ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

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FUNDAMENTAL CHEMISTRY OF THE UNIVERSAL EXTRACTANT (UNEX) FOR THE SIMULTANEOUS SEPARATION OF MAJOR RADIONUCLIDES (CESIUM, STRONTIUM, ACTINIDES AND LANTHANIDES) FROM RADIOACTIVE WASTES

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INTRODUCTION

Research conducted by the Idaho National Engineering and Environmental Laboratory and the Khlopin Radium Institute has led to the development of the Universal Extraction (UNEX) process[1,2]. The UNEX extraction process removes cesium, strontium and the actinides from acidic radioactive waste in a single process step. The UNEX process utilizes an organic phase solvent containing a dilute mixture of chlorinated cobalt dicarbollide (CCD), polyethylene glycol (with a nominal molecular weight of 400, (PEG-400) and diphenyl-*N*,*N*-di-*n*-butylcarbamoylmethylphosphine oxide (CMPO), all dissolved in trifluoromethylphenyl sulfone.

While the UNEX process has been demonstrated on a laboratory scale in counter-current flowsheet tests with both surrogate solutions and actual waste solutions, further development of the UNEX process is hampered by a lack of understanding of the details of the extraction mechanism. The process chemistry is unique, but complicated, since the extractants operate synergistically to extract the radionuclides. Results indicate that water dissolved in the organic phase dramatically impacts the process chemistry. The impact of dissolved water on an extraction system has been reported for other systems[3]. In order to investigate this phenomenon, we have varied the amount of water dissolved in the organic phase by using several different organic diluents.

MATERIALS AND METHODS

The concentration of water dissolved in different organic diluents was determined by coulometric Karl Fischer titration (Mettler-Toledo DL-39). All titrations were performed on a mass basis.

All cesium and strontium distribution coefficients were measured using ^{137}Cs and ^{85}Sr tracers (Isotope Products), respectively. Before performing the distribution measurement all organic solutions were pre-equilibrated by contacting three times with an appropriate acid solution. All distribution coefficient measurements were performed by contacting equal volumes of pre-equilibrated organic solutions with fresh aliquots of acidic solutions containing the appropriate radiotracers. The activity in each phase was determined by γ-spectrometry. In general, distribution coefficients were reproducible to within ±5%.

RESULTS AND DISCUSSION

Water contents were determined for the diluents alone and for solutions of CCD and PEG-400 dissolved in the diluents. In all cases the organic solutions were equilibrated with various concentrations of nitric acid. In general, the concentration of water present in the various organic solutions showed little dependence upon the aqueous nitric acid concentration. The equilibrium concentrations of water dissolved in the organic diluents with and without CCD/PEG-400 are presented in Figure 1. The addition of CCD and PEG-400 resulted in a significant increase in the equilibrium concentration of water dissolved in the organic solvents.

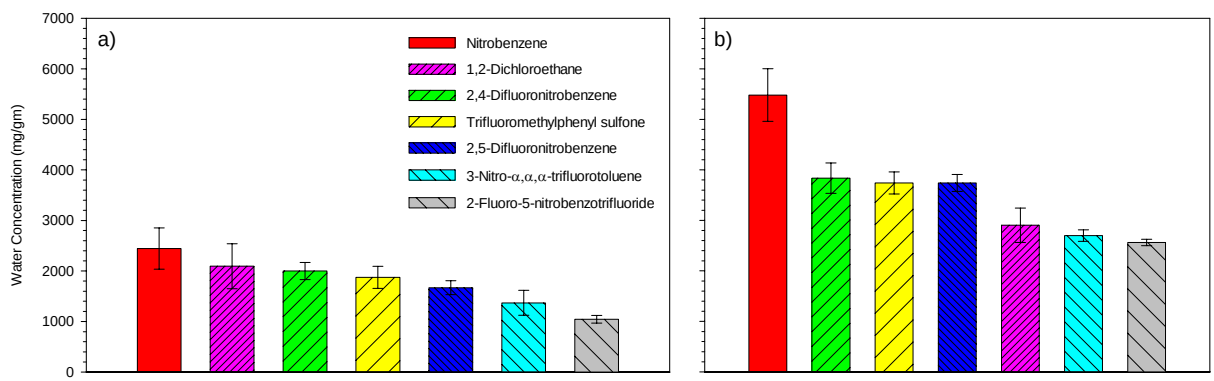

Figure 1. Concentration of water dissolved in (a) organic diluents without CCD/PEG-400 and (b) organic diluents containing 0.06 M CCD and 0.03 M PEG-400.

The ^{137}Cs and ^{85}Sr distribution coefficients were determined for solutions containing 0.06 M CCD and 0.03 M PEG-400 dissolved in the various organic diluents. The distribution coefficients from 0.5 M HNO_3 are plotted versus the concentration of dissolved water in Figure 2. No simple correlation between the magnitude of the ^{137}Cs and ^{85}Sr distribution coefficients and the concentration of dissolved water is observed. The lack of a simple correlation points to the fact that simple hydration effects alone

cannot explain the interaction of dissolved water and cationic species in the UNEX process. Other factors such as solvent polarity need to be considered and are currently being investigated.

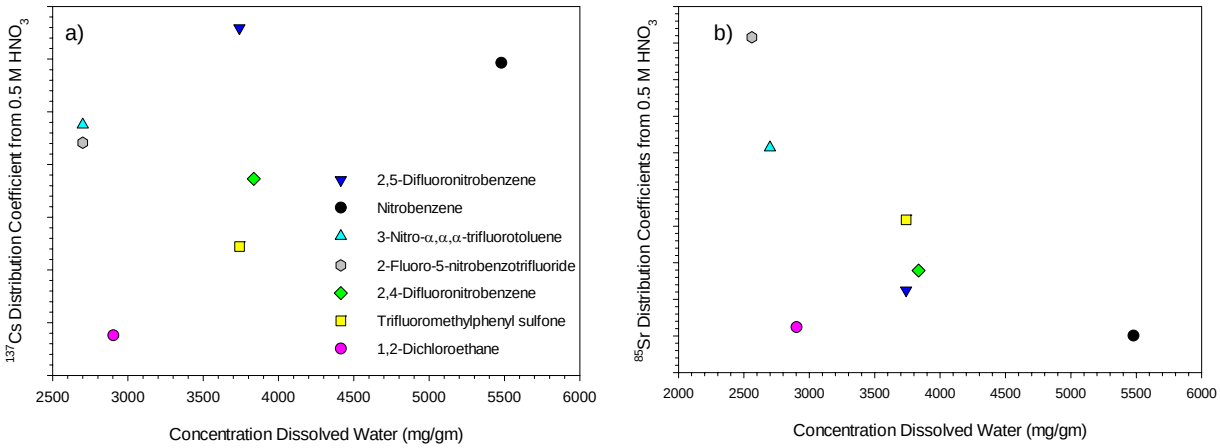

Figure 2. Cesium-137 (a) and strontium-85 (b) distribution coefficients for solutions containing 0.06 M CCD and 0.03 M PEG-400 dissolved in various organic solvents plotted versus concentration of dissolved water.

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