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

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AQUEOUS BIPHASIC SYSTEMS BASED ON SALTING-OUT POLYETHYLENE GLYCOL OR IONIC LIQUID SOLUTIONS: STRATEGIES FOR ACTINIDE OR FISSION PRODUCT SEPARATIONS

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INTRODUCTION

Traditionally, the application of separations' processes to the nuclear industry have focused on three primary areas: 1) the isolation of fissile materials for the fabrication of nuclear fuels, 2) the processing of spent nuclear fuel for the recovery of uranium and plutonium and 3) the clean-up of nuclear tank wastes. From an environmental standpoint, the clean-up of nuclear tank wastes is of paramount concern due to the threat to water supplies, soil and ultimately human health. The remediation of tank wastes is primarily focused on reducing the immense volume of liquid effluent that remains encased in above- and underground storage bins at most major U.S. national laboratory sites. While tanks contain supernatant (liquid), sludge and salt-cakes, the major thrust is to transform high-level liquid waste to low-level liquid waste *via* the removal of high-activity radionuclides, the majority of which are ^{137}Cs and ^{99}Tc, including small amounts of actinides. The bulk of these other elements, such as ^{90}Sr, ^{239}Pu and ^{235}U are found as precipitates in the sludge and salt-cake due to the highly alkaline nature of the tanks. By reducing the volume of high-level waste, the amount that must be stored in long-term repositories (due to long-lived radionuclides) is considerably reduced.[1]

The major hurdle in the clean-up of these tanks is the great diversity in their compositions. In an attempt to minimize tank waste corrosion, most legacy tanks (those involved with the weapons development programs) were made highly alkaline *via* the

addition of copious amounts of sodium hydroxide to neutralize the acid used in processing schemes such as PUREX. Thus, the challenge in remediation is developing separations' schemes that are effective under both caustic and highly radiolytic conditions. Many separations' processes, including those for processing and tank waste clean-up, involve contacting an organic phase, such as odorless kerosene or dodecane that contains an extractant molecule, with the aqueous processing of waste solutions.[2] The extractant (which prefers the organic phase) selectively removes the desired metal from the aqueous waste stream. Some extractants that have demonstrated or show potential use in such processes include tri-*n*-butyl phosphate (TBP) and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO).[3]

While diluents such as kerosene and dodecane are widely used and highly studied as organic phases for nuclear separations schemes, they, as well as many other industrial organic solvents, are falling into disregard due to issues of volatility, flash point, and flammability, as well as significant environmental impact. As a result, the Rogers' group at The University of Alabama has been investigating alternative "greener" solvent systems for use in nuclear-based separations' schemes. Our group has been focusing on the use of both polyethylene glycol (PEG) and Ionic Liquids (ILs) in separations of actinide and fission products using traditional biphasic extractions from acidic media, as well as more challenging extractions from tank waste conditions. Here, we will present results which illustrate the applicability of PEG and ILs as suitable media for biphasic extractions.

IONIC LIQUIDS

Ionic Liquids (ILs) have recently become highly studied solvents for use in a variety of scientific applications, including synthesis, catalysis, separations and biochemical transformations.[4] ILs are salts that are liquid at or near room temperature and are composed of organic cations and organic/inorganic anions. As a class, they offer many advantageous properties, particularly for separations, including low volatility, high thermal stability and tunable physical properties (*e.g.*, hydrophobicity) based upon suitable alterations to either the cationic or anionic component. Traditionally, separations' applications involving ILs have been limited to the hydrophobic type; these ILs typically have an expensive, perfluorinated anion that renders them, from an environmental standpoint, non-benign.[5]

It was recently shown that hydrophobic ILs are no longer the limiting factor in the formation of biphasic systems for separations' schemes. Aqueous solutions of hydrophilic ILs, such as 1-butyl-3-methylimidazolium chloride, can form biphasic systems with the addition of certain water-structuring salts, such as K_3PO_4. This IL/salt system has an IL-rich upper phase and K_3PO_4-rich lower phase, with phase divergence increasing with increasing inorganic salt concentration.[6] This phenomenon is also accessible with various other IL cations, including phosphonium, ammonium and pyridinium, but not limited to these.

The alkaline nature of the aqueous phase in these IL/salt systems has definite relation to the nature of tank waste supernatant. In fact, hydroxides, carbonates and some

sulfates have also shown the ability to salt-out ILs, all of which are components of actual tank waste. We have recently begun to apply this salting-out technology to the removal of certain fission products, in particular $^{99}TcO_4^-$, from simple kosmotropic salt solutions, with the goal of using more complex waste simulants. Figure 1 shows the partitioning of $^{99}TcO_4^-$ from increasing concentrations of aqueous K_3PO_4 solutions (represented by increasing tie line length, a term that relates upper and lower phase concentrations). Due to the relatively hydrophobic nature of the pertechnetate anion, it quantitatively partitions to the more hydrophobic IL-rich phase, with partitioning increasing with increasing K_3PO_4 concentration and without the need for an extractant.

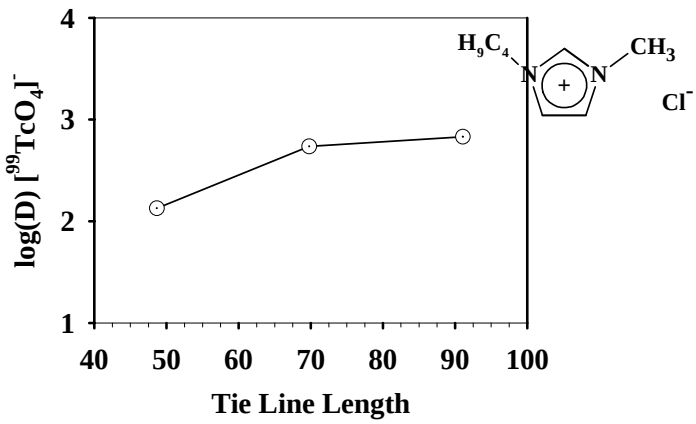

Figure 1. Partitioning data for $^{99}TcO_4^-$ from IL/K_3PO_4 biphasic systems.

The above proof of principle illustrates the applicability of hydrophilic ILs to the formation of biphasic systems for fission product separations. With further fine tuning, it should be possible to develop extractant-based partitioning as well as solid support-based partitioning using these biphases, with the goal of applying these principles to removing both actinides and fission products from waste simulants.

PEG

PEG-based aqueous biphasic systems (ABS) are constructed from the combination of water-soluble polymers, here polyethylene glycols, and certain water-structuring inorganic salts at specific concentrations. The nature of the biphase formation has been shown to be dependent upon the Gibb's free energy of hydration of the salt; as the free energy becomes more negative, the phase divergence increases. While the fundamentals of PEG-ABS are more well understood, it appears that similar principles may govern biphase formation in IL/salt systems. As two-phase systems, PEG-ABS are suitable for carrying out liquid/liquid separations and have, in fact, been studied for over 50 years for the gentle, nondenaturing separation of biomolecules and particulates. The two phases are aqueous in nature (the only solvent present, water, is over 80% on a molar basis) and can be fine tuned toward the separation of interest.[7]

The ABS systems represent a safe, environmentally benign extraction media for industrial and analytical separations and environmental applications. PEG-ABS can also be used with traditional solvent extraction equipment. The covalent attachment of PEG molecules to resin backbones (ABEC) has found use as effective solid-support extraction media for various applications.[8] These resins have been used for the removal of fission products (*e.g.*, $^{99}TcO_4^-$ and $^{129}I^-$) from solutions of high concentrations of sodium hydroxide, simulating radioactive tank wastes (Figure 2). The fission products can be removed without the need for pretreatment or the use of an extractant.

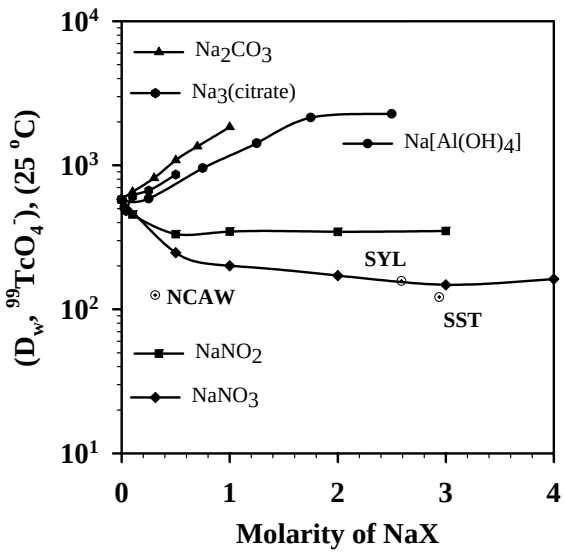

Figure 2. D_w for TcO_4^- with ABEC Resin XL72 vs. Molarity of [NaX] in 4 M NaOH.

The PEG-based systems have also demonstrated the ability to remove actinides from caustic solutions but with the aid of an extractant. For example, the distribution ratios (in 5 and 6 M NaOH) for ^{241}Am decrease with increasing concentration of the extractant Tiron over the range10^{-6}-10^{-3} M (distribution ratios are < 1 in most cases); high distribution ratios are observed for the extraction of ^{241}Am using the extractant, Pyrocatechol Violet (PCV), in 3 and 5 M NaOH, with little ligand dependency. Strong ligand dependency is observed at 1 M NaOH, with distribution ratios falling off sharply at greater that 10^{-4} M PCV.

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