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Robin D. Rogers[a]; Andrew H. Bond[a]; Cary B. Bauer[a]
[a] Department of Chemistry, Northern Illinois University DeKalb, IL

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# AQUEOUS BIPHASE SYSTEMS FOR LIQUID/LIQUID EXTRACTION OF f-ELEMENTS UTILIZING POLYETHYLENE GLYCOLS

Robin D. Rogers,* Andrew H. Bond, and Cary B. Bauer
Department of Chemistry
Northern Illinois University
DeKalb, IL 60115

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## ABSTRACT

Aqueous biphasic systems formed by adding a $H_2O$ soluble polymer (polyethylene glycol) to an aqueous salt solution ($(NH_4)_2SO_4$ or $K_2CO_3$) have been investigated for use in extracting aqueous $Am^{3+}$, $Pu^{4+}$, $UO_2^{2+}$, and $Th^{4+}$ ions into the polymer-rich phase. Extraction occurs only in the presence of complexing dyes which preferentially partition to the polymer-rich phase. Three such dyes, arsenazo III, alizarin complexone, and xylenol orange were investigated. Arsenazo III extracts all four metal ions from $SO_4^{2-}$ media but not from $CO_3^{2-}$ solutions. Alizarin complexone quantitatively extracts $Th^{4+}$ and $Pu^{4+}$ from $SO_4^{2-}$ media, while $Am^{3+}$ is the best extracted ion in $CO_3^{2-}$ solution. Xylenol orange extracts only $Am^{3+}$ from $CO_3^{2-}$ media. In $SO_4^{2-}$ solutions low concentrations of xylenol orange extract $Th^{4+}$ and $Pu^{4+}$, while $Am^{3+}$ and $UO_2^{2+}$ are extracted at higher concentrations of xylenol orange. $H_2SO_4$ can be used to strip the metal ions, while $NH_4OH$ often but not always enhances the extraction.

## INTRODUCTION

Aqueous mixtures of two dissimilar polymers or of a polymer and an inorganic salt are known to separate into two distinct layers (1,2). Each layer consists of 80% or more $H_2O$ on a molar

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* Corresponding author

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basis. The large concentration of $H_2O$ in each phase allows fully hydrated species to be extracted. It also allows the use of $H_2O$ soluble extractants which have an affinity for the polymer phase. Aqueous biphasic systems have been used for over forty years for the separations of biomaterials such as proteins, blood cells, etc., thus, a significant amount of research has been devoted to the optimization of these systems for specific tasks (2).

We have begun to investigate liquid/liquid extraction of dissolved metal ions with aqueous biphasic systems composed of polyethylene glycol (PEG) as the polymer and an inorganic salt. PEGs are inexpensive, commercially available, nonflammable, nontoxic, and durable. The PEG phases are easily separated by centrifugation. Phase separation times are highly dependent on system composition and temperature, however, dispersion numbers (3) (eq. 1) are comparable to many oil/water systems in use today (e.g., $N_{D_i} = 1.7 \times 10^{-3}$ at 50°C for the $(NH_4)_2SO_4$/PEG-2000 systems investigated in this study).

$$N_{D_i} = \left(\frac{1}{t_B}\right)\sqrt{\Delta Z/g} \qquad (1)$$

a) $N_{D_i}$ = dispersion number, b) $t_B$ = time (s) needed for phase disengagement to result in a constant height interface, c) $\Delta Z$ = total system height (cm), d) g = the gravitational constant (980.665 cm/s$^2$).

A phase diagram for the $(NH_4)_2SO_4$/PEG-2000 system (data from reference 4) is presented in Figure 1. The curve represents the binodial, below which compositions result in a single phase and above which aqueous biphasic systems are observed. The binodial depends on the type of polymer and its molecular weight and concentration, the nature of the inorganic salt and its concentration, and other variables including temperature (5). PEGs preferentially distribute to the top phase and are thus represented as the ordinate. The straight lines connecting two points (nodes) on the binodial are tie lines. Preparing a system

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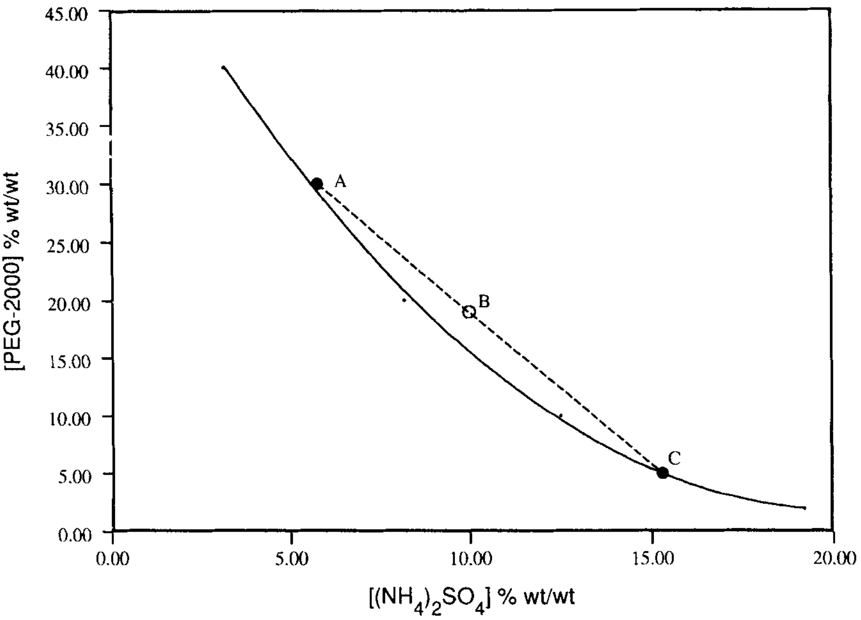

FIGURE 1. $(NH_4)_2SO_4$/PEG-2000 System. (Phase Diagram Data from Reference 4).

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by adding the individual components in amounts anywhere along the tie line will result in a total system composition represented by the open circle on the tie line, and individual phase compositions represented by the nodes. The approximate phase ratio can be estimated as the ratio of the length along the tie line from the upper phase composition to the system composition over the system composition to the lower phase ($\overline{AB}/\overline{AC}$). The point on the binodial where the tie line has a length of one point is called the critical point. Concentrations of solutes in each phase are independent of phase volume (1,2).

Our work with PEGs (6) initially concentrated on the complexation chemistry of low molecular weight PEGs with salts of the lanthanides, La, Y, Th, U, Bi, Pb, Cd, and Hg. We have studied the crystal structures of well over two hundred of these complexes. In our work with triethylene through heptaethylene glycol, we observed the formation of biphasic systems and became interested in the possibility of metal ion extraction with these nontraditional biphases.

As we learned more about these biphasic systems in order to explain our experimental results, it became obvious that although a significant number of papers have been published concerning aqueous biphase systems utilizing PEGs for separation of particulates or biomaterials (1,2), very little research has been carried out on the extraction of metal ions from the salt-rich to PEG-rich phases. The majority of the work in metal ion extraction utilizing aqueous biphasic systems has come from Russian laboratories and generally falls into two categories: a) extraction into the PEG-rich phase by addition of a $H_2O$ soluble extractant which partitions to the PEG phase (7-12), or b) extraction by addition of an inorganic anion which enhances extraction of the metal ion into the PEG-rich phase (4,13-14).

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This paper focuses on the extraction of actinides (specifically, $Th^{4+}$, $UO_2^{2+}$, $Pu^{4+}$, and $Am^{3+}$) from $SO_4^{2-}$ and $CO_3^{2-}$ solutions utilizing PEG-2000 and the water soluble complexing dyes arsenazo III, alizarin complexone, and xylenol orange (15). Our results are compared to similar studies (where available) published in the Russian literature.

## EXPERIMENTAL

Reagent grade $(NH_4)_2SO_4$ (Baker), $K_2CO_3$ (Baker), PEG-2000 (Aldrich), $NH_4OH$ (Fisher), and $H_2SO_4$ (Fisher) were used as received. Arsenazo III, alizarin complexone, and xylenol orange were purchased from Aldrich and used as received.

Stock solutions of 40% wt/wt PEG-2000 and 40% wt/wt $(NH_4)_2SO_4$ or $K_2CO_3$ were prepared with distilled then deionized $H_2O$. For the studies involving acid or base, PEG-2000 and $(NH_4)_2SO_4$ stock solutions (40% wt/wt) were prepared in either 1M $NH_4OH$ or 3M $H_2SO_4$. When extractants were added, they were prepared by dissolution in the PEG-2000 stock solutions to a known molarity. Generally, extractant concentrations above 0.01M were too deeply colored to effectively study. Reasonable results were, however, obtained with 0.10M xylenol orange.

The systems studied were prepared as follows. A 1 mL aliquot of aqueous salt stock solution was added to 1 mL of PEG-2000 stock solution (with extractant where appropriate) in a glass culture tube. The system was equilibrated prior to use by vortexing for 2 min. followed by 2 min. of centrifugation. This method of system preparation results in approximately equal volumes of salt-rich and PEG-rich phases. Final system compositions were determined to be: a) sulfate system - 21.2% $(NH_4)_2SO_4$, 18.8% PEG-2000; b) carbonate system - 22.5% $K_2CO_3$, 17.5% PEG-2000.

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Tracer levels of the metal ions studied were added to these equilibrated systems then vortexed and centrifuged for 2 min. each. The phases were separated and measured aliquots removed for counting. All distribution ratios were measured at 25°C, and are reproducible to within ±5%. The tracer scale experiments were carried out with $^{241}$Am, $^{239}$Pu, $^{233}$U, and $^{230}$Th. The plutonium tracer was kept in 7.33M $HNO_3$ to ensure that it remained in the +4 oxidation state prior to use. The distribution ratios were determined radiochemically from equivalent volumes of each phase as:

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

## RESULTS AND DISCUSSION

It became apparent from our early results (Table 1) and a few reports in the Russian literature (7-11), that the PEG phase itself would not extract the metal ions investigated from aqueous solution. We noted, however, that certain complexing dyes which

TABLE 1. $D_{An}$ IN THE ABSENCE OF EXTRACTANT

| Metal Ion | $(NH_4)_2SO_4$ System | $K_2CO_3$ System |
|---|---|---|
| $Am^{3+}$ | 0.013 | 0.12 |
| $Pu^{4+}$ | 0.023 | 0.022 |
| $UO_2^{2+}$ | 0.082 | 0.0065 |
| $Th^{4+}$ | 0.040 | 0.025 |

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quantitatively partition to the PEG-rich phase were reported to accomplish the desired extraction (7-11).

In sulfate media, arsenazo III was reported to separate $Th^{4+}$ and $Pu^{4+}$ from trans-plutonium and lanthanide metal ions when extracted from acid at pH $\approx$ 2 (7,8,11). The trans-plutonium and lanthanide ions were extracted in the range pH = 3.5-4.5. $Am^{3+}$ and $Cm^{3+}$ were extracted from weakly acidic media in a very narrow range of pH. Separation factors of over 100 are reported for the Th/Eu pair. Stripping was accomplished by adjusting the pH.

The extraction of actinides from carbonate media has also been reported. Alizarin complexone, xylenol orange, and methyl thymol blue were used to extract $Am^{3+}$, $UO_2^{2+}$, $Np^{5+}$, and $Pu^{4+}$ from $K_2CO_3$, $Na_2CO_3$, or $(NH_4)_2CO_3$/PEG-2000 systems (9,10). The $Na_2CO_3$ systems were most effective for the +3 and +4 metal ions. $K_2CO_3$ was better for separation of ions in different oxidation states. Xylenol orange and alizarin complexone extracted the $An^{3+}$ ions but not $U^{6+}$ or $Pu^{4+}$. An effective separation of actinides and lanthanides was accomplished by addition of an extractant (xylenol orange) and a masking agent (hydroxyethylenediphosphonic acid-HEDPA). Using such a system separation factors of 4.5-5.6 were found for the Am/Eu pair.

With these published hints at the utility of PEG biphasic systems for actinide extraction, we focused our initial studies on two extraction media (the slightly acidic $(NH_4)_2SO_4$ system and the slightly basic $K_2CO_3$ system) and three complexing dyes (arsenazo III, alizarin complexone, and xylenol orange). Our results are represented in Figures 2-7.

## Dispersion Numbers

Dispersion numbers (3) were calculated based on separation times for the $(NH_4)_2SO_4$ and $K_2CO_3$ systems at 25 and 50°C. Utilizing the system compositions described in the experimental section, separation times of 77s and 118s were observed for the $(NH_4)_2SO_4$ and $K_2CO_3$ systems, respectively, at 25°C. These correspond to $N_{D_i}$'s of $6.2 \times 10^{-4}$ ($SO_4^{2-}$) and $4.0 \times 10^{-4}$ ($CO_3^{2-}$). Separation times ($t_B$) were dramatically reduced by elevating the temperature to 50°C: $SO_4^{2-}$: $t_B = 28s$, $N_{D_i} = 1.7 \times 10^{-3}$; $CO_3^{2-}$: $t_B = 20s$, $N_{D_i} = 2.4 \times 10^{-3}$. Addition of a complexing dye to the systems had little or no effect on the dispersion numbers obtained.

## Arsenazo III

Arsenazo III is by far the best extractant from sulfate media for all the metal ions studied. Three metal ions, $Th^{4+}$, $UO_2^{2+}$, and $Pu^{4+}$ exhibit almost identical extractant dependencies (Figure 2). Distribution ratios are already well over 10 at $10^{-4}$M arsenazo III. $Am^{3+}$ is also extracted and exhibits a similar extractant dependency, however, higher concentrations of the extractant are required. Distribution ratios of 10 and above for $Am^{3+}$ are not achieved until the extractant concentration reaches $1.5 \times 10^{-3}$M.

In carbonate media arsenazo III extracts the metal ions studied poorly (Figure 3). $Am^{3+}$ exhibits the highest D values followed by $Pu^{4+}$ and then $Th^{4+}$ and $UO_2^{2+}$ which are nearly identical.

## Alizarin Complexone

The extractant dependency data for alizarin complexone from sulfate media are given in Figure 4. Alizarin complexone has been

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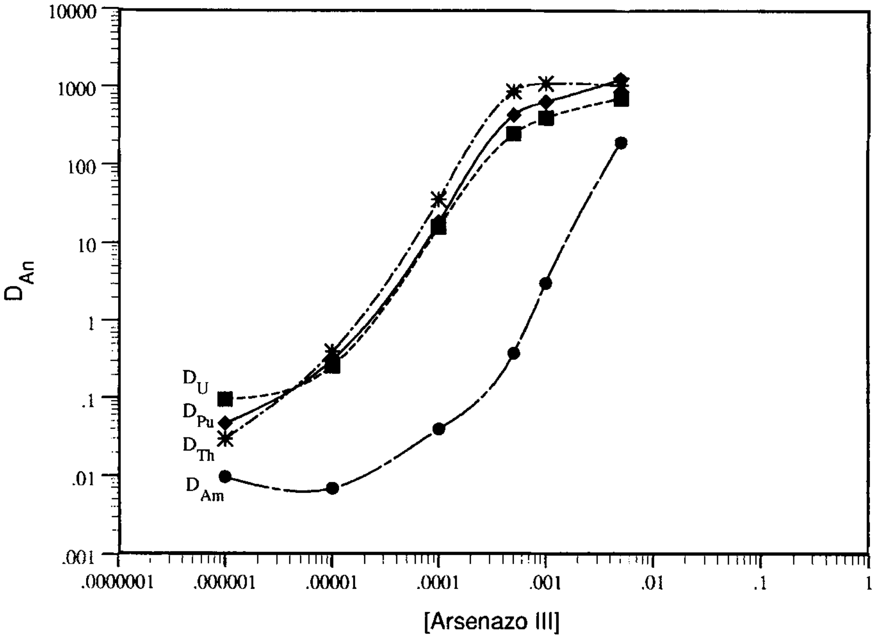

FIGURE 2. $D_{An}$ vs. [Arsenazo III] for the $(NH_4)_2SO_4$/PEG-2000 System.

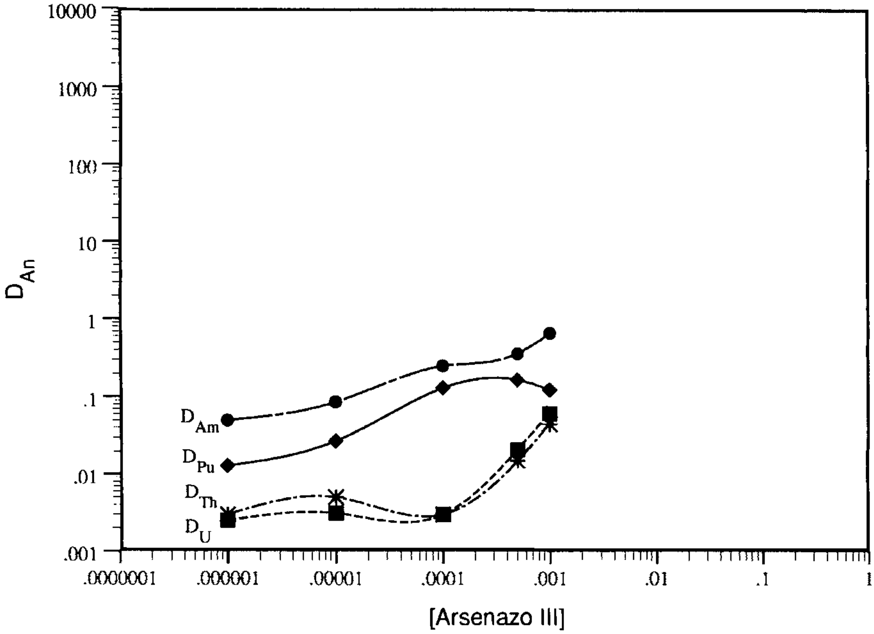

FIGURE 3. $D_{An}$ vs. [Arsenazo III] for the $K_2CO_3$/PEG-2000 System.

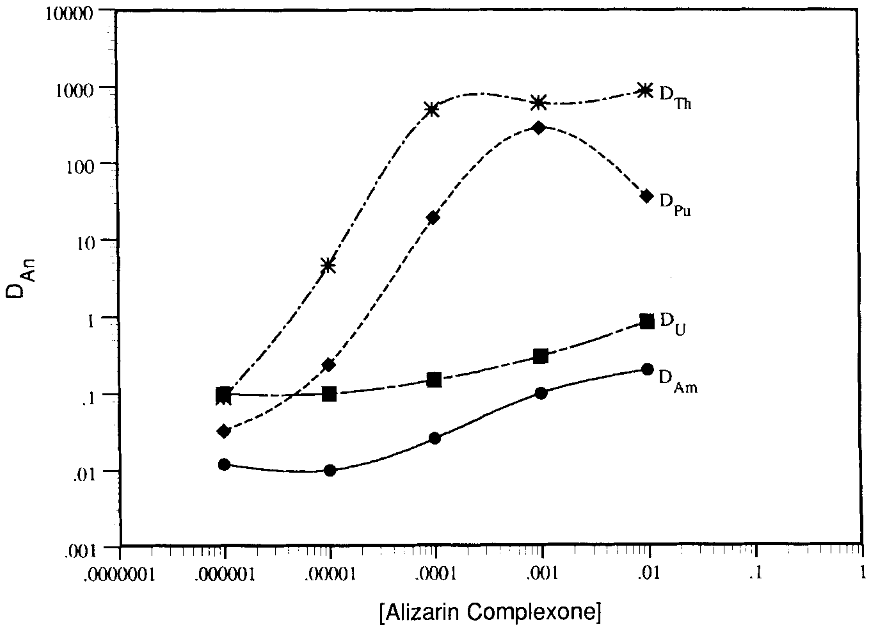

FIGURE 4. $D_{An}$ vs. [Alizarin Complexone] for the $(NH_4)_2SO_4$/PEG-2000 System.

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shown to distinguish between $Th^{4+}$ and $UO_2^{2+}$. In fact, both +4 metal ions ($Th^{4+}$ and $Pu^{4+}$) are extracted by alizarin complexone.

From carbonate media (Figure 5), $Am^{3+}$ has the highest D values (they were the lowest in $SO_4^{2-}$ systems) followed by $Pu^{4+}$, $UO_2^{2+}$, and $Th^{4+}$. Distribution ratios over one are achieved for $Am^{3+}$ and $Pu^{4+}$ at 5 x $10^{-5}$M and 3 x $10^{-4}$M alizarin complexone, respectively. The $D_U$ value approaches one only at $10^{-2}$M extractant, while $Th^{4+}$ would require much higher concentrations of extractant. Extrapolation of our data for $Am^{3+}$ yields a $D_{Am}$ value of 30 at 2 x $10^{-2}$M alizarin complexone. A value of 57.8 is reported for this extractant concentration in reference 10.

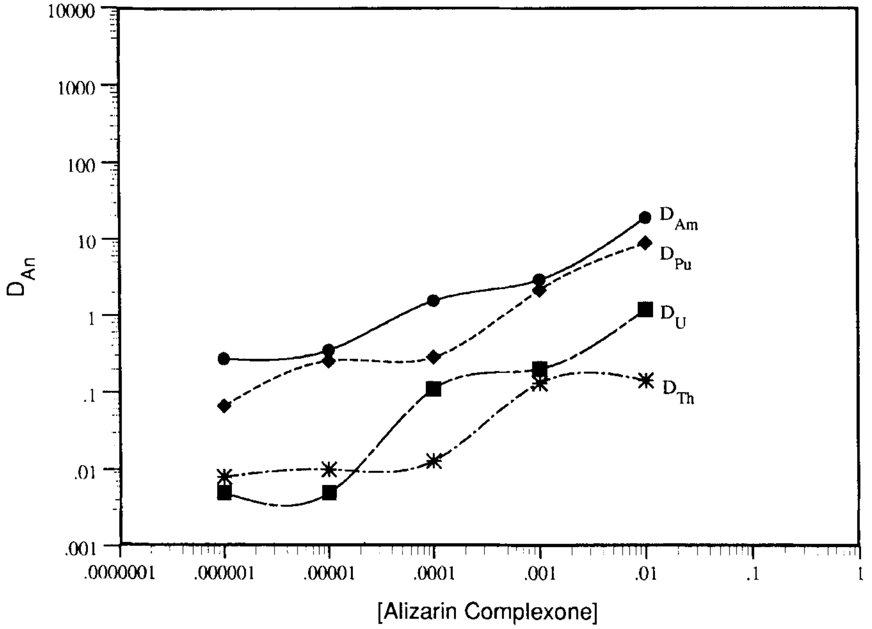

FIGURE 5. $D_{An}$ vs. [Alizarin Complexone] for the $K_2CO_3$/PEG-2000 System.

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Xylenol Orange

At low concentrations of xylenol orange in sulfate media (Figure 6), the extractant dependencies are similar to those observed for alizarin complexone. D values for $Th^{4+}$ and $Pu^{4+}$ increase rapidly, while $D_U$ and $D_{Am}$ are essentially flat. As the concentration of xylenol orange is increased, however, the $D_{Th}$ and $D_{Pu}$ curves tail off, while $D_{Am}$ and $D_U$ increase until at 0.1M xylenol orange, $D_{Am}$ is actually the highest value.

Again, when changing from $SO_4^{2-}$ media to $CO_3^{2-}$ media, the $D_{Am}$ values go from lowest to highest (Figure 7). The remaining three metals show virtually no extraction dependence and are not extracted. Our results indicate much higher $D_{Am}$ values than reported in reference 10 ($D_{Am}$ = 32.7 for 2 x $10^{-2}$M xylenol orange in reference 10).

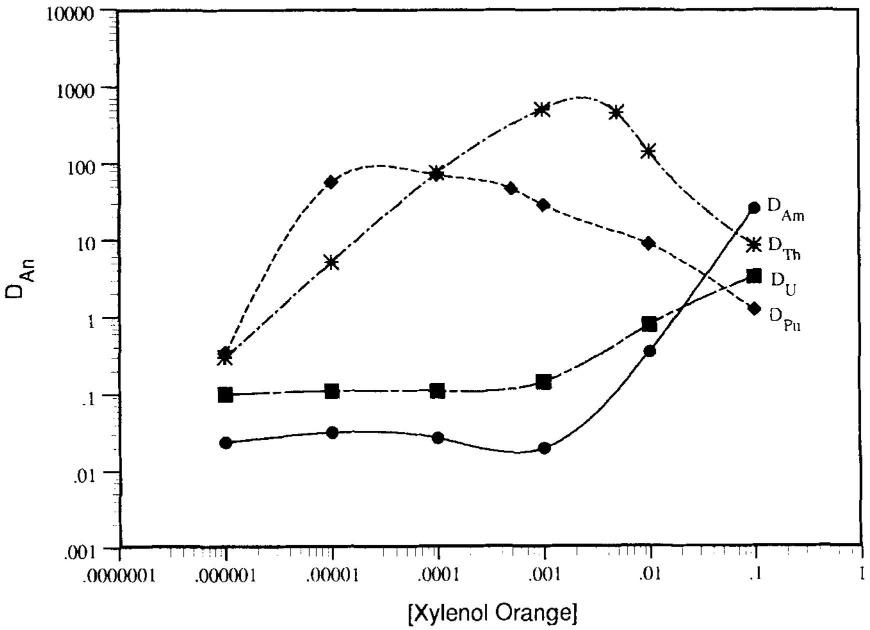

FIGURE 6. $D_{An}$ vs. [Xylenol Orange] for the $(NH_4)_2SO_4$/PEG-2000 System.

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## pH Dependence

A tremendous amount of research could be carried out investigating these three extractants as a function of pH. Several reports in the literature (7,8,11) suggest pH to be a critical factor in determining the distribution ratios. Optimization of pH could lead to useful systems for the separation of similar metal ions.

We have briefly investigated the effects of base and acid on the D values obtained for the $(NH_4)_2SO_4$ system. The effects of base were studied by preparing each stock solution in 1M $NH_4OH$, while acid side studies were conducted in 3M $H_2SO_4$.

Our results are presented in Table 2. It is clear that acid strips the metal ions from the PEG phase and this could serve as a

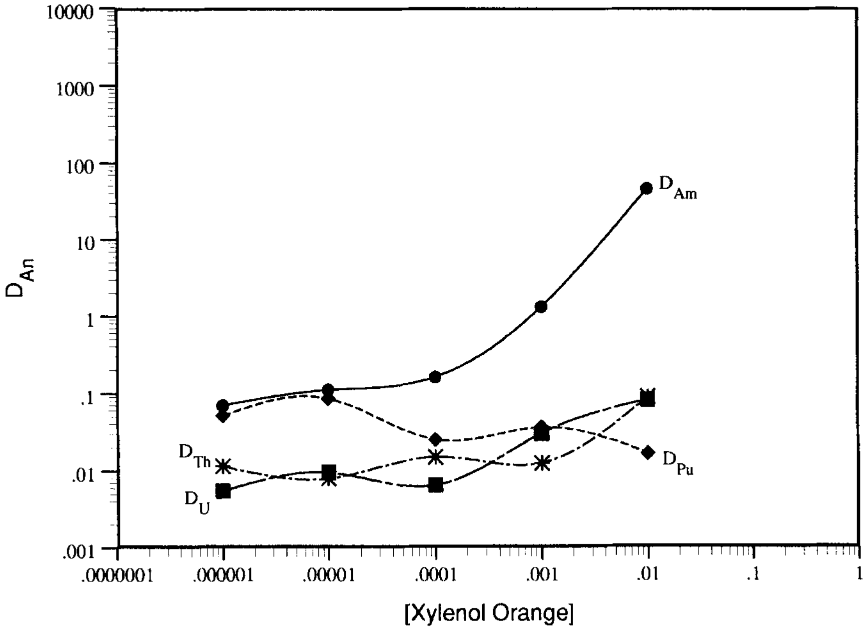

FIGURE 7. $D_{An}$ vs. [Xylenol Orange] for the $K_2CO_3$/PEG-2000 System.

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reasonable strip stage in any separations process. The effect of 1M $NH_4OH$ is less clear, although in general the D values are higher when base is used. There are four exceptions to this, three of which involve arsenazo III. D values above one are still observed but much lower than the values of 250-870 found without base.

We have been investigating the effects of both acid and base on the biphasic system itself and have observed clues to system behavior that must be fully detailed before the effects of pH can be clearly sorted out. First, high acid concentrations tend to move the binodial toward higher compositions and thus tend to destroy the biphase. The hydroxide ion on the other hand forms a

TABLE 2. THE EFFECTS OF $H_2SO_4$ AND $NH_4OH$ ON $D_{An}$ FOR THE $(NH_4)_2SO_4$/PEG-2000 SYSTEM

| Metal Ion | Extractant | Extractant Concentration,M | $D_{An}$ Aqueous | 3M $H_2SO_4$ | 1M $NH_4OH$ |
|---|---|---|---|---|---|
| $Am^{3+}$ | alizarin complexone | $1.0 \times 10^{-3}$ | 0.10 | 0.093 | 84 |
| $Am^{3+}$ | xylenol orange | $1.0 \times 10^{-3}$ | 0.020 | 0.099 | 79 |
| $Am^{3+}$ | arsenazo III | $5.0 \times 10^{-4}$ | 0.38 | 0.099 | 4.4 |
| $Pu^{4+}$ | alizarin complexone | $1.0 \times 10^{-3}$ | 280 | 0.076 | 400 |
| $Pu^{4+}$ | xylenol orange | $1.0 \times 10^{-3}$ | 28 | 0.070 | 37 |
| $Pu^{4+}$ | arsenazo III | $5.0 \times 10^{-4}$ | 440 | 0.064 | 4.3 |
| $UO_2^{2+}$ | alizarin complexone | $1.0 \times 10^{-3}$ | 0.30 | 0.19 | 100 |
| $UO_2^{2+}$ | xylenol orange | $1.0 \times 10^{-3}$ | 0.14 | 0.19 | 3.0 |
| $UO_2^{2+}$ | arsenazo III | $5.0 \times 10^{-4}$ | 250 | 0.20 | 17 |
| $Th^{4+}$ | alizarin complexone | $1.0 \times 10^{-3}$ | 610 | 0.070 | 440 |
| $Th^{4+}$ | xylenol orange | $1.0 \times 10^{-3}$ | 510 | 0.075 | 1.6 |
| $Th^{4+}$ | arsenazo III | $5.0 \times 10^{-4}$ | 870 | 0.086 | 14 |

biphase by itself and thus serves to salt out more of the PEG. Both effects must be considered in future evaluation of pH effects.

## CONCLUSIONS

We have demonstrated the possibility of actinide extraction and separation using aqueous biphasic systems based on PEGs. Our results complement the limited data available in the Russian literature. The use of complexing dyes, however, negates many of

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the advantages (e.g., the dyes may be expensive and toxic) of aqueous biphasic systems, and further work in this area should focus on finding other viable $H_2O$ soluble complexing agents.

While we will continue to study this area as time allows, our focus will shift to areas where the unique properties of aqueous biphasic systems present unique opportunities for extraction (i.e., where oil/$H_2O$ compositions are unworkable or undesirable). The areas currently under investigation include extraction of metal ions via the addition of an inorganic anion, extraction from highly alkaline media, and extraction directly into the PEG-rich phase without the addition of any complexant or complexing anion.

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