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METAL SEPARATIONS USING AQUEOUS BIPHASIC PARTITIONING SYSTEMS*

D. J. Chaiko, B. Zaslavsky, A. N. Rollins†, Y. Vojta, J. Gartelmann, and W. Mego

Argonne National Laboratory
Chemical Technology Division
9700 South Cass Avenue
Argonne, Illinois 60439-4837

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Abstract

Aqueous biphasic extraction (ABE) processes offer the potential for low-cost, highly selective separations. This countercurrent extraction technique involves selective partitioning of either dissolved solutes or ultrafine particulates between two immiscible aqueous phases. The extraction systems that we have studied are generated by combining an aqueous salt solution with an aqueous polymer solution.

We have examined a wide range of applications for ABE, including the treatment of solid and liquid nuclear wastes, decontamination of soils, and processing of mineral ores. We have also conducted fundamental studies of solution microstructure using small angle neutron scattering (SANS). In this chapter we review the physicochemical fundamentals of aqueous biphase formation and discuss the development and scaleup of ABE processes for environmental remediation.

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Introduction

Aqueous biphasic extraction (ABE) is a highly adaptable separation technique that can be used in a wide range of applications. We have been evaluating various types of ABE systems for possible applications in the treatment of solid radioactive wastes (1,2), liquid nuclear wastes (3,4), and contaminated soils (5-7), and in the removal of organics from aqueous salt solutions (8). We have also conducted fundamental studies of the solution microstructure of ABE systems using small angle neutron scattering (SANS) (9).

The extraction systems are generated by combining an aqueous salt solution and an aqueous polymer solution. This produces two distinct liquid layers that are as immiscible as oil and water, yet each liquid layer contains at least 70 to 80 wt % water. The biphasic systems that we have been working with consist of immiscible polyethylene glycol (PEG) and salt solutions. Some inorganic salts that promote biphase formation with PEG solutions include the sodium/potassium salts of sulfate, carbonate, phosphate, and hydroxide (10).

The selective partitioning of particulates in ABE systems is based on physicochemical interactions between the particle surface and the liquid phases, rather than on bulk phase properties such as density. Consequently, particle size should be small enough that particle settling due to gravity is low compared to the rate of liquid/liquid phase separation. In general, we have found that an upper size limit of about 150-200 μm can be accommodated during continuous, countercurrent extractions (6,7).

Bench-scale tests have shown that, in general, ultrafine metal oxide particulates (such as PuO_2, UO_2, CeO_2, Fe_2O_3, TiO_2, and Al_2O_3) partition preferentially into the salt-rich phase in PEG/salt systems (1). The only exceptions to this partitioning behavior that we have found so far are the crystalline silicates (e.g., quartz and cristobalite), layered silicates (e.g., clays such as kaolinite and montmorillonite), and glass. Clays partition into the PEG-rich phase with partition coefficients of about 100, regardless of pH (we looked at pH values ranging from 2 to 12). On the other hand, the partition behavior of crystalline silicates and glass depends on the degree of surface ionization. At pH values near the point-of-zero charge (PZC), these materials partition into the PEG-rich phase, while partitioning into the salt-rich phase occurs when the pH is either above or below the PZC (11).

When contaminated soil is being treated, the fine soil particles (-100 mesh) are suspended in the aqueous polymer solution (e.g., polyethylene glycol), which is then contacted in a countercurrent fashion with an aqueous salt solution (e.g., sodium carbonate). The liquid/liquid extraction is carried out in a Karr column because of the ability to handle solids without blockage. During the liquid/liquid contact, heavy-metal contaminants, such as uranium and thorium, are selectively partitioned from the polymer solution to the salt solution, while the cleaned soil particles remain dispersed in the polymer phase. Typically, 99 to 99.5% of the soil can be recovered in the cleaned soil fraction while only 0.5 to 1% of the soil feed is recovered in the contaminant concentrate (5-7).

In addition to pH, phase transfer agents (PTAs) can be used to alter the partitioning behavior of ultrafine particulates (10). For example, water-soluble complexants, such as arsenazo III, can be used to selectively transfer PuO_2 or UO_2 particles from the salt-rich phase into the PEG-rich phase (1,2). In general, the partition coefficients of metal ions, including silicic acid, are in the range of 0.1-0.5 (6,9). However, complex species that possess a significant rotational contribution to the entropy loss of water during solvation, like polymeric plutonium and uranyl carbonate, exhibit extremely low partition coefficients, in the range of 0.001 to 0.01 (9).

One can use water-soluble complexants to selectively extract the metal ions from high-ionic-strength salt solutions into a PEG-rich phase. In this regard, ABE systems are analogous to conventional oil/water extraction systems. But, unlike conventional solvent extraction systems, the two immiscible phases in an ABE system share a common diluent -- water. Therefore, the potential for process upset due to excess mass transfer of water must be carefully considered. If one wishes to prevent the net mass transfer of water between the liquid phases, the polymer-rich and salt-rich phases can be contacted at compositions defined by the tie lines from the appropriate polymer/salt/water phase diagram.

In the scaleup of an ABE process, the rate of phase separation becomes an important system characteristic that directly impacts extraction efficiency. We have found that phase separation times for the biphase systems we are evaluating are comparable with typical values of oil/water solvent extraction systems (1,6). Thus, the ABE systems described in this chapter are compatible with conventional contacting equipment, such as mixer/settlers, pulsed columns, and centrifugal contactors.

In this chapter, we review the physicochemical factors leading to biphase formation in aqueous polymer/salt systems and present an advanced extraction flowsheet, which includes the back extraction of metal ions from PEG-rich phases, together with the recovery and recycle of PEG.

Experimental Details

Materials

Polyethylene glycol (PEG) of various molecular weights (MWs) and methoxypolyethylene glycol (mPEG) (MW = 5,000) were purchased from Aldrich Chemicals and Sigma, respectively. In addition, a branched PEG (bPEG) (8 arms, MW = 10,000) was purchased from Shearwater Polymers, while polyvinylpyrrolidone (PVP) (MW = 10,000) was purchased from Aldrich Chemicals. Inorganic salts were purchased from either Fisher Scientific, Aldrich Chemicals, or Malinckrodt. All were of analytical reagent grade. The anion exchange resin, AG-MP1 (Cl-form) was purchased from Bio-Rad, while arsenazo III [2,2'-(1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo)bisbenzenearsonic acid] and chlorophosphonazo III [2,7-bis(4-chloro-2-phosphonbenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid] were purchased from Aldrich Chemicals and Fluka, respectively. Deionized (18 MΩ-cm) water was prepared using a Barnstead E-Pure ion-exchange unit.

Measurements

Cloud Point Measurements. The cloud points in aqueous PEG/salt solutions were measured over the temperature range of 20 to 85°C, using sealed glass test tubes immersed in a thermostated water bath that was regulated to within 0.1°C. The samples were allowed to equilibrate at least 20 to 30 min between incremental adjustments in temperature. The polymer concentration in all measurements was fixed at 10 wt %.

Partition Measurements. The partition coefficients for Pu(IV), PEG, n-butanol, carbonate, and sulfate in various liquid/liquid systems were measured using ^{239}Pu, ^{3}H-labeled PEG-4000, ^{14}C-labeled n-butanol and carbonate, and ^{34}S-labeled sulfate, respectively. The partition coefficients, or D values, for the ^{239}Pu radiotracer and the radiolabeled species were determined by counting the activity present in aliquots of each liquid phase by liquid scintillation counting using Ultima Gold scintillation cocktail (Packard) and a Packard 2200 CA scintillation counter.

The $^{239}Pu(IV)$ stock solution was prepared using the following procedure. A 200 μL aliquot of a 0.023 M ^{239}Pu solution in 3 M HNO_3 was added to 600 μL of 6 M HNO_3, capped, and left to equilibrate at room temperature overnight. This procedure was performed to convert any plutonium in the +3 and +6 oxidation states to the tetravalent state (12). An anion exchange column was prepared by slurrying 0.20 g of AG-MP1 resin in 2 mL of water and then pouring the slurry into a glass Pasteur pipet containing a glass wool plug. The resin was converted from the chloride form to the nitrate form by consecutive additions of five, 1-mL aliquots of 8 M HNO_3 to the column. The ^{239}Pu solution, prepared the previous day, was then loaded onto the ion-exchange resin. The Pu(IV) was retained in a thin green band at the top of the column. The column was then washed with five, 1-mL aliquots of 8 M HNO_3 to remove any ^{239}Pu daughter products as well as plutonium in any oxidation state other than +4. The remaining Pu was stripped from the column with 5 mL of 1 M HCl. The Pu/HCl solution was converted to a HNO_3 solution by slowly evaporating the HCl solution with intermittent additions of 6 M HNO_3 until approximately 150 μL of a dark-green solution remained. The volume was then increased to about 1.15 mL by the addition of 1 mL of 6 M HNO_3. The percentage of ^{239}Pu and daughter product impurities in the stock solution was determined by preparing another anion exchange column (AG-MP1) and performing the same separation as described above, using a 10 μL aliquot of the ^{239}Pu solution in 6 M HNO_3. Since only the green hexanitrato $[Pu(NO_3)_6^{2-}]$ complex is retained on the column (13), the fraction of tetravalent plutonium relative to other oxidation states and the daughter products can be estimated from the fraction of the activity retained in the column. From this procedure, we estimate the purity of the $^{239}Pu(IV)$ radiotracer to be 99.93%.

Results and Discussion

Biphase Formation in PEG/Salt Systems

In collaboration with the Argonne National Laboratory (ANL) Intense Pulsed Neutron Source (IPNS) and the Los Alamos Neutron Science Center, we carried out small angle neutron scattering studies of various PEG/salt solutions (9). In addition, anion effects on biphase formation were investigated by cloud point measurements in H_2O and D_2O. In the presence of $NaNO_3$ (i.e., a salt that does not promote biphase formation at room temperature), PEG behaves like a random coil with no evidence of aggregation, whereas the presence of either Na_3PO_4 or Na_2CO_3 (i.e., salts that promote biphase formation at room temperature) leads to aggregate formation. The aggregate size increased with increasing salt concentration until a discontinuity appeared at the point of biphase formation, where the polymer in the PEG-rich phase forms an entangled mesh with loss of chain identity. In the monophasic regime, the aggregates were elongated with a radius of approximately 19 Å and a length which varied with salt type and concentration and polymer molecular weight (9).

It was first shown by Ananthapadmanabhan and Goddard (10,14,15) that phase separation in PEG/salt/water systems is similar to the well-known phenomenon of clouding that occurs in polymer solutions on heating (16). Clouding in aqueous PEG solutions containing different inorganic salts was examined by Bailey and Callard (17) and Florin et al. (18), and clouding in salt-containing aqueous PVP solutions was reported by Sekikawa et al. (19) and Guner and Ataman (20). All these authors reported that the salt effect on the suppression of the cloud point temperature of PEG and PVP in aqueous solutions follows the lyotropic series. It was shown, in particular, that the salt effect on the cloud point of aqueous PEG solution correlates linearly with the salt molal surface tension increment, suggested by Melander and Horvath (21) as a measure of the salt influence on water structure.

More recently, our analysis of the effects of electrolytes on the cloud points of PEG in H_2O and D_2O suggests that the PEG phase behavior in solution is entropy driven. We have found that the cloud point lowering of PEG by inorganic salts correlates linearly with the change in water entropy (ΔS_{II}) upon the addition of electrolytes (9). Salt effects on cloud points and biphase formation follow the well-known Hofmeister series (9). Anions leading to increased structuring of water lower the cloud point. This is illustrated in Figure 1, in which the cloud points (T_{CP}) for 10 wt % PEG-10,000 solutions are plotted as a function of salt type and concentration. The data can be described by the following equation:

$$T_{CP} = T^{o}_{CP} + \sum \alpha_i C_i \qquad (1)$$

where T_{CP} is the cloud point of the polymer/salt solution, and α_i is the slope of the straight line relating the change in cloud point with the concentration (C_i) of salt *i*. The cloud point of the salt-free polymer solution (T^{o}_{CP}) can be estimated by extrapolating the straight line fit of the data to zero salt concentration. The T^{o}_{CP} value of 125 $\pm$ 1 °C for a 10 wt % PEG-10,000 solution agrees well with the value reported by Bae et al. (22).

The measured and calculated values of T_{cp} for 10 wt % PEG-10,000 solutions containing various mixtures of Na_3PO_4 and Na_2SO_4 are shown in Table I. The good agreement between the calculated and measured cloud points suggests that, at least for the two salts examined, the salt effects are additive.

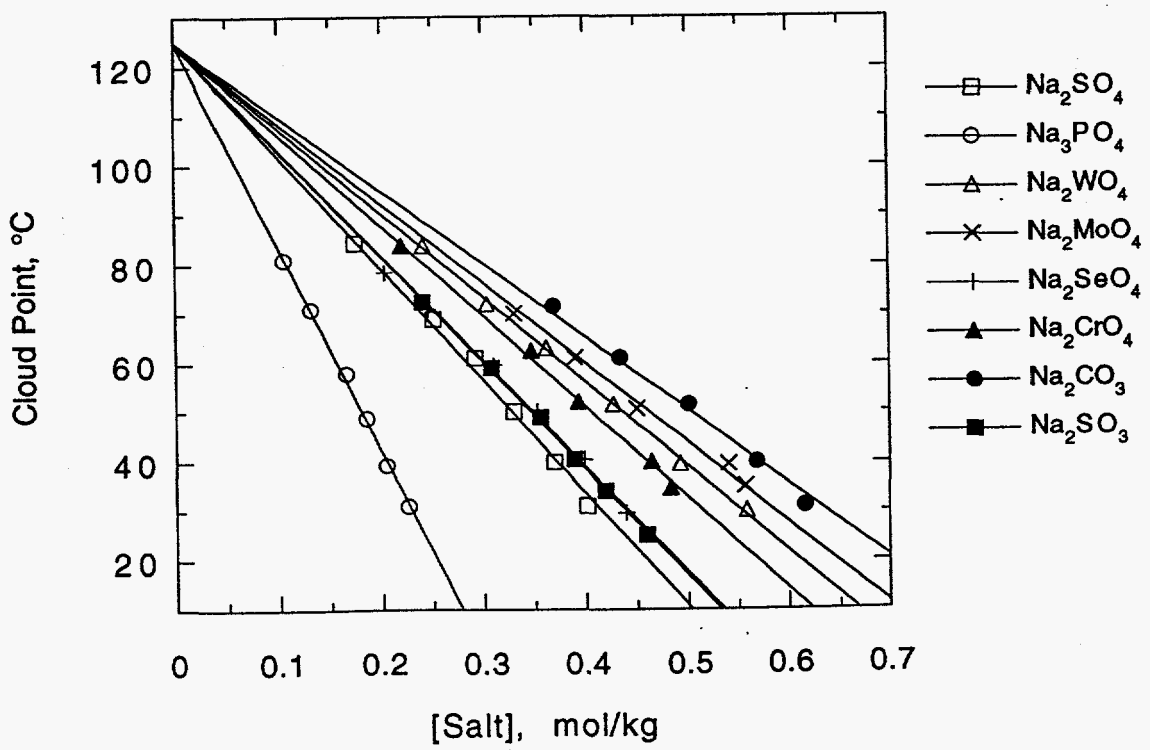

Figure 1 - Effects of salt type and concentration on the cloud point of PEG-10,000. T^{o}_{CP} = 125 $\pm$ 1 °C.

Table I Cloud Points of 10 wt% PEG-10,000 Solutions Containing Salt Mixtures*

$[Na_3PO_4]$, mol/kg	$[Na_2SO_4]$, mol/kg	T_{CP}, °C	
		Experimental	Calculated
0.071	0.290	28.0	28.8
0.067	0.273	35.0	34.4
0.062	0.252	40.0	41.3
0.055	0.224	50.0	50.7
0.041	0.167	70.0	69.7

*The values of T_{CP} were calculated using Eq 1 and the appropriate values of α_i, which are 414.6 $\pm$ 3.8 °C kg/mol and 231.6 $\pm$ 4.9 °C kg/mol for Na_3PO_4 and Na_2SO_4, respectively.

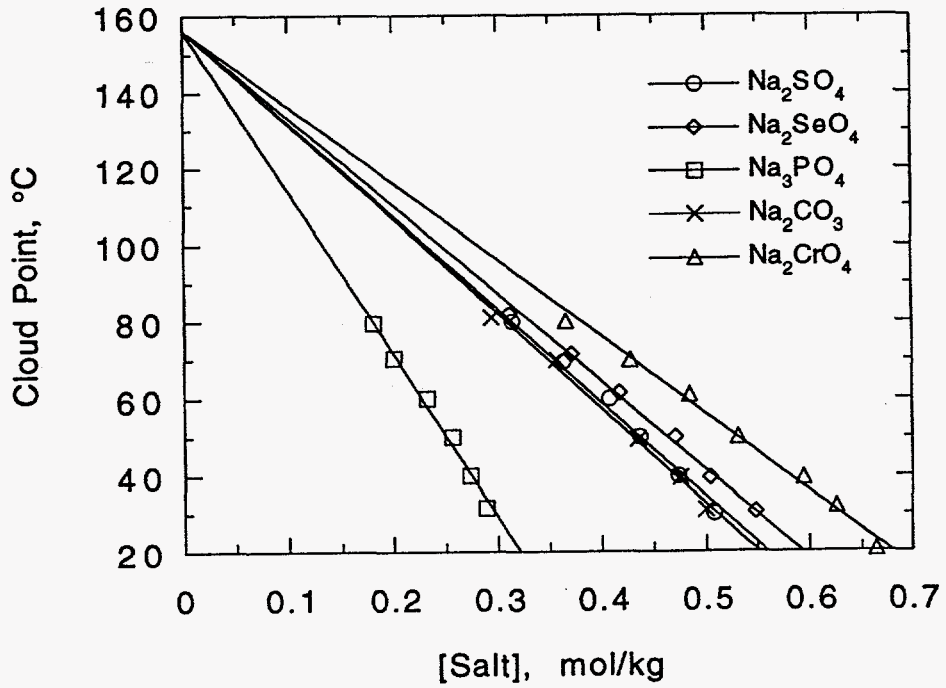

Figure 2 - Effect of salt type and concentration on the cloud points of 10 wt % bPEG-10,000. $T^{o}_{CP} = 156 \pm 4$ °C.

We have begun to expand our studies to include cation effects, polymer structures (e.g., linear versus branches), and type on cloud points and biphase formation. Thus far, we have found that the effects of biphase-forming salts (e.g., Na_3PO_4, Na_2CO_3, Na_2SO_4, Na_2SO_3, Na_2CrO_4, Na_2WO_4, and Na_2MoO_4) on the cloud points of bPEG and PVP correlate linearly (see Figures 2 and 3) with salt concentration in a manner similar to that observed for PEG.

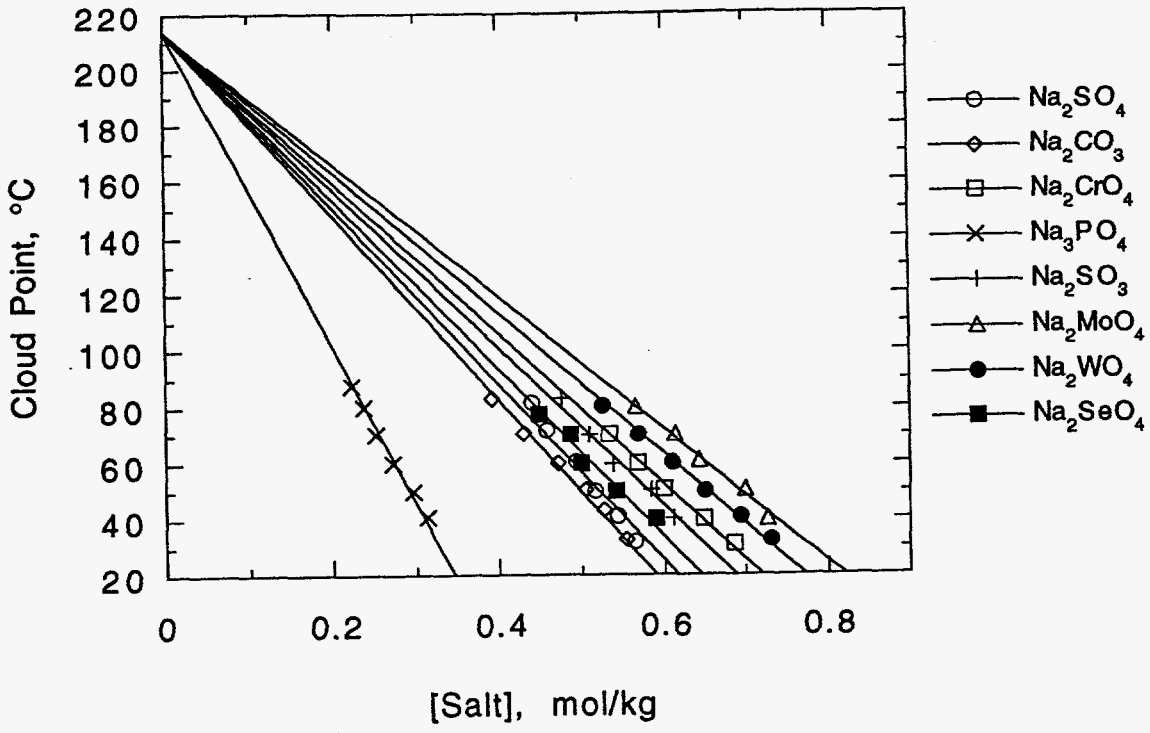

Figure 3 - Effect of salt type and concentration on the cloud points of 10 wt % PVP-10,000. $T°_{CP} = 214 \pm 16°C$.

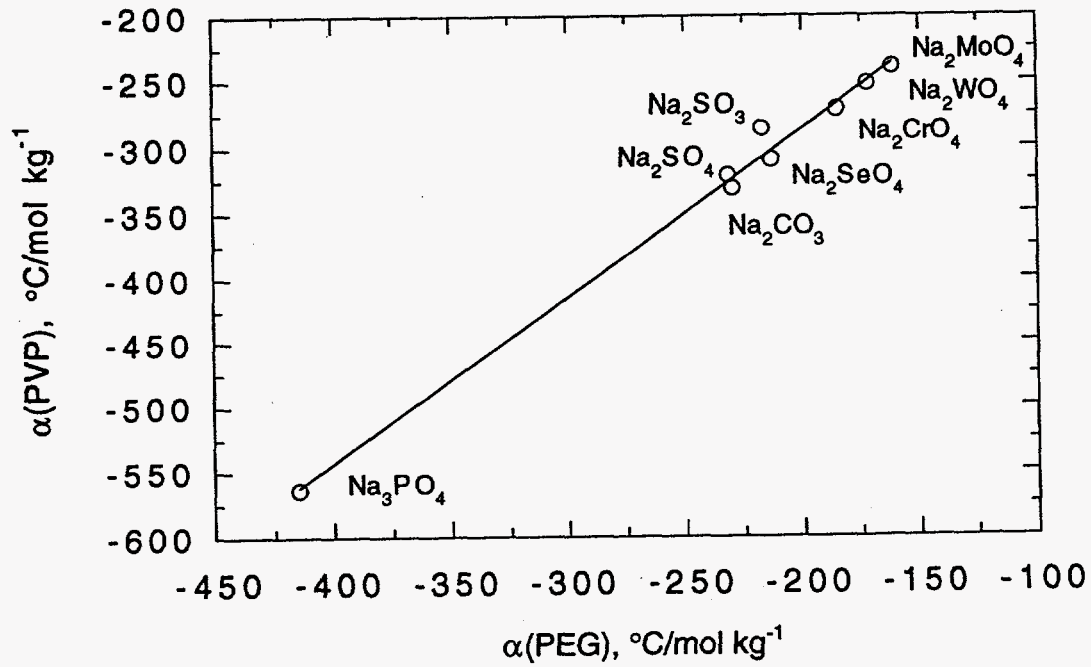

Figure 4 - Relationship between the rate of cloud point lowering (α_i) for PEG-10,000 and PVP-10,000 in different polymer/salt systems.

The α_i values for the linear and bPEGs are very similar, implying that the conformation of the polymer chain (e.g., linear or branched) is not the dominant factor in salt-induced clouding and aqueous biphase formation. This contradicts the view of Karlstrom (23), who presented a thermodynamic model for predicting critical solution temperatures in polyethylene oxide (PEO)/salt solutions. The model was based on the assumption that the temperature-dependent conformation of PEO and its effects on the van der Waal's attraction between PEO molecules was predominantly responsible for the observed phase diagrams.

Our view is that increased structuring of water by lyotropic ions provides the driving force behind the observed aggregation and phase separation in PEG, PVP/salt systems. A comparison of the α_i values for PEG-10,000 and PVP-10,000 is shown in Figure 4. The linear relationship, again, suggests that the phase behavior of PEG and PVP is dominated by the influence of salt on the water structure. The difference in T_{CP} values between PEG and PVP at any given salt concentration reflects the influence of the polymer on the water structure.

Metal Separations

A major difficulty encountered when designing ABE systems for metal ion extraction has been an inability to efficiently back extract solutes from the polymer-rich phase. This is primarily due to the fact that relatively high salt concentrations are required to maintain the aqueous biphase system. The phase diagram for the PEG-10,000/Na_2SO_4 system illustrates this point (see Figure 5). Proposed flowsheets that involve treating the loaded, polymer phase with ion-exchange resins (24) or back extraction into secondary, salt-rich phases (25) are inefficient and generate significant amounts of waste.

To address these shortcomings, we have been investigating the use of an alternative approach to back extraction that significantly reduces secondary waste generation. Below, we illustrate the key elements of these advanced flowsheets, which take advantage of the temperature-driven partitioning behavior of high-molecular-weight PEGs in organic/water systems.

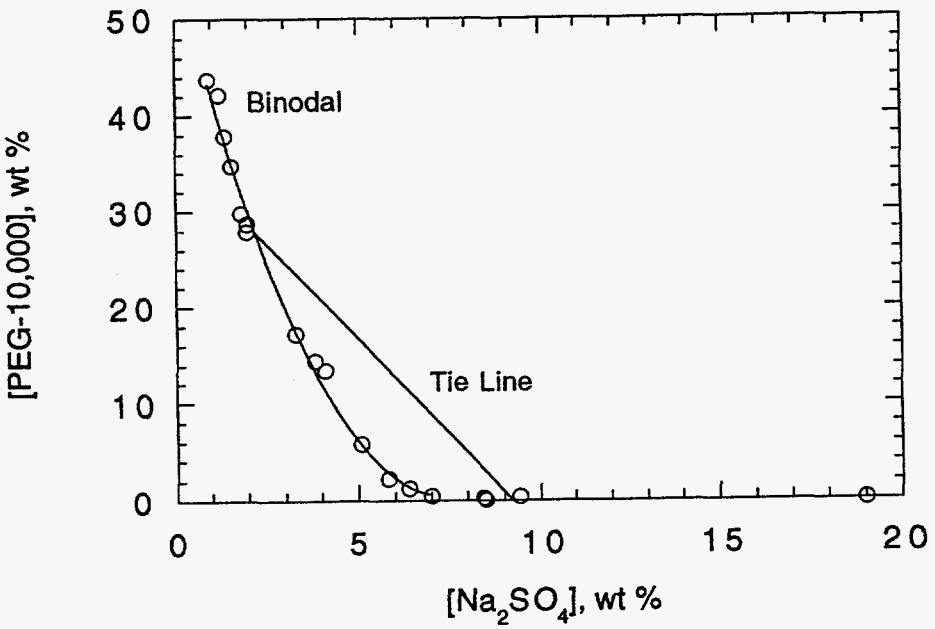

Figure 5 - Phase diagram for the PEG-10,000/Na_2SO_4 system at 60°C.

Certain metal ions can be selectively extracted from high-ionic-strength salt solutions directly into a PEG-rich phase. The extraction of pertechnetate (TcO_4^-) from Hanford Tank supernatants is an example (4,24,25) of quantitative partitioning of metal ions into PEG-rich phases. Thus, the separation of pertechnetate from a broad range of anions (e.g., NO_3^-, NO_2^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}) can be achieved by countercurrent extraction using aqueous PEG solutions without the need for complexants (or extractants) as in conventional oil/water solvent extraction systems (4).

However, the more common situation is one in which the metal ions do not possess any special affinity for the polymer phase In this case, complexants can be used to achieve selective partitioning. But unlike conventional oil/water solvent extraction systems, both the extractants and their metal complexes must be water soluble since both phases in ABE systems are aqueous.

In general, complexants containing sulfonated aromatic rings are quantitatively extracted into PEG-rich phases (2,26). Two examples of complexants that are compatible with ABE systems are arsenazo III and chlorophosphonazo III (see Figure 6 for chemical structures). In studies of plutonium(IV) extraction, excellent extraction performance was obtained at low extractant concentrations (e.g., 0.005-0.01 wt %), giving D_{Pu} values well in excess of 100 (see Figures 7 and 8).

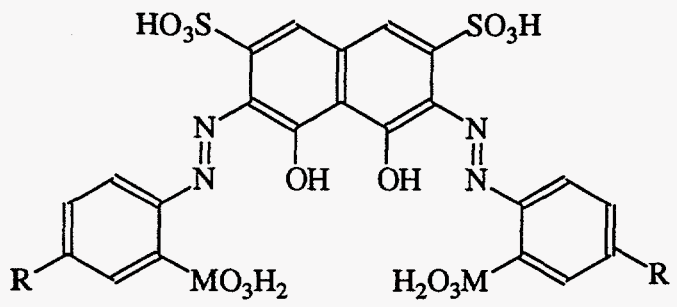

Figure 6 - Chemical structures of arsenazo III and chlorophosphonazo III; R = H, M = As for arsenazo III; R = Cl, M = P for chlorophosphonazo III.

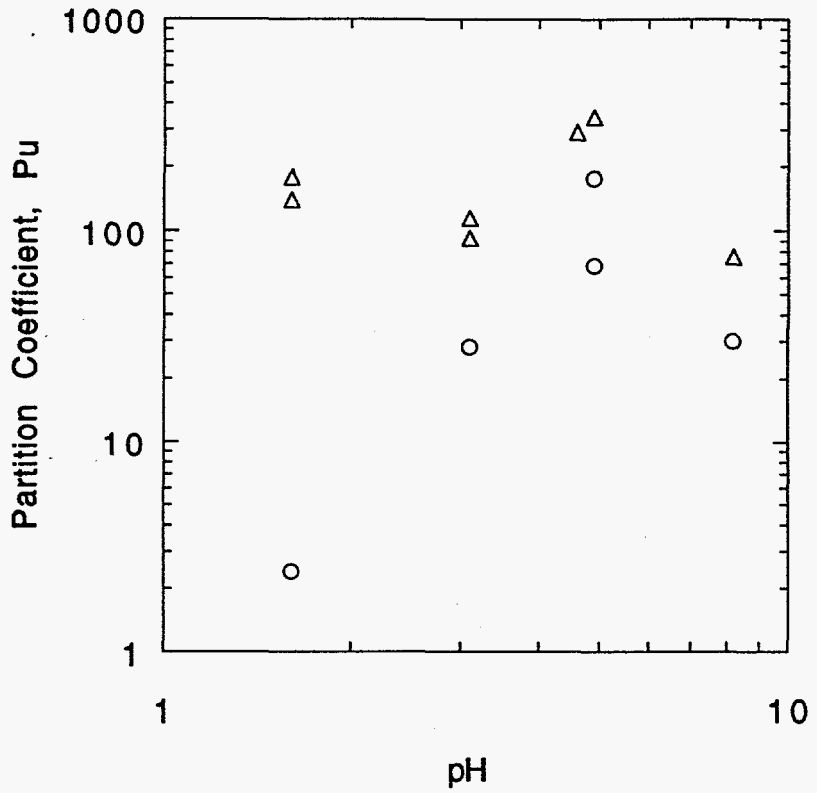

Figure 7 - Extraction of Pu(IV) by Arsenazo III (O's) and Chlorophosphonazo III (Δ's) as a function of PEG-phase pH in the PEG-3400/$(NH_4)_2SO_4$ system at 25°C. Extractant concentrations were 0.0075 wt %.

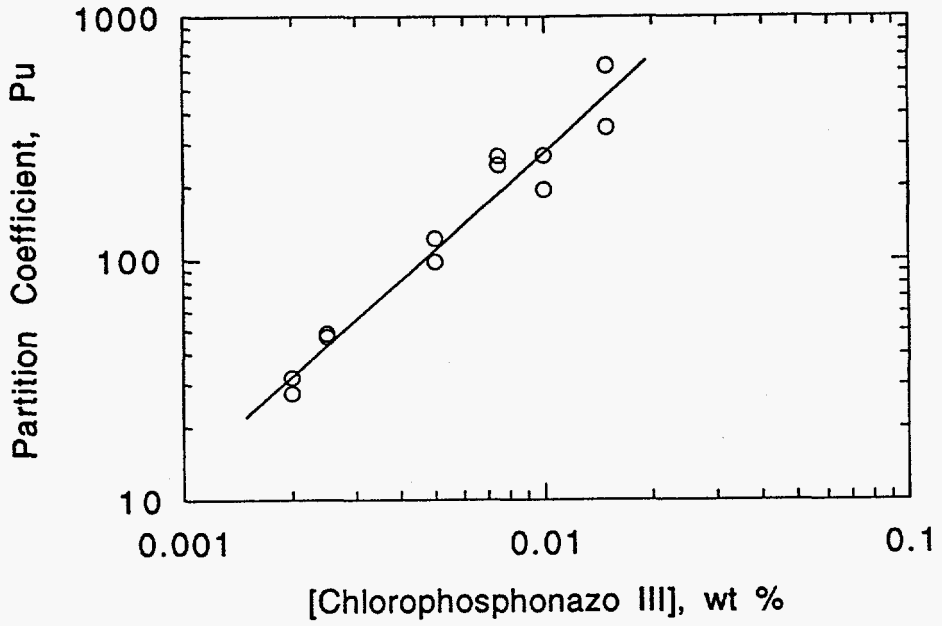

Figure 8 - Extraction of Pu(IV) as a function of chlorophosphonazo III concentration in the PEG-3400/$(NH_4)_2SO_4$ system at 25°C.

Recovery of the extracted metal complex can be achieved by contacting the loaded PEG-rich phase with a water-immiscible alcohol phase (e.g., butanol, or pentanol if using mPEG) at elevated temperatures. The elevated temperature (e.g., 60-80°C) provides the thermodynamic driving force for the selective partitioning of the PEG from the aqueous phase into the alcohol phase. The partition coefficient for PEG-4000 in the n-butanol/water/salt/PEG system is ≥ 15, while the partition coefficient for the salts is $\leq 10^{-3}$ (see Table II). The mass transfer of PEG into the alcohol phase results in significant phase volume change so that even though the partition coefficient for PEG is marginal, we still achieve >99.4% PEG recovery. In general, increasing temperature and PEG molecular weight leads to more favorable partitioning of the polymer into the alcohol phase. Partition data for the butanol/water system are summarized in Table II. It should be remembered that, to a certain extent, the partition coefficients depend on the concentrations of PEG and salt, which, in turn, will be a function of the tie line chosen for the aqueous biphasic system.

The polymer can be recovered from the alcohol phase by back extraction into a dilute salt solution at low temperature. The tie-line composition of the polymer-rich phase from the PEG/salt/water phase diagram can be used as a guide in choosing the appropriate salt composition for this back extraction step. Partition coefficients for PEG-4000 and n-butanol during back extraction are given in Tables III and IV, respectively.

Table II Partitioning in the n-Butonal/Water/Sulfate/PEG System at 60°C

Species	Partition Coefficient*
PEG-4000	~15
PEG-10,000	~35
Sulfate	0.001
n-Butanol	12.7

*The PEG phase was prepared by equilibrating equal volumes of 15 wt % PEG-3400 and 12 wt % Na_2SO_4 solution at 60°C. An initial phase volume ratio of butanol/PEG solution of 1 produced an equilibrium phase volume ratio of 5.

Table III Back Extraction of PEG-4000 from n-Butanol

$[Na_2SO_4]$, wt %	PEG-4000 Partition Coefficient	
	20°C	5°C
0	0.048	0.025
0.01	0.044	0.028
0.05	0.047	0.028

Table IV Partitioning of n-Butanol during Back Extraction of PEG

$[Na_2SO_4]$, wt %	n-Butanol Partition Coefficient	
	20°C	5°C
0	10.1	10.4
0.01	10.4	--
1.0	10.9	11.0
5.0	--	13.5

The data in Tables III and IV show that temperature is the primary factor in determining partitioning behavior of the polymer. As in the forward extraction, there is also a large phase volume change during back extraction due to the mass transfer of large amounts of polymer. For the three cases listed in Table III, initial phase volume ratios (polymer-to-a salt) of one produced, at equilibrium, phase volume ratios of 0.3.

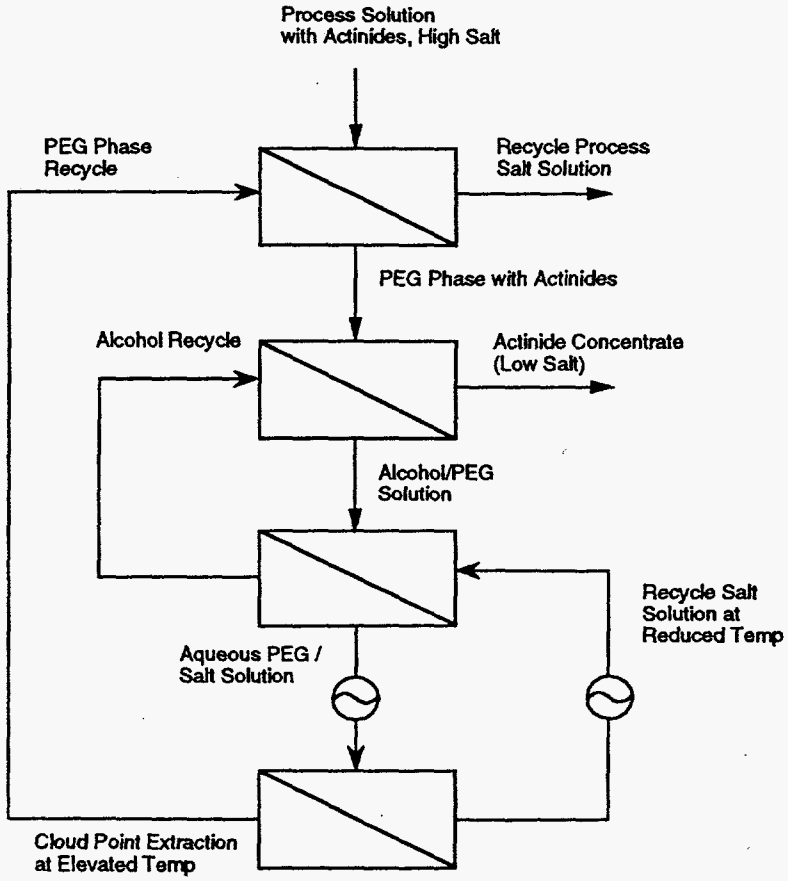

Figure 9 - ABE flowsheet for actinide removal from high-ionic-strength salt solutions.

An example flowsheet for the removal of actinides from high-ionic-strength salt solutions, similar to those used in the decontamination of concrete surfaces (27), is shown in Figure 9. Prior to the first extraction section, chlorophosphonazo III would be added to the salt stream at a concentration of 0.005-0.01 wt % to selectively complex the actinides (e.g., Pu^{4+}, UO_2^{2+}, Th^{4+}). In the first extraction section, any excess chlorophosphonazo III and the complexed actinides are extracted into the PEG-rich phase. This produces an actinide-free salt solution that can be recycled back to the decontamination operation. The net result of the first two extraction sections in Figure 9 is the production of an aqueous stream in which the actinide concentrations increase while the salt concentration decreases. The actinide concentrate can then be sent directly to a vitrification process prior to final disposal.

In the last section of the flowsheet (see Figure 9) a cloud point extraction is used to generate a polymer solution for recycle. This is achieved by raising the temperature of the polymer/salt solution above its cloud point, causing it to split into two phases -- a polymer-rich phase and a salt-rich phase. Both solutions can then be recycled, as shown in Figure 9.

Summary and Conclusions

In this chapter, we have briefly reviewed some of the results from our studies of biphase formation and partitioning in ABE systems. From SANS measurements, we know that the presence of biphase-forming salts (e.g., Na_2CO_3, Na_2SO_4, Na_3PO_4) leads to the formation of PEG aggregates, whose length increases with increasing salt concentration up to the consolute point. The SANS measurements, coupled with cloud point data in H_2O and D_2O, suggest that increased structuring of water by lyotropic ions provides the driving force behind polymer aggregation and phase separation.

In this chapter, we also described a new approach to solute stripping from ABE systems that utilizes the temperature-dependent partitioning of polymers, like polyethylene glycol and methoxypolyethylene gylcol, in water/alcohol systems. An example flowsheet was presented which offers an inexpensive approach to radionuclide removal from process solutions used in decontamination operations. It is especially attractive for the treatment of process solutions that contain high concentrations of salts, like sodium carbonate, sulfate, or phosphate. The technology permits metal recovery under conditions that, because of high salt concentration, are not amenable to treatment by ion exchange. Because of the highly efficient extracting ability of the ABE system, waste volume reductions of at least 100-fold can be expected.

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