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Can Kosmotropic Salt/Chaotropic Ionic Liquid (Salt/Salt Aqueous Biphasic Systems) be Used to Remove Pertechnetate From Complex Salt Waste?

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Abstract: Aqueous solutions of water-structuring, kosmotropic salts (e.g., salts of PO_4^{3-}, HPO_4^{2-}, CO_3^{2-}) will salt-out water-destructuring chaotropic ionic liquids (ILs) (e.g., 1-butyl-3-methylimidazolium chloride, ([C_4mim]Cl)) forming salt/salt aqueous biphasic systems (ABS). The chaotropic pertechnetate (TcO_4^-) anion will partition without the use of an extractant into the IL-rich phase. These complex salt/salt ABS are not unlike the complex and salt-rich Hanford tank waste, and thus have been used here as a simple model to show effectiveness in the partitioning of TcO_4^- from such tank waste into an IL-rich phase.

Keywords: Aqueous biphasic systems, ionic liquids, pertechnetate, kosmotropic, chaotropic

INTRODUCTION

Separation of certain radiological isotopes for repository storage has become more important with the future opening of Yucca Mountain (1). From spent fuel, the most important isotopes to separate are those with long half-lives, strong heat generation, and/or highly environmentally mobile isotopes. One

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such isotope of specific concern is ^{99}Tc, commonly found as $^{99}TcO_4^-$ in alkaline media. $^{99}TcO_4^-$ exhibits high environmental mobility and has a long biological half-life (2.111×10^5 years) that makes bioaccumulation a concern in case of an accidental release into the ecosphere (2, 3).

Previous work in our group studying the remediation of TcO_4^- from aqueous systems have centered on use of poly(ethylene glycol) (PEG)/kosmotropic salt aqueous biphasic systems (ABS) in both liquid/liquid (4) and solid/liquid modes (5). Kosmotropic ions (e.g., PO_4^{3-}, CO_3^{2-}, SO_4^{2-}, OH^-, etc.) have large negative Gibbs free energies of hydration (ΔG_{hyd}), indicating strong interactions with H_2O, and are thus water-structuring. Chaotropic ions have weak to unfavorable interactions with H_2O (slightly negative to positive ΔG_{hyd}) and are considered to be water-destructuring (6).

PEG/salt ABS are based on the salting-out of the PEG polymer in aqueous solutions of kosmotropic salts, such that two immiscible phases are formed, both mainly aqueous but one phase is richer in PEG and the other mostly kosmotropic salt. In PEG/salt ABS the phase divergence (essentially the degree of separation of the phase forming components measured by their concentration differences between the phases) can be directly correlated with solute distribution ratios, with the more hydrophobic (chaotropic) species preferring the more chaotropic upper PEG-rich phase (4).

Like some quaternary ammonium functionalized anion exchange resins, PEG can also be chemically attached to a solid support and used as aqueous biphasic extraction chromatographic resins (ABEC). The TcO_4^- anion can be loaded onto the ABEC resin from a kosmotropic salt solution and stripped by simply eluting with water (5).

Hanford and Savannah River's nuclear tank wastes are stored in alkaline solutions that have moderate to high concentration of kosmotropic salts (e.g., OH^-, SO_4^{2-}, PO_4^{3-}, etc.) (7). These salts and tank simulations have been shown to salt-out PEG-2000 forming ABS, and extraction of TcO_4^- has been demonstrated (8) in both liquid/liquid and chromatographic modes (4, 5).

Industrial anionic separation is commonly conducted through anion exchange resins due to their ease of use and predictability in separation particularly from a wide range of anion matrices. Most anion exchange resins utilize quaternary onium functionality with variable alkyl length to control the relative hydrophobicity of the resin, allowing for fine-tuning for a specific anionic species to be chemically preferred. Commonly used anion exchange resins for TcO_4^- include Dowex SRB-OH (9) and Reillex HPQ (10), which have been shown to efficiently extract TcO_4^- from nitric acid systems. The extraction of TcO_4^- is driven by the more chaotropic nature of TcO_4^- (compared to the other ions in the effluent) and the sacrificial anion that is preloaded on the resin (e.g., OH^-) (9, 10).

Recently, we (11, 12) and others (13–16) have begun to use ABS, where aqueous solutions of kosmotropic salts salt-out aqueous solutions of hydrophilic, chaotropic ionic liquids (IL) to produce biphasic systems. The phase diagrams obtained for these systems (e.g., see Fig. 1) by cloud point

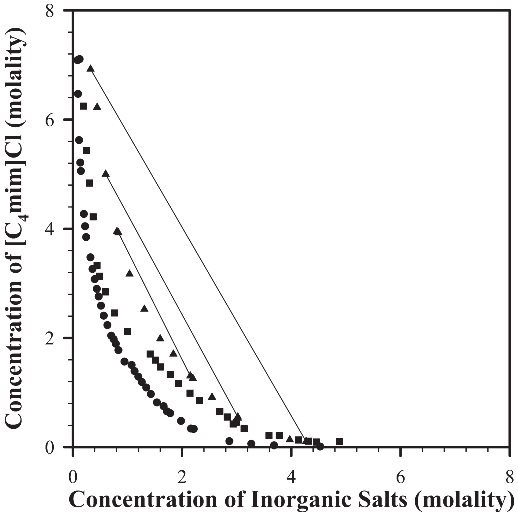

Figure 1. Three salt/salt ABS phase diagrams: (●) [C_4mim]Cl/K_3PO_4; (■) [C_4mim]Cl/K_2HPO_4; (▲) [C_4mim]Cl/K_2CO_3 (with three tie lines illustrated). Figure reproduced from data provided in references 11 and 12.

titration at room temperature are not unlike those previously determined for PEG/salt ABS. The most kosmotropic cation and anion partition into the same (lower) phase to yield the most structured phase possible, while the other ions form the (upper) chaotropic phase (11, 12). As observed for PEG/salt ABS, the salting-out strength of the kosmotropic salt follows the Hofmeister series (17) and increasing concentrations of salt leads to increasing phase divergence (12). In Fig. 1, this is shown for three tie lines which join the upper and lower phase compositions on the binodal. As the tie line lengths (TLLs) increase, the upper and lower phases show increasing differences in concentrations, in other words the separation of the chaotropic and kosmotropic components increases; the upper phase becomes more chaotropic and the lower phase becomes more kosmotropic.

Herein, we report our investigations of the distribution of TcO_4^- in three different salt/salt ABS formed using the ionic liquid, 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) and the comparison of these results to those previously obtained using PEG/salt ABS. Attempts to strip technetium by reduction with $SnCl_2$ are also reported.

EXPERIMENTAL

All chemicals (K_3PO_4, K_2HPO_4, K_2CO_3, $SnCl_2$, 1-methylimidazole, and 1-chlorobutane) were purchased from Aldrich (Milwaukee, WI) and used as received, except 1-methylimidazole which was distilled before use. Pertechnetate tracer ($NH_4^{99}TcO_4$) was purchased from Isotope Products Laboratories (Valencia, CA) and diluted in 0.01 M NaOH (ca. 0.035 μCi/μL). Fisher ScintiSafe Econo1 (Fairlawn, NJ) liquid scintillation cocktail was used as received. [C_4mim]Cl was synthesized using previously reported procedures and the purity was confirmed through ^{1}H NMR, and found to be greater than 99% (12).

All salt/salt ABS were made by addition of equal volumes of varying aqueous IL solutions (30–70% w/w) to an aqueous solution of 40% w/w of kosmotropic salt (K_3PO_4, K_2HPO_4, or K_2CO_3). The mixtures were vortexed and allowed to stand for 12 h at ambient temperature before equal volumes (1 mL) of top and bottom phases were removed and combined in a separate vial for radiological tracer experiments.

To these ABS, 2 μL of the $^{99}TcO_4^-$ solution was added. The mixtures were vortexed for 1 min, centrifuged for 1 min, and this procedure was repeated twice. Aliquots of 100 μL were removed from each phase, placed separately in 5 mL of scintillation cocktail, and mixed thoroughly before counting on a Packard 1900TR liquid scintillation (Meridien, CT). Counting times were limited to 5 min due to disengagement (after ca. 3 h) of the organic scintillation cocktail from the aqueous salt solutions caused by high concentrations of kosmotropic salt. All samples were vortexed within one hour of being counted to ensure that the phases had not disengaged before measurement.

Duplicates of all systems where conducted simultaneously, and error bars are plotted in the figures. Since equal aliquots of each phase were counted, the distribution ratios could be calculated from Eq. (1):

$$D = \frac{[^{99}\mathrm{Tc}]_{\mathrm{cpm,\ top\ phase}}}{[^{99}\mathrm{Tc}]_{\mathrm{cpm,\ bottomphase}}} \tag{1}$$

For the stripping experiments, a known mass of $SnCl_2$ was added to a vial and dissolved to the appropriate volume of the salt/salt ABS bottom (kosmotropic) phase so as to yield a 2 mmol $SnCl_2$ solution. Thereafter, 1 mL of this 2 mmol $SnCl_2$ in kosmotropic salt solution was transferred to a fresh vial where an equal volume (1 mL) of chaotropic phase was added. Distribution experiments utilizing $^{99}TcO_4^-$ were then carried out in these systems as described above.

RESULTS AND DISCUSSION

The phase diagrams obtained for the salting-out of [C_4mim]Cl with K_3PO_4, K_2HPO_4, or K_2CO_3 have been previously determined and are reproduced in Fig. 1 (12). The apparent salting-out strength is related to the kosmotropic salt anions' ΔG_{hyd} (6). After phase separation the chaotropic phase is comprised mostly of $[C_4mim]^+$ and Cl^- and the kosmotropic phase is mostly kosmotropic salt (e.g., K_3PO_4), with only small amounts of other ions in the opposing phase (12). As the concentrations of the salts increase, the tie line lengths (TLLs) increase representing the decreasing concentrations of contaminating ions from the opposing phase, and thus providing the upper phase with an increasingly chaotropic and the lower phase an increasingly kosmotropic nature.

The distribution ratios of TcO_4^- between the phases of three salt/salt ABS ($[C_4mim]Cl/K_3PO_4$, $[C_4mim]Cl/K_2HPO_4$, $[C_4mim]Cl/K_2CO_3$) are shown in Fig. 2. The distribution ratios increase in a nearly linear fashion as a function of TLL (and thus phase divergence) until a certain TLL is reached and the distribution ratios start to plateau. The increasing distribution ratios are due to the increased kosmotropicity of the lower phase which increases the preference of chaotropic solutes for the upper phase. This has been observed previously for the distribution ratios of short chain alcohols in salt/salt ABS (11) and for TcO_4^- in PEG/salt ABS (4, 18).

In order for TcO_4^- to partition into the chaotropic phase, the charge balance of both phases must be maintained, and the most logical mechanism at lower TLLs is anion exchange (TcO_4^-, $\Delta G_{hyd} = -251$ kJ/mol (6), exchanging with the slightly more kosmotropic Cl^-, $\Delta G_{hyd} = -347$ kJ/mol (6)). An anion exchange mechanism would be more favorable at shorter TLLs as the lower phase would be less kosmotropic, however, transfer of an ion pair cannot be ruled out.

As TLLs become longer, the lower phase not only becomes more kosmotropic, but the $[C_4mim]Cl$ concentration in the chaotropic phase increases

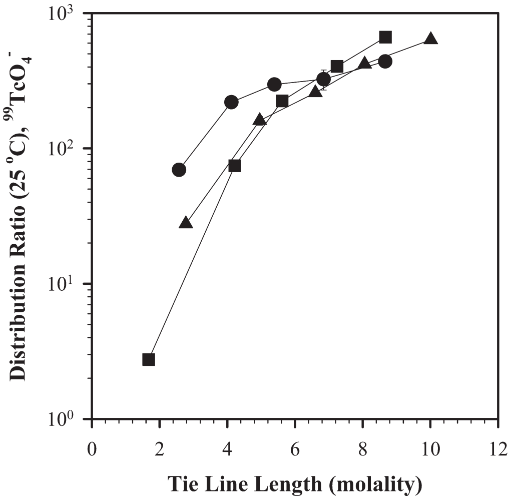

Figure 2. Distribution ratios of TcO_4^- in three salt/salt ABS: (●) $[C_4mim]Cl/K_3PO_4$; (■) $[C_4mim]Cl/K_2HPO_4$; (▲) $[C_4mim]Cl/K_2CO_3$.

causing aggregation of $[C_4mim]Cl$ (19). These aggregates may decrease the availability of Cl^- as the interactions between $[C_4mim]^+$ and Cl^- increase, leading to the observed leveling of the distribution ratios, but this has not yet been confirmed.

Reduction of the chaotropic $Tc^{VII}O_4^-$ and $Tc^{V}O^{3-}$ was successfully utilized to strip this anion from the PEG-rich phase in PEG/salt ABS (4), and our attempts to reproduce this stripping strategy here are shown in Fig. 3, where 2 mmol $SnCl_2$ (relative to kosmotropic salt stock solution) was added to each ABS prior to measuring the distribution ratios. Though the distribution ratios never decreased to less than one, the decreases in distribution ratios do indicate that at least partial reduction was possible. Understanding the stripping behavior will require a more detailed study into all of the possible reduction products. Each reduced species will have to compete with the remaining chaotropic and kosmotropic ions and will have an influence on the distribution ratio observed for ^{99}Tc in these ABS.

The difference in stripping between the K_3PO_4 and K_2HPO_4 ABS could be due to the differences in the pH of the kosmotropic salt-rich phase (K_3PO_4, pH ~13.0–14.2; K_2HPO_4, pH ~ 9.7–10.5). A better model system to study the stripping would be a SO_4^{2-}-based salt/salt ABS, where a wide range of pH could be used. However, $[C_4mim]Cl$ will not form salt/salt ABS with $(NH_4)_2SO_4$ due to the precipitation of NH_4Cl before concentrations leading to phase separation can be reached (12).

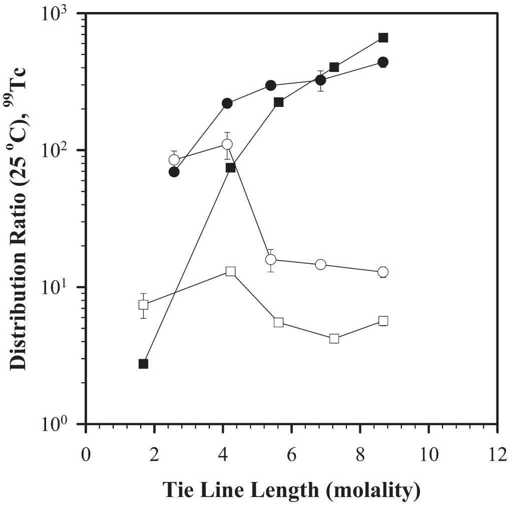

Figure 3. Distribution ratios without (filled symbols) and with (open symbols) 2 mmol $SnCl_2$: (•) $[C_4mim]Cl/K_3PO_4$; (■) $[C_4mim]Cl/K_2HPO_4$. (A reaction of $SnCl_2$ with CO_3^{2-}, yielding CO_2, prevented stripping experiments from being conducted in the $[C_4mim]Cl/K_3CO_3$ ABS.)

CONCLUSIONS

The partitioning of the pertechnetate anion from kosmotropic phases to chaotropic phases in salt/salt ABS has been demonstrated. However, stripping of the technetium from the system was not entirely successful. Salt/salt ABS may be useful in studying the anion's behavior in complex waste systems, however, many operational difficulties would have to be overcome before any such complex system could find practical application.

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