Crown ethers as actinide extractants in acidic aqueous biphasic systems: partitioning behavior in solution and crystallographic analyses of the solid state

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Abstract

The partitioning behavior of UO_2^{2+}, Pu^{4+}, Th^{4+}, and Am^{3+} has been investigated in aqueous biphasic systems formed by the addition of polyethylene glycol of average molecular weight 2000 (PEG-2000) and $(NH_4)_2SO_4$. Water-soluble crown ethers 18-crown-6 and 15-crown-5 have been utilized as extractants. A positive correlation has been observed between crown ether concentration and metal ion partitioning with D_{An} decreasing in the order $UO_2^{2+} > Pu^{4+} > Th^{4+} > Am^{3+}$. A distribution ratio above unity, however, has only been observed for UO_2^{2+} at very high (1.25 M) concentrations of 18-crown-6. In general the distribution ratios for 15-crown-5 are all lower. Matrix ions introduced as NH_4NO_3, H_2SO_4, or HNO_3 drastically reduce the observed distribution ratios and level the extractant dependencies.

1. Introduction

Mixtures of certain inorganic salts and water-soluble polymers, or of two dissimilar polymers, are known to separate into two distinct phases [1, 2] with each phase consisting of greater than 80% water on a molar basis. These aqueous biphasic systems have been studied for over 40 years, primarily because they offer the possibility of gently separating fragile biomolecules such as proteins [2]. Our interest in aqueous biphasic systems has arisen from their unexplored ability to separate metal ions. These unique systems allow for the use of water-soluble extractants and may even allow fully hydrated metal ions to be partitioned between the aqueous phases. We recently reviewed all of the literature devoted to metal ion partitioning in aqueous biphasic systems [3] and found the area to be virtually ignored.

We have been investigating the partitioning behavior of dissolved metal ions in aqueous biphasic systems composed of high molecular weight polyethylene glycols (PEGs) and inorganic salts such as $(NH_4)_2SO_4$, K_2CO_3, and NaOH [4–6]. These systems offer several advantages including the following: (1) PEGs are inexpensive, nontoxic, and commercially available; (2) the use of an organic diluent is not required; (3) new classes of water-soluble complexants can be utilized. In addition, phase separation times are comparable with those of many traditional extraction systems, especially at elevated temperatures.

Actinide partitioning in aqueous biphasic systems has been studied by our group [4] and that of Myasoedov [7–12] (Myasoedov and coworkers have recently reviewed their actinide partitioning results [13]). Certain water-soluble complexing dyes (*e.g.* Arsenazo III, Alizarin Complexone, Xylenol Orange), which both chelate the actinides and distribute quantitatively to the PEG-rich phase, can extract actinides from high ionic strength solutions. Unfortunately, these dyes are toxic, expensive, and very hard to use.

Utilizing our background in crown ether chemistry and metal ion recognition [14–27], we wanted to show that water-soluble crown ethers could also be used to extract metal ions using aqueous biphasic systems. We chose two fairly water-soluble crown ethers that are readily available: 18-crown-6 and 15-crown-5. We have previously used these crown ethers to extract group 1 and 2 cations from alkaline aqueous biphasic media and found a good correlation between $\log K$ (metal:crown ether) values and the observed distribution ratios [5].

The literature has several examples of crown ether extraction of actinides in oil–water systems and several of these present the usual cavity size–metal ion size arguments to explain the results [28–37]. It is interesting to note, however, that the vast majority of crystal structures containing actinides (typically uranium, uranyl, or thorium) and crown ethers exhibit second-sphere hydrogen-bonded coordination [19–24, 26, 27, 31, 35, 38–41]. The isolation and characterization of

directly coordinated crown ether–actinide complexes (e.g. [UO$_2$(dicyclohexano-18-crown-6)][ClO$_4$]$_2$ [42]) is rare and usually involves crystallization from anhydrous solvents and the use of weakly coordinating anions. Under acidic conditions we have isolated only hydronium ion–crown ether complexes stabilized by large uranyl complex ions (e.g. [(H$_5$O$_2$)$_2$(18-crown-6)][UO$_2$Cl$_4$] [19]) or we have characterized neutral second-sphere hydrogen-bonded complexes (e.g. [UO$_2$(SO$_4$)(OH$_2$)$_3$]·0.5(18-crown-6) [19]). We have only observed the latter behavior for thorium and have characterized hydrogen-bonded complexes of 15-crown-5 [20] and 18-crown-6 [21–24] for several Th^{4+} salts.

We chose to pursue crown ether–actinide partitioning in aqueous biphasic systems precisely because of these second-sphere complexes observed in the solid state. The salting out of PEG by certain inorganic anions is thought to be a result of the very different hydrogen bonding environments generated in each phase [43, 44]. We anticipated that the hydrogen bonding environment of the PEG phase would be similar to the polymeric crown ether–water–metal ion hydrogen bonding observed in the solid state and that these complexes would then partition to the PEG-rich phase.

2. Experimental details

Reagent grade (NH$_4$)$_2$SO$_4$ (Baker), PEG-2000 (Aldrich), NH$_4$NO$_3$ (Fisher), 18-crown-6 and 15-crown-5 (Aldrich) and ultrapure H$_2$SO$_4$ and HNO$_3$ (Fisher) were used as purchased.

The systems studied were prepared by the addition of 1 mL aliquots of an (NH$_4$)$_2$SO$_4$ salt stock solution and a PEG-2000 stock solution. The reference system was prepared with a 40% (by weight) (NH$_4$)$_2$SO$_4$(aq) and a 40% (by weight) PEG-2000(aq) stock. The crown ethers used as extractants were diluted to known molarity with the 40% PEG-2000(aq) solution to give a new PEG stock. When NH$_4$NO$_3$ was used it was diluted to a known molarity with the 40% (NH$_4$)$_2$SO$_4$(aq) to give a new salt stock. When acids were used, the salt stock solution was prepared in that acid, e.g. for the 2 M H$_2$SO$_4$ system enough (NH$_4$)$_2$SO$_4$ was diluted with 2 M H$_2$SO$_4$ to give a new acidic 40% salt stock. The PEG was always kept in water. After the initial mixing of the two stock solutions, the systems were equilibrated by vortexing for 2 min followed by 2 min centrifugation.

Tracer solutions of ^{241}Am, ^{233}U, and ^{230}Th were prepared and stored in dilute nitric acid. For the Pu^{4+} studies, ^{239}Pu tracer in HCl was taken up in 8 M nitric acid and several drops of 30% H$_2$O$_2$ were added. This solution was gently evaporated to dryness and the procedure was repeated. The plutonium was then taken up in 8 M nitric acid to ensure that it remained in

the +4 oxidation state prior to use. To prepare the PuO$_2$$^{2+}$ tracer solution, ^{239}Pu in HCl was gently heated to dryness. An aliquot of an oxidizing solution consisting of 0.09 M (NH$_4$)$_2$S$_2$O$_8$ and 0.009 M AgNO$_3$ in 1.0 M H$_2$SO$_4$ was added and gently swirled in the vial. The solution was gently heated at 60 °C for 5 min and allowed to stand at 25 °C for 10 min. A white precipitate formed which was removed by centrifugation. The supernatant was used in the studies of PuO$_2$$^{2+}$ distribution.

Tracer quantities (2–10 μl) of each metal ion solution were added to each system followed by 2 min of vortexing and 2 min of centrifugation. The phases were then separated and equal aliquots of each phase were removed for counting. All distribution ratio measurements were carried out at 25 °C and are accurate to within ±5%. Each distribution ratio was then calculated as

$$D_{An} = \frac{\text{activity in PEG-rich phase}}{\text{activity in salt-rich phase}}$$

Crown ether containing PEG stock solutions for the phase diagrams were prepared as above. (NH$_4$)$_2$SO$_4$ solutions in HNO$_3$ or H$_2$SO$_4$ were also prepared similarly. (NH$_4$)$_2$SO$_4$ solutions with NH$_4$NO$_3$ were prepared by addition of the NH$_4$NO$_3$ solution to a known mass of (NH$_4$)$_2$SO$_4$ to yield the desired weight percentage. The turbidity titrations were carried out according to the method of Albertsson [1].

Crown ether distribution ratios were obtained as follows. For each distribution ratio measured a system was prepared and equilibrated as described above. The two phases were quantitatively separated and placed in separate containers. Each phase was then contacted with 1 ml of hexane followed by 1 min of vortexing and 1 min of centrifugation. The hexane layers were removed and placed into 5 ml volumetric flasks. This procedure was repeated five times. The solutions were then diluted to volume with hexane. Aliquots of each phase were removed for gas chromatographic analyses. The crown ether distribution ratios were calculated as the ratio of the integrated peaks (PEG-rich phase wash/salt-rich phase wash).

3. Results

Aqueous biphasic systems are sensitive to a variety of variables including pH, polymer molecular weight and concentration, salt selection and concentration, temperature, total system composition, and other matrix ions or molecules present. In order to define more fully the PEG-2000–(NH$_4$)$_2$SO$_4$ systems we were investigating, several phase diagrams were prepared bracketing the system in use (Figs. 1 and 2). The curves illustrated
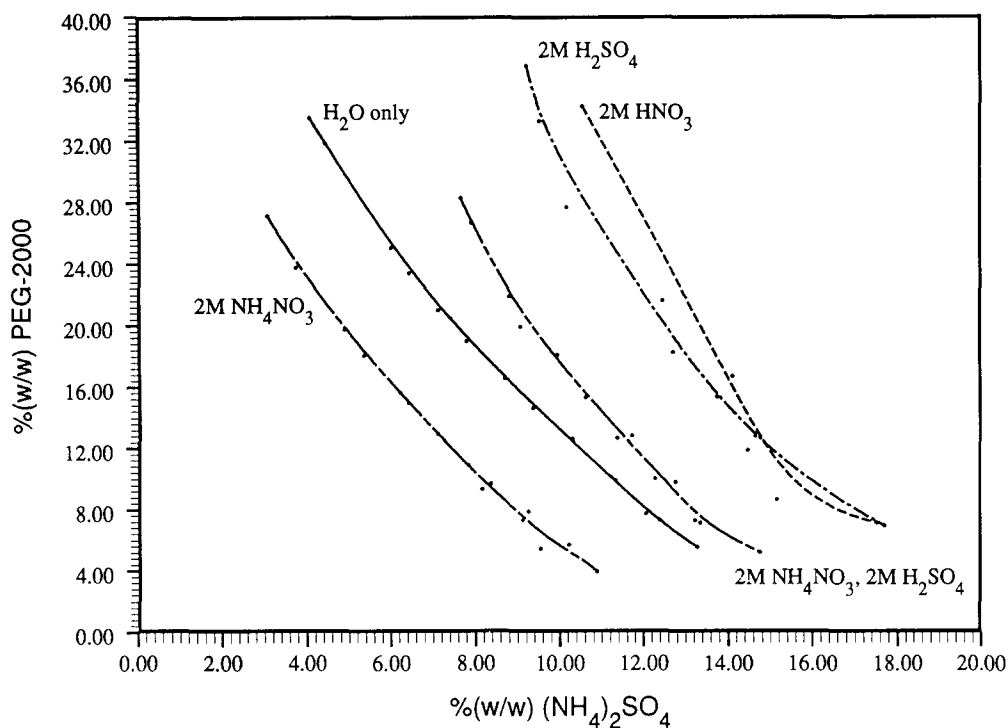
Fig. 1. Phase diagrams at 25 °C for the PEG-2000–$(NH_4)_2SO_4$ system without extractant. The percentage by weight for PEG-2000 and $(NH_4)_2SO_4$ refer to the total system composition (including NH_4NO_3, H_2SO_4, and HNO_3 if present). The concentrations of NH_4NO_3, H_2SO_4, and HNO_3 given refer to the initial concentration in the salt stock solution. To prepare each system, equal volumes of PEG-2000 stock solution and salt stock solution were mixed.
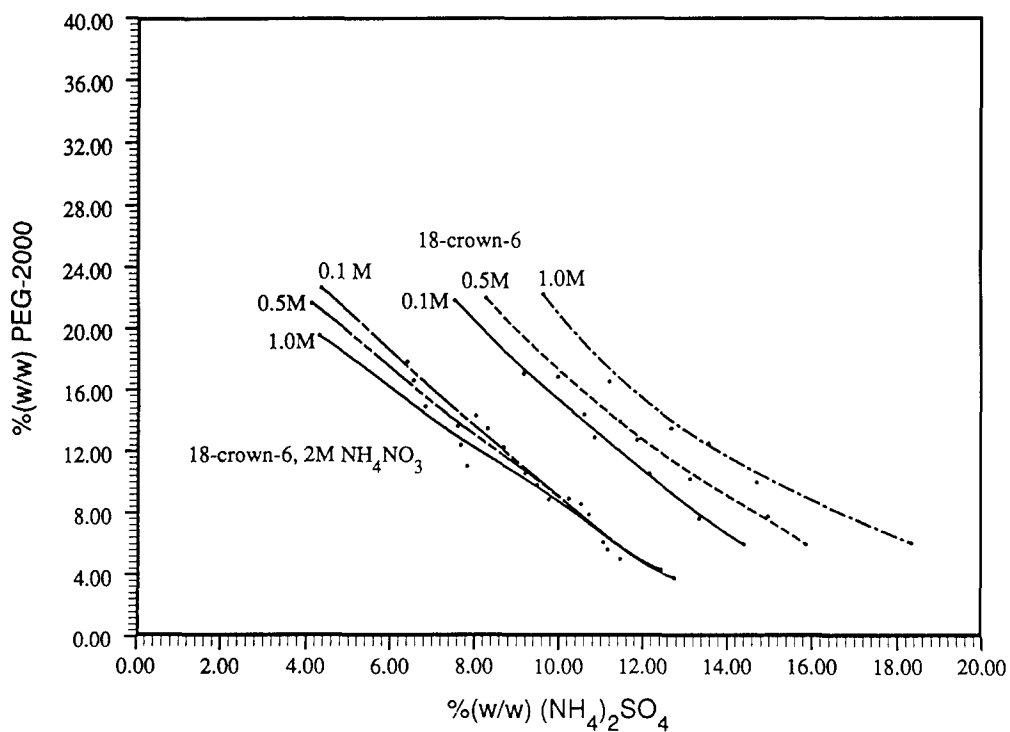

Fig. 2. Phase diagrams at 25 °C for the PEG-2000–$(NH_4)_2SO_4$ systems with extractant. The concentrations of 18-crown-6 given are the initial concentrations in the PEG-2000 stock solutions.

represent the binodials: system compositions below the binodial are monophasic, those above are biphasic. The ordinate and abscissa represent the total system weight percent (including any added NH_4NO_3, acid, or crown ether) of PEG-2000 and $(NH_4)_2SO_4$ respectively. The concentrations noted for NH_4NO_3, H_2SO_4, and HNO_3 refer to the initial concentration in the salt stock solution, prior to mixing with an equal volume of 40% PEG-2000. Similarly the concentrations of crown ether represent the initial crown ether concentration in the PEG-2000 stock solution.

As we have observed previously [4] at low pH the binodial shifts upward (Fig. 1) requiring more salt to form a biphasic solution. Nitric and sulfuric acid give very similar results. It is very interesting, however, that the addition of NH_4NO_3 pushes the binodial so far down. The combination of both NH_4NO_3 and H_2SO_4 nearly cancels out the effect of each. Even if the NO_3^- anion is not needed to aid in metal ion extraction (as it is for group 1 and 2 metal ions [5]) the addition of NH_4NO_3 may be helpful in reducing the total salt concentration necessary to maintain a biphase. This is somewhat surprising since the nitrate anion itself does not form a biphasic solution with PEG-2000 [45].

The addition of large amounts of 18-crown-6 tends to shift the binodial higher as the initial concentration of crown ether is increased although the shifts are relatively small (Fig. 2). The presence of NH_4NO_3 tends to overwhelm the effect of the crown ether and the binodial shifts downward to nearly where it is located when only NH_4NO_3 is added to the system.

The PEG-2000-$(NH_4)_2SO_4$ system without an extractant does not provide for any significant partitioning of UO_2^{2+}, Pu^{4+}, Th^{4+}, or Am^{3+} from the salt-rich to PEG-rich phases. The slightly acidic system prepared by mixing equal volumes of 40% PEG-2000 stock solution with 40% $(NH_4)_2SO_4$ stock solution exhibits D_{An} values that range from 0.0096 (Am^{3+}, Table 1) to 0.085 (UO_2^{2+}). The D values are in general even lower in the systems with NH_4NO_3, H_2SO_4, or HNO_3.

We chose to test the feasibility of using crown ethers to extract actinides in aqueous biphasic systems with 18-crown-6 and 15-crown-5. Both have good water solubility, and, although cyclic, both have the same

polyether backbone found in the linear PEG-2000. Unfortunately, these crown ethers are evenly distributed between the PEG-rich and salt-rich phases. D_{CE} values of ca. 1 were observed for all systems tested (Table 2). Ideally the extractant should be quantitatively partitioned to the PEG-rich phase as observed for certain chelating dyes [4, 7–13]. Nonetheless, it is still possible to discuss trends in the actinide partitioning behavior.

The best results were obtained from the 40% PEG-2000–40% $(NH_4)_2SO_4$ system. The 18-crown-6 extractant dependence profiles are illustrated in Fig. 3. Each is linear with slopes which range from 0.72 (Am^{3+}) to 0.94 (Th^{4+}). A 1.25 M (concentration in the initial 40% PEG-2000 stock solution) 18-crown-6 system actually gives a $D_{UO_2^{2+}}$ value above unity (1.2). The order of extraction is $UO_2^{2+} > Pu^{4+} > Th^{4+} > Am^{3+}$.

15-crown-5 gives generally similar extraction profiles, but at lower D values. The exception is Pu^{4+} which is actually elevated slightly from the 18-crown-6 results and is almost identical to UO_2^{2+}. The slopes of the best fit lines depicted in Fig. 4 range from 0.29 (UO_2^{2+}) to 0.61 (Th^{4+}).

By analogy to our work partitioning group 1 and 2 elements from alkaline media using crown ethers [5], where the addition of NO_3^- enhanced extraction by providing an extractable anion, we hoped to increase D_{An} by the addition of NH_4NO_3. Instead NH_4NO_3 tended to depress the D_{An} values and to flatten the extractant dependencies. The highest D_{An} observed was $D_{UO_2^{2+}} = 0.046$ (1.25 M 15-crown-5). In addition, when NH_4NO_3 was used the PEG-rich phases containing the higher concentrations of 18-crown-6 tended to crystallize.

The results using H_2SO_4 and HNO_3 were similarly disappointing. The highest D_{An} achieved were $D_{UO_2^{2+}} = 0.16$ (2 M H_2SO_4 system at 1.25 M 18-crown-6) and $D_{UO_2^{2+}} = 0.060$ (2 M HNO_3 system at 1.25 M 18-crown-6).

4. Discussion

Substituted crown ethers dibenzo-18-crown-6 and di-cyclohexano-18-crown-6 have received the most atten-

TABLE 1. Actinide distribution ratios in the absence of extractant

PEG-2000 stock solution[a]	Salt stock solution[a]	$D_{UO_2^{2+}}$	$D_{Pu^{4+}}$	$D_{Th^{4+}}$	$D_{Am^{3+}}$
40% PEG-2000	40% $(NH_4)_2SO_4$	0.085	0.045	0.026	0.0096
40% PEG-2000	2 M HNO_3 in 40% $(NH_4)_2SO_4$	0.039	0.013	0.015	0.0083
40% PEG-2000	2 M H_2SO_4 in 40% $(NH_4)_2SO_4$	0.065	0.018	0.016	0.011
40% PEG-2000	2 M NH_4NO_3 in 40% $(NH_4)_2SO_4$	0.019	0.013	0.0068	0.0041

[a] D_{An} were measured in an aqueous biphasic system prepared by mixing equal volumes of PEG-2000 stock solution with salt stock solution. Percentages are by weight.

TABLE 2. Distribution ratios of 18-crown-6 and 15-crown-5

PEG-2000 stock solution[a]	Salt stock solution[a]	D_{CE}
0.10 M 18-crown-6 in 40% PEG-2000	40% $(NH_4)_2SO_4$	1.1
1.0 M 18-crown-6 in 40% PEG-2000	40% $(NH_4)_2SO_4$	1.1
1.0 M 18-crown-6 in 40% PEG-2000	2 M HNO_3 in 40% $(NH_4)_2SO_4$	1.1
1.0 M 18-crown-6 in 40% PEG-2000	2 M H_2SO_4 in 40% $(NH_4)_2SO_4$	0.94
1.0 M 18-crown-6 in 40% PEG-2000	2 M NH_4NO_3 in 40% $(NH_4)_2SO_4$	1.1
1.0 M 15-crown-5 in 40% PEG-2000	40% $(NH_4)_2SO_4$	1.1
1.0 M 15-crown-5 in 40% PEG-2000	2 M HNO_3 in 40% $(NH_4)_2SO_4$	1.1
1.0 M 15-crown-5 in 40% PEG-2000	2 M H_2SO_4 in 40% $(NH_4)_2SO_4$	1.0
1.0 M 15-crown-5 in 40% PEG-2000	2 M NH_4NO_3 in 40% $(NH_4)_2SO_4$	1.1

[a] D_{CE} was measured in an aqueous biphasic system prepared by mixing equal volumes of PEG-2000 stock solution with salt stock solution. Percentages are by weight.
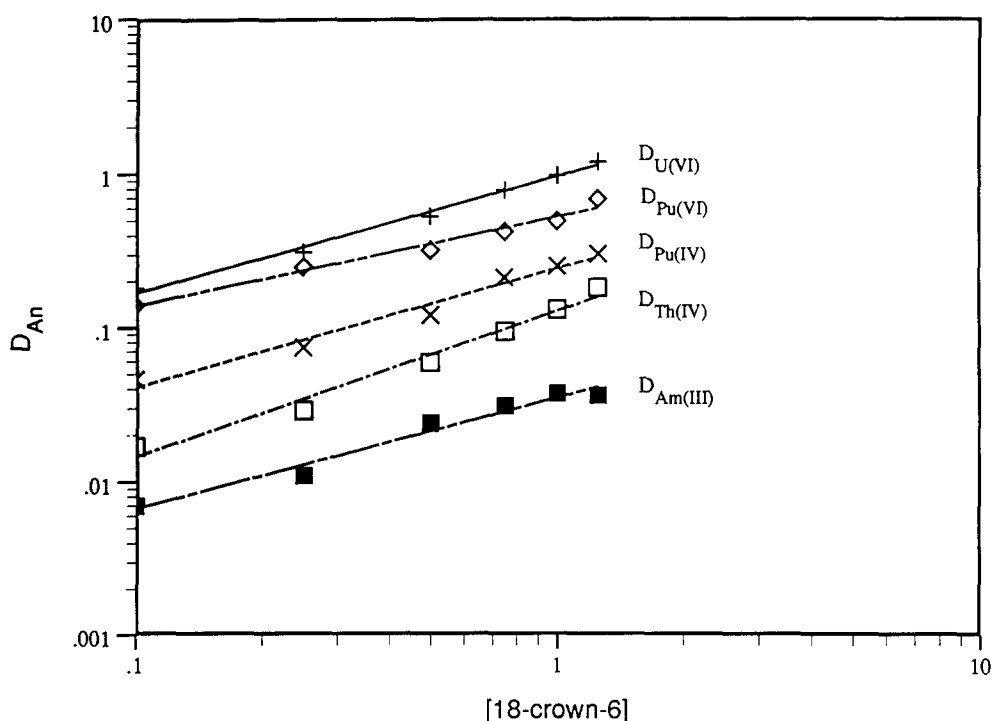

Fig. 3. Extractant dependence profile for 18-crown-6 in the 40% (by weight) PEG-2000–40% (by weight) $(NH_4)_2SO_4$ system. The concentration of 18-crown-6 given refers to the initial concentration in the PEG-2000 stock solution prior to mixing with the salt stock solution.

tion as actinide extractants in oil–water systems owing to their low aqueous solubilities [29–34] although a few studies utilizing the simple 18-crown-6 and 15-crown-5 ligands have appeared [35–37]. Several of these papers make reference to a cavity size–cation size relationship, especially when the uranyl ion is being discussed.

Our structural investigations of the solid state do not support the idea of crown ether inner sphere coordination [19–27], a necessity for true molecular recognition of cations. Instead the crystal structure database suggests polymeric hydrogen-bonded second-sphere coordination complexes. This idea is also supported by the molecular dynamics simulations of ur-anyl–18-crown-6 complexation in water carried out by

Guilbaud and Wipff [46]. Starting with a simulated inner sphere complex between $UO_2(NO_3)_2$ and 18-crown-6 in H_2O, they observed dissociation to form a second-sphere hydrogen-bonded complex. A similar study of Eu^{3+} revealed complete dissociation of 18-crown-6 to form a primary and secondary coordination sphere of water molecules. (Since Am^{3+} and Eu^{3+} are of such similar size and charge it is reasonable to assume they behave similarly in solution.)

The partitioning data obtained for actinides in aqueous biphasic media do not exhibit an obvious cavity size–cation size relationship. Both 18-crown-6 and 15-crown-5 enhance partitioning to the PEG-rich phase of all four actinide ions studied but the order of
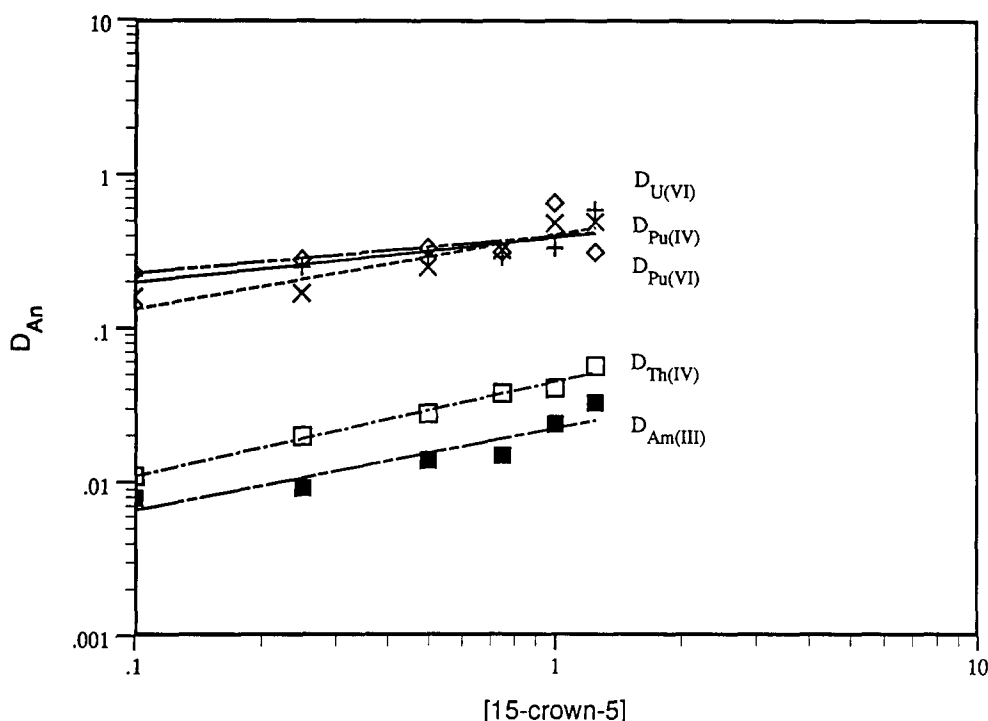
Fig. 4. Extractant dependence profile for 15-crown-5 in the 40% (by weight) PEG-2000–40% (by weight) $(NH_4)_2SO_4$ system. Concentrations of 15-crown-5 are reported for the initial PEG-2000 stock solutions.

extraction $(UO_2^{2+} > Pu^{4+} > Th^{4+} > Am^{3+})$ remains the same and the slopes of the extractant dependence profiles are very similar. The same order of extraction is even observed when no crown ether is present at all.

If, however, partitioning to the PEG-rich phase is a function of the presence of the actinide aquo ion and the formation of second-sphere hydrogen-bonded crown ether complexes, we might expect some correlation between the stability of the actinide aquo ion and the distribution ratios. Although we cannot fully explain it yet, we have discovered such a correlation. Figure 5 plots the $\log D_{An}$ values vs. the standard enthalpy of formation of the aquo ion [47]. There is good correlation with UO_2^{2+}, Th^{4+}, and Am^{3+} (e.g. in the absence of extractant the correlation coefficient r for these three points is 99.6%), but not for Pu^{4+} which falls much higher than we would predict.

We noted that if our plutonium tracer were actually in the form of PuO_2^{2+} the data would fit very nearly on the lines generated in Fig. 5. In order to test the validity of our Pu^{4+} data we prepared tracer quantities of $^{239}PuO_2^{2+}$ and repeated the distribution measurements for the 40% PEG-2000–40% $(NH_4)_2SO_4$ system with both 18-crown-6 and 15-crown-5. We also measured $D_{PuO_2^{2+}}$ in the absence of crown ether ($D_{PuO_2^{2+}} = 0.12$).

The Pu(VI) data in Fig. 3 (18-crown-6 dependence) exhibit elevated D values (falling between our original

Pu^{4+} and UO_2^{2+} extractant dependencies) but have the same extractant dependence profile as Pu(IV). However, there is virtually no difference in the Pu^{4+} and PuO_2^{2+} distribution ratios in the presence of 15-crown-5 (Fig. 4).

Returning to Fig. 5 and the correlation of D_{An} with the standard enthalpy of formation of the aquo ion, we find that the $D_{PuO_2^{2+}}$ value in the presence of 18-crown-6 has a much closer fit than the $D_{Pu^{4+}}$ value. (The correlation coefficient for the four data points represented is 99.8%.) While it is possible that our Pu^{4+} tracer solutions were at least partially oxidized, given the very complex aqueous chemistry of plutonium we feel that it is essential to investigate more fully the partitioning behavior of plutonium in these systems before such conclusions are drawn.

Further support for the observed correlation can be found in the published data of Myasoedov and coworkers [7, 8] for an aqueous biphasic system reported to have a total system composition of 15% PEG-2000–14.4% $(NH_4)_2SO_4$. The distribution ratio data for Th^{4+}, Cm^{3+}, Am^{3+}, and Cf^{3+} have a similar correlation with the standard enthalpy of formation of the aquo ion as we have observed. It is also noted that Am^{3+} and Cm^{3+} have nearly identical values of ΔH_f^o for the aquo ion [47] and their distribution ratios are also nearly identical. (That the D_{An} values themselves are higher than ours probably is related to the different system compositions utilized.)
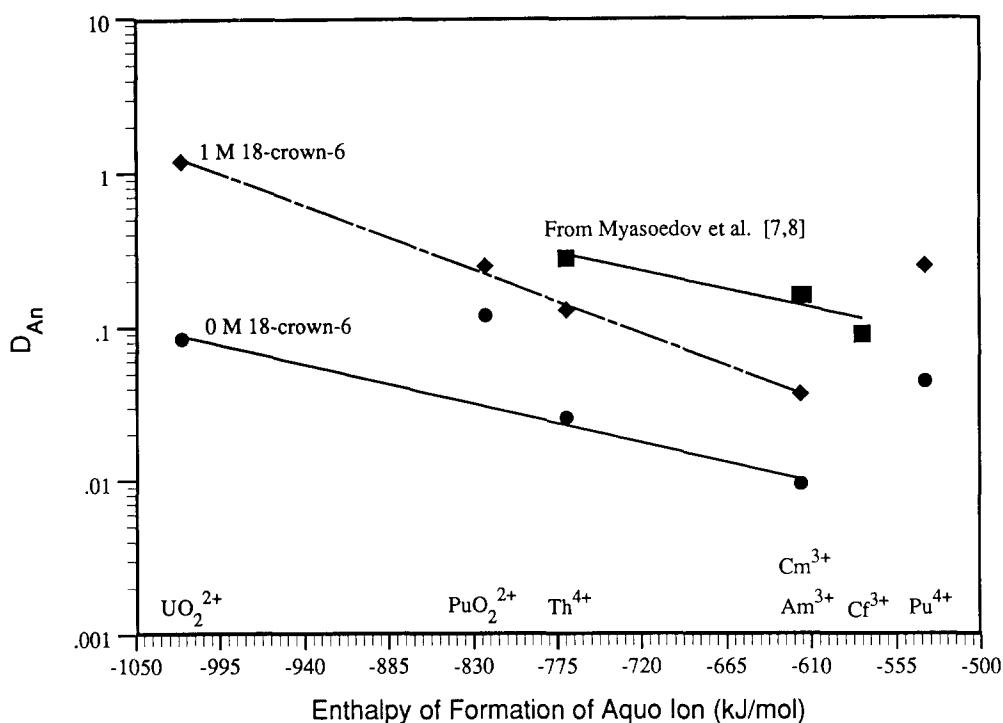
Fig. 5. Correlations between D_{An} in the 40% (by weight) PEG-2000–40% (by weight) $(NH_4)_2SO_4$ system vs. the standard enthalpy of formation of the aquo ion. The four data points from Myasoedov and coworkers [7, 8] correspond to a total system composition of 15% (by weight) PEG-2000–14.4% (by weight) $(NH_4)_2SO_4$.

The interesting correlation between stability of the aquo ion and D_{An} may also shed light on why NH_4NO_3 and HNO_3 have such a big effect on D_{An}, lowering them substantially and leveling out any extractant dependence. The donating ability of the nitrate anion is much better than sulfate and the presence of excess NO_3^- could easily lead to mixed aquo–nitrato complexed metal ions which disrupt the hydrogen bonding environment.

The presence of hydronium ion species may also account for some of the effects noted for HNO_3 and H_2SO_4. Large uranyl ions with crown ethers are known to stabilize higher-order hydronium ions (*e.g.* $[(H_5O_2)(H_9O_4)(benzo-15-crown-5)_2][UO_2Cl_4]$ [19]). The crown ether hydrogen bonding patterns for these species are much different from that generated by aquated metal ions.

5. Conclusions

We have demonstrated that, under certain conditions at least, crown ethers can influence actinide partitioning in aqueous biphasic media. We have not clearly shown, however, that the concepts of molecular recognition apply to this actinide extraction with crown ethers. On the contrary, our results tend to support the idea that the formation of hydrogen-bonded second-sphere crown ether complexes is responsible for the observed behavior. In order to bring molecular recognition to aqueous biphasic systems we must find more suitable macrocyclic extractants. We are currently investigating the development of new water-soluble crown-ether-like ligands that will partition to the PEG-rich phase and which contain softer N or S donor atoms more likely to form direct actinide coordination complexes. We will be able to tailor these extractants to exploit fully the precepts of molecular recognition and to apply them to novel extractions utilizing aqueous biphasic systems.

It is evident that a tremendous amount of work is left to define fully the chemistry of both aqueous biphasic systems and metal ion partitioning in them. Studies such as this do, however, clearly show the potential for exploiting the clean, inexpensive nature of aqueous biphasic systems for metal ion separations.

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