet sensitive method for the analysis of uranium in complex matrices. The accuracy and precision of the method were verified by the analysis of a NIST standard sample, NIST 610 trace elements in glass. The photometric analysis employed dibenzoyl methane and gave a linear dynamic range from 500 parts per trillion (ppt) to 1 part per million (ppm) with a limit of detection of 160 ppt. The results of this study will be submitted as an invited paper for a special edition of the Journal Analytica Chimica Acta.

After analyzing the sorbant properties, the polymers were used to fabricate ion selective electrodes. Ground polymer of an appropriate size, 60 mesh, was cast in a polyvinylchloride (PVC) membrane. The membrane was adhesively bonded to a PVC support tube and assembled into a standard polymer membrane electrode. The selectivity and stability of the templated polymer give this electrode advantages over traditional ion selective electrodes. An extensively used electrode does not display a loss of function resulting from solubility of the active ingredient. The templated polymer has greater selectivity for the target ion than does either the monomeric ionophore or the untemplated polymer. The selectivity of the uranyl ion electrode is very high with selectivity coefficients log KU,M around 5 for the interferents tested. A variety of membrane and solution compositions were examined to obtain optimal performance.

Planned Activities

The characterization and optimization of the uranyl polymers will continue. This Summer we are planning a first visit to the Transuranium Laboratory of the Oak Ridge National Laboratory in order to test the polymers with actinide ions other than uranyl. This is expected to occur annually for all three years of the project as more sophisticated resins are developed. The ion selective electrode data will be collected for publication in about six months. The data from the tests with other actinide ions will be used in the next two years to develop both a actinyl complexing resin and resins for individual actinyl and other actinide ions.

Other Access To Information

http://www.rsc.org/is/journals/current/analcoms/anpc9708.htm.