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Partitioning of Polymeric Plutonium(IV) in Winsor II Microemulsion Systems

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Partitioning of Polymeric Plutonium(IV) in Winsor II Microemulsion Systems

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Abstract

The hydrolysis and polymerization of Pu(IV) can cause serious problems during the aqueous processing of spent fuel and nuclear wastes. Several studies describing the liquid/liquid extraction behavior of polymeric Pu(IV) have been reported in the literature. In many cases, poor plutonium extraction was accompanied by the appearance of an interfacial crud or third phase. Invariably, poor mass balances were observed during the extraction of aged, colloidal Pu(IV). Extraction of colloidal Pu(IV) by microemulsion-based solvent extraction systems, however, is capable of attaining bulk phase mass balances for Pu of 100%. The Winsor II microemulsions discussed in this paper consisted of sodium bis(2-ethylhexyl) sulfosuccinate in hexane with either octylphenyl-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide or tributyl phosphate as coextractant. Backextraction of plutonium from microemulsion phases was achieved by Pu encapsulation in silica particles that were produced by the acid-catalyzed hydrolysis and polymerization of tetraethoxysilane within the aqueous microdroplets of the microemulsion.

INTRODUCTION

The hydrolysis and polymerization of Pu(IV) can cause serious problems during the aqueous processing of spent fuel and nuclear wastes. The polymer is resistant to extraction by ion exchange and leads to emulsification and interfacial crud formation during solvent extraction (*1*). In aqueous solutions, the polymeric Pu(IV) species is easily distinguished from the monomeric Pu(IV) species by the intense green color of the polymer. The polymer exhibits a marked resistance toward depolymerization, which increases with aging at high temperatures or for extended periods of time at room temperature. The aging process is believed to involve the replacement of hydroxy bridges between Pu atoms by oxo bridges (*2*). The polymer carries a net positive charge and is readily adsorbed onto a wide variety

of surfaces (*3*). The reported molecular weight of polymeric Pu(IV) varies widely—from a low of about 4000 to a maximum of 10^{10} (*1*). Polymer formation is highly dependent on temperature, the concentrations of Pu(IV) and hydrogen ion, and the presence of other metal ions in solution (*1*, *4*).

The ability of Pu(IV) to form hydrous polymers is not unique. Other tetravalent ions (such as Zr, Hf, Ce, Th, and U) also form polymeric species. With the exception of U and Pu, however, the polymeric species are in equilibrium with low molecular weight intermediates. In the case of U and Pu, hydrolysis leads to very rapid polymerization, producing particles of colloidal dimensions that appear not to be in equilibrium with each other or with the monomeric species (*5*). The existence of hydrolyzed Pu dimers, trimers, and other such low molecular weight species has never been demonstrated experimentally (*1*, *5*).

Several studies concerning the partitioning of polymeric Pu(IV) in liquid/liquid extraction systems have been reported in the literature. Ockenden and Welch (*3*) found only negligible extractability of the polymer by dibutylcarbitol, trifluorothiophenoxylacetone, and tributyl phosphate (TBP). Each of these solvents is known to be effective for monomeric Pu(IV) extraction. Only dibutyl phosphate was able to promote reasonably high partition coefficients for polymeric Pu(IV). The authors also noted the formation of an interfacial crud during all of the partition experiments.

In a more recent study, Muscatello et al. (*6*) reported that the extraction of polymeric Pu(IV) could be achieved with the neutral extractant TOPO (trioctylphosphine oxide) and the bifunctional extractants DHDECMP (dihexyl-*N*,*N*-diethylcarbamoylmethyl phosphonate) and CMPO (octylphenyl-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide). However, poor Pu mass balances were observed during all extractions of aged Pu polymer, and extractions by DHDECMP were accompanied by severe emulsion and interfacial crud formation. The appearance of interfacial cruds has also been reported during the extraction of aged polymeric Pu(IV) with HDHoEP (bis(hexoxyethyl) hydrogen phosphate) and H_2MEHP (2-ethylhexyl dihydrogen phosphate) (*7*).

The use of water-in-oil microemulsion systems for the separation and recovery of metal ions (*8–10*), amino acids (*11–14*), and proteins (*15–18*) from aqueous solutions has received considerable attention over the past 10 years. And while the successful extraction of a hydrolyzed metal species ($FeOH^{2+}$) from weakly acidic solutions by a microemulsion system consisting of dinonylnaphthalene sulfonic acid (HDNNS) and 5,8-diethyl-7-hydroxy-6-dodecanone oxime has been reported (*19*, *20*), microemulsion-based solvent extraction systems have not previously been examined for possible applications in the separation and recovery of hydrous, polymeric species.

Because of the dynamic nature of reversed micelles, the interior aqueous phase and the surfactants are rapidly exchanged between interacting micelles and the macro oil/water interface (*21*, *22*). Thus, a mechanism exists for the direct transfer of hydrated species from the bulk aqueous phase to the aqueous micelle core. This feature permits protein extraction and separation while retaining the primary hydration shell surrounding the protein and thus preserving enzyme activity. Hydrous metal polymers represent yet another type of macromolecule for which microemulsion-based extraction systems may provide enhanced extraction performance.

In the present work, the partitioning behavior of polymeric Pu(IV) between aqueous HNO_3 solutions and organic phases containing the extractants CMPO and TBP was studied. The performance of these conventional solvent systems is compared with microemulsion formulations containing these extractants in combination with the surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT). Plutonium partitioning data are discussed in terms of an extraction mechanism that involves the competitive adsorption of the Pu-extractant complex between the macro liquid/liquid interface and the micro liquid/liquid interface of reversed micellar aggregrates. A novel approach to backextraction from loaded microemulsion solvents is presented, which involves the encapsulation of the extracted metal species in an SiO_2 network. The encapsulation network is generated *in situ* by the hydrolysis of tetraethoxysilane (TEOS).

EXPERIMENTAL SECTION

Materials

TEOS (tetraethoxysilane, 99+%) and gold-labeled TBP were purchased from Aldrich. CMPO (99+%) was supplied by the Separation Science and Technology Section, Chemical Technology Division, Argonne National Laboratory (ANL). The aged, polymeric plutonium(IV) was supplied by H. Diamond, Chemistry Division (ANL). The details of its preparation are given elsewhere (*7*). All other chemicals were reagent grade or better.

Methods

Distribution ratios of polymeric Pu(IV) between aqueous HNO_3 solutions and organic solvents containing either CMPO, TBP or CMPO/AOT, TBP/AOT mixtures were measured at an aqueous/organic phase ratio of 1 and a total liquid volume of either 1 or 2 mL. All equilibrations were carried out at 25°C using a thermostated water bath. With the exception of the TBP/AOT system, extraction equilibrium was reached after 1 min of contact using a vortex mixer. The phases were separated by centrifugation for a period of 10 min to produce two clear phases. For the TBP/

AOT systems, the two phases were vortexed for 1 min and then placed in a thermostated bath at 25°C where the two phases were allowed to remain in contact overnight (>12 h). All ^{239}Pu distribution ratios, D_{Pu}, were determined by measuring the alpha activity in appropriate aliquot sizes from each phase with a liquid scintillation counter (Packard TriCarb). Extraction equilibrium was considered to have been reached when the Pu distribution ratios were the same regardless of whether the Pu polymer was added first to the organic phase or to the aqueous phase. Organic phase water concentrations were measured by Karl Fischer titration using a Metrohm 652 KF-Coulometer. The organic phase hydrogen ion concentrations were measured by direct titration of organic phase aliquots with standardized isopropanol solutions of tetrabutylammonium hydroxide.

Plutonium partitioning between bulk aqueous and organic phases and the liquid/liquid interface was measured using the following procedure. The organic and aqueous phases were equilibrated, and portions of the top and bottom phases were removed and placed in separate vials for sampling. The remaining interphase region and the bulk phase samples were then recombined, and a sufficient volume of a 1:1 acetone:Triton X-100 solution was added to produce a homogeneous, optically transparent emulsion. The amount of Pu adsorbed at the liquid/liquid interface was determined from a mass balance of the alpha activity present in the individual bulk phases and the recombined-emulsified sample. The amount of Pu adsorbed at the liquid/solid interface in the test tube was determined from a mass balance of the alpha activity originally put into the system and the amount recovered from the bulk phases and the liquid/liquid interface.

Samples for transmission electron microscopy (TEM) were prepared by depositing 8 μL droplets of the particle suspensions on Formvar-coated copper grids and drying on filter paper at room temperture. Before deposition, the particle suspensions were diluted 1:100 with *n*-hexane and sonicated for 15–30 s.

RESULTS AND DISCUSSION

Polymeric Pu(IV) Structure

In past studies of polymeric Pu(IV) extraction, detailed information on the size and shape of the polymeric species was not available. Questions regarding the effect of polymer molecular weight and structure on extractability, therefore, remain unanswered. In the present study, the polymeric Pu(IV) was previously characterized by small angle neutron scattering (SANS) (*7*). It is identified as Sample 4 from Table 1 in the publication

by Thiyagarajan et al. (*7*). The SANS data indicated that in aqueous solutions the polymer is an elongated particle having a diameter of 22 ± 3 Å and a length of 120 ± 10 Å. The x-ray diffraction lines agreed with those of crystalline PuO_2, indicating a crystal structure that is of the fluorite-type with eight oxygen atoms surrounding each plutonium atom. The crystal structure of PuO_2 is known to be isomorphous with UO_2, ThO_2, and CeO_2 (*23*).

We are attempting to further characterize the polymer by photon correlation spectroscopy and have recently succeeded in obtaining crystals of the polymer to be used in structural determination by single-crystal x-ray diffraction. These results will be reported in future publications.

Extraction by TBP and CMPO

TBP extracts a variety of tetravalent metal ions, including Pu, from acidic nitrate solutions as $M(NO_3)_4(TBP)_2$. Under low acid conditions, the hydrolyzed species $M(OH)(NO_3)_3(TBP)_2$ have also been detected in hydrated TBP solvents (*24–27*). CMPO is a selective extractant for actinides in their III, IV, and VI oxidation states and is capable of removing Am and Pu(IV) from acidic nitrate and chloride wastes, producing very high decontamination factors (*28*, *29*). Unlike TBP, however, the ability of CMPO to complex monomeric hydrolyzed metal species has not been reported.

In an attempt to gain further insight into the reasons for the poor extractability of polymeric Pu in solvent extraction systems, we carried out a series of extractions using 1.4 *M* TBP, 0.2 *M* CMPO, and the TRUEX solvent consisting of 1.4 *M* TBP and 0.2 *M* CMPO in combination. The aqueous phases contained an initial plutonium concentration of 0.03 m*M* and either 1 *M* HNO_3 or 1 *M* HNO_3/4.4 *M* $NaNO_3$.

The partitioning data in Table 1 show that a significant fraction of the Pu polymer adsorbs at the liquid/liquid (L/L) and liquid/solid (L/S) interfaces. The amount of Pu adsorbed to the glass surface of the test tube and at the oil/water interface is calculated relative to the total Pu present in the system. The remaining Pu was distributed between the bulk aqueous and organic phases. In each of the extraction systems listed in Table 1, a white interfacial precipitate was observed. It should be noted that no interfacial precipitates are produced when monomeric Pu is used.

The adsorption of polymeric Pu(IV) onto glass is believed to occur through attractive, electrostatic interactions between the cationic polymer and a negatively charged SiO_2 surface (*1*). Kinetic measurements recently made in our laboratory have indicated that, in concentrated electrolyte solutions (including 1 *M* HNO_3), approximately 50% of the equilibrium adsorption is reached within the first 3 min of contact (*30*).

TABLE 1
Partitioning of Polymeric Pu(IV) in Oil/Water Systems

Aqueous phase	Organic phase[a]	D_{Pu}	% Pu at respective interface	
			L/L	L/S
1 *M* HNO_3	0.2 *M* CMPO	0.77	77	22.9
	1.4 *M* TBP	1.43	49	47
	TRUEX	22.5	54	33
1 *M* HNO_3/4.4 *M* $NaNO_3$	0.2 *M* CMPO	0.026	79	20
	1.4 *M* TBP	0.12	44	34
	TRUEX	0.24	39	45

[a]The organic diluent in each case was *n*-dodecane.

Extraction by CMPO/AOT

In a separate study dealing with the adsorption of polymeric Pu onto SiO_2 surfaces from concentrated electrolyte solutions, it was found that the presence of small amounts of AOT (0.1 wt% or less) could completely inhibit polymer adsorption (*30*). Contacting these aqueous solutions with an equal volume of *n*-dodecane resulted in the transfer of the Pu to the organic phase, giving D_{Pu} values of about 100 and, more significantly, nearly complete recovery of plutonium in the bulk liquid phases. To expand on those earlier studies, the extraction of polymeric Pu(IV) by CMPO/AOT mixtures was measured. These results are shown in Fig. 1 for the extraction of Pu from 1 *M* HNO_3 solutions as a function of the organic phase AOT concentration. The organic phase concentration of CMPO was held constant at 0.2 *M*. Because of a tendency toward macroemulsion formation with aqueous phases of low ionic strengths, *n*-hexane was used as the diluent in place of *n*-dodecane.

As the AOT concentration in CMPO/AOT mixtures is increased, D_{Pu} values increase dramatically and become substantially larger than those obtained with either CMPO or AOT alone. A maximum D_{Pu} of about 2000 is obtained at a CMPO:AOT molar ratio of 1. Equally dramatic is the effect of AOT on the bulk phase recovery (R_{Pu}) of polymeric Pu(IV). The results shown in Fig. 2 indicate a linear increase in R_{Pu} as the ratio of [AOT]/[CMPO] increases from 0 to 0.5. Also shown in Fig. 2 are data for the extraction of water from 1 *M* HNO_3 solutions as a function of the organic phase AOT concentration. The sudden increase in the slope of the extraction isotherm at a [AOT]:[CMPO] ratio of 0.5 marks a transition to the microemulsion system containing large water-swollen micelles.

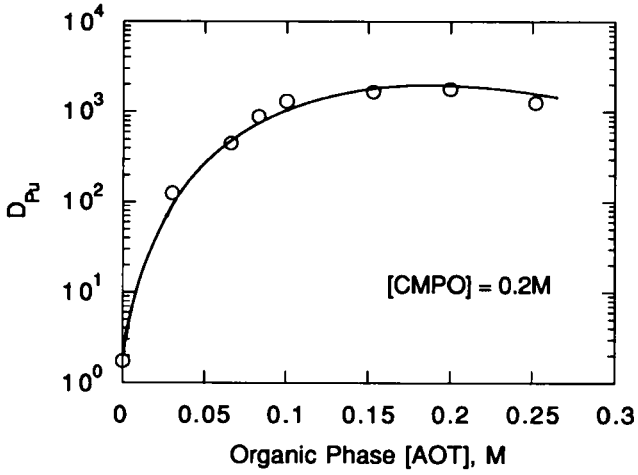

FIG. 1. Effect of [AOT] on polymeric Pu(IV) extraction. Initial aqueous phase [HNO_3] = 1.0 *M*.

Examination of Fig. 2 indicates that polymeric plutonium recovery is sensitive to the organic phase water concentration. This type of solubilization dependency has also been observed in other macromolecular systems. For example, the solubility of proteins in reversed micellar systems is dramatically reduced when the water content of the micellar phase (*W*), measured as the ratio [H_2O]/[surfactant], is decreased to values less than

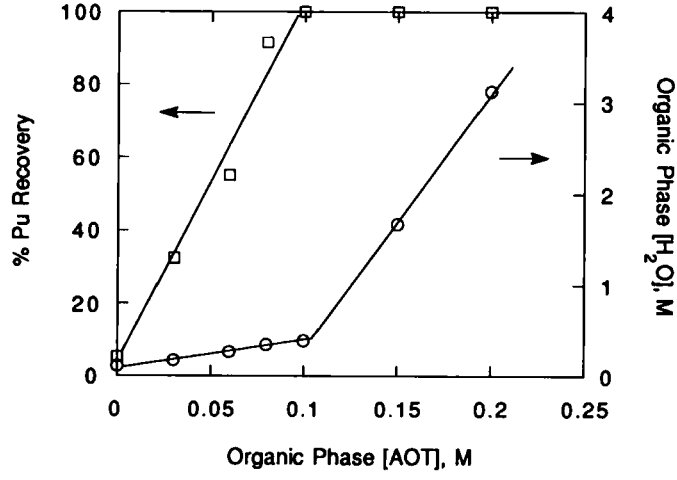

FIG. 2. Effect of [AOT] on bulk phase recovery of polymeric Pu(IV) and water extraction. [CMPO] was held constant at 0.2 *M*.

1–2 (*31*). The water extraction data in Fig. 2 thus provide evidence for the participation of inverted AOT micelles in the polymeric plutonium extraction process. The extraction mechanism can be viewed as a two-stage process in which the plutonium polymer is initially complexed by CMPO and AOT at the macro L/L interface, with subsequent transfer of the Pu-extractant complex to the bulk organic phase, where it is adsorbed at the micro L/L interface of the inverted AOT micelles. The larger interfacial area provided by the inverted micelles thus competes with the macro interface for the adsorption of the plutonium polymer.

The extraction of polymeric Pu as a function of the equilibrium HNO_3 concentration in the aqueous phase is shown in Fig. 3. Polymer extraction increases rapidly with increasing HNO_3 concentration until a maximum in D_{Pu} of 3000 is reached at 0.4 *M* HNO_3. At all HNO_3 concentrations shown in Fig. 3, the bulk phase Pu recovery was 100%. The lowest plutonium partition coefficient measured (D_{Pu} = 24) was at an aqueous HNO_3 concentration of 0.04 *M*. Lower acid concentrations resulted in the formation of a macroemulsion that could not be broken by brief centrifugation. Because of the net positive charge on the plutonium polymer, its extraction by neutral extractants like CMPO or TBP requires the coextraction of nitrate to maintain electroneutrality. Due to the ability of CMPO and TBP to extract HNO_3, a competition between the metal ion and HNO_3 for

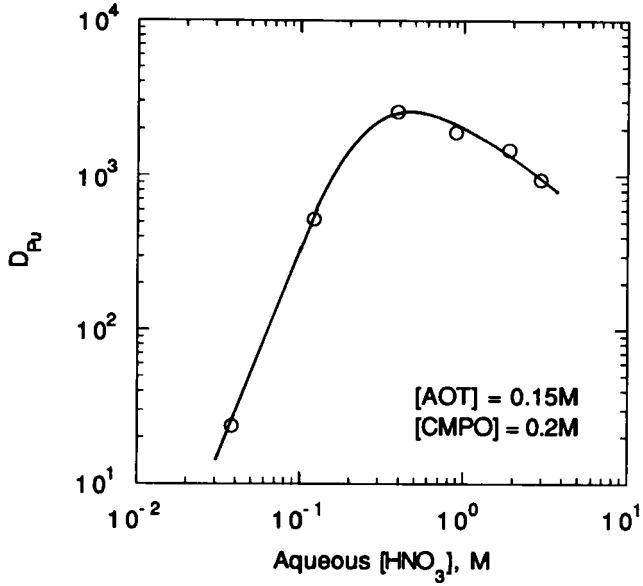

FIG. 3. Effect of equilibrium [HNO_3] on polymeric Pu(IV) extraction.

complexation by free extractant molecules leads to a maximum in the metal extraction isotherm (*32*). In the CMPO/AOT system, however, AOT itself would be capable of functioning as a counterion to the positively charged plutonium polymer. The effect of increasing HNO_3 concentration on plutonium extraction in Fig. 3 may, in fact, be related more to its effect on the organic/aqueous partitioning of AOT and the organic phase micelle size than to its function as a source of counterions to the positively charged plutonium polymer.

Extraction by TBP/AOT

The extraction data in Fig. 4 show that mixtures of TBP and AOT in hexane are also capable of promoting enhanced polymeric Pu(IV) extraction from aqueous HNO_3 solutions. However, the D_{Pu} values were consistently lower than those of the CMPO/AOT system. As with the nonmicellar extraction systems listed in Table 1, the relative values of the plutonium partition coefficients in Figs. 1 and 4 reflect the complexation affinities of CMPO and TBP for plutonium.

In other respects, however, the extraction behavior of polymeric Pu is quite different between the two micellar extraction systems. Unlike the CMPO/AOT system, the bulk phase recovery of polymeric Pu was independent of the organic phase AOT concentration. Pu recoveries of 100% were obtained at all AOT concentrations shown in Fig. 4. In the absence of AOT, a D_{Pu} value of 0.008 was obtained for extraction from 1 *M* HNO_3 by 0.2 *M* TBP in hexane with a R_{Pu} value of 35%. The extraction kinetics

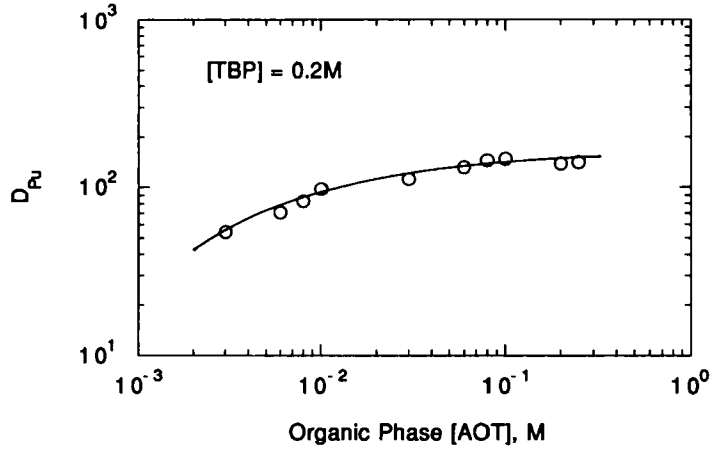

FIG. 4. Effect of [AOT] on polymeric Pu(IV) extraction. Initial aqueous phase [HNO_3] = 1.0 *M*.

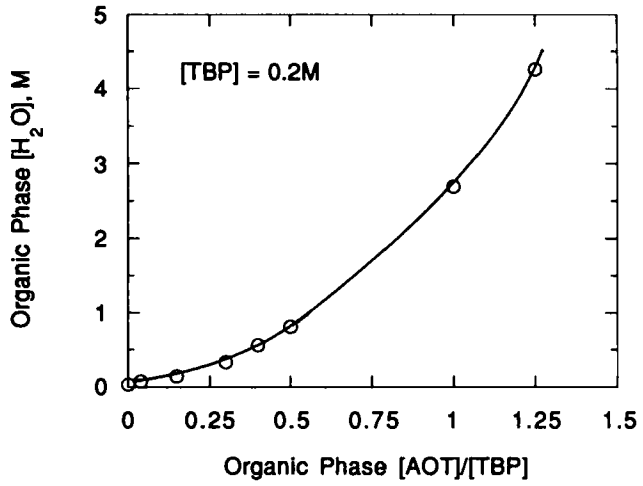

FIG. 5. Extraction of water by AOT/TBP mixtures from 1 *M* HNO_3.

for the two extractant systems were also very different. In the CMPO/AOT system, equilibrium was reached after vortex mixing of the oil/water phases for 1 min whereas in the TBP/AOT system the two phases had to be kept in contact overnight in order to reach equilibrium.

The extraction of water by the TBP/AOT system from 1 *M* HNO_3 solutions was also measured, and these data are plotted in Fig. 5. The high level of organic phase water concentration attained in TBP/AOT mixtures is consistent with a microemulsion system.

Solubilization Site

The water extraction data in Figs. 2 and 5 were analyzed in terms of the amount of water extracted per mole of surfactant (w). In the mixed surfactant systems, this ratio is modified to account for the water that is coextracted by CMPO and TBP. The organic phase water content is therefore expressed in terms of a W_o value, where $W_o = ([H_2O] - [H_2O]_o)/[AOT]$. The water of hydration associated with either TBP or CMPO, $[H_2O]_o$, was measured at zero AOT concentration and was assumed to be a constant.

The data in Table 2 indicate that the number of water molecules solubilized per AOT molecule is influenced by the AOT concentration and by the presence of either CMPO or TBP. As the AOT concentration increases, the micelle diameter must increase to accommodate the additional water extracted per AOT molecule in the organic phase. Comparison of the Pu

TABLE 2
Water Solubilization by AOT[a]

	W_o	
[AOT], *M*	TBP/AOT system	CMPO/AOT system
0.03	3.7	2.0
0.06	5.0	2.6
0.08	6.6	2.9
0.10	7.8	2.8
0.15	ND	10.4
0.20	13.3	15.0
0.25	17.0	ND

[a][CMPO] = 0.2 *M*, [TBP] = 0.2 *M*.

and water extraction data suggests that the swollen AOT micelles are better able to accommodate the plutonium polymer, thus leading to higher Pu recoveries.

At minimal W_o values ($W_o < 1$), the icosahedral packing of the polar head groups in single-component AOT reversed micelles produces a micelle core with a diameter of about 8.8 Å (*33*). For solutions of 0.1 *M* AOT in heptane, the diameter of the micelle core increases to 18 Å at $W_o = 3$ and to 36 Å at $W_o = 9$ (*34*). For the extraction systems described in this paper, 100% Pu recoveries were achieved when W_o was approximately 3 or greater. Thus, a minimum core diameter of about 18 Å is required to produce enhanced Pu polymer extraction and recovery, discounting any effect that the presence of CMPO or TBP might have on the micelle size.

The relationship between micelle size and the size of the extracted species has received considerable attention in the literature. For the systems under discussion here, this question is complicated by the uncertainty about the actual length of the extracted Pu polymer. In a previous extraction study using the extractants H_2MEHP and HDHoEP, SANS measurements on the organic phase indicated that during extraction, the Pu polymer was broken into smaller segments of 200 Å in length from an original polymer length of about 2000 Å (*7*). The organic phase polymer did, however, retain its aqueous phase diameter and its characteristic UV-VIS adsorption spectrum. It is also possible that a similar reduction in polymer length occurs during extraction in the CMPO/AOT and TBP/AOT systems. On the other hand, a plausible argument can also be made in support of an extraction mechanism in which the micelle size increases to accommodate an intact Pu polymer. Studies (*35*) on protein extraction have shown that significant structural changes in reversed micelles can be brought about by the solubilization of macromolecules which are comparable in size to the

micelle. A small-angle x-ray scattering study (*35*) of micelle-solubilized rhodopsin in hexane solutions revealed two distinct micelle populations—one composed of empty micelles and the other composed of larger, protein-filled micelles. In this case, micelles of approximately 22 Å radius solubilized the much larger protein by surrounding the polar regions of the protein while the hydrophobic regions of the protein acted as crosslinks between the inverted micelles, producing a dumbbell-shaped micellar aggregate. The micelle-solubilized rhodopsin had a radius of gyration in excess of 160 Å (*35*).

Photon correlation spectroscopy studies are planned to provide information regarding the size of the extracted Pu polymer in the CMPO/AOT and TBP/AOT systems.

Backextraction of Polymeric Pu(IV)

The extraction data in Fig. 3 indicate the difficulty encountered when attempting to backextract the Pu polymer from a loaded microemulsion phase. Even at the lowest acid concentration compatible with the Winsor II system, the D_{Pu} values were still too large to permit efficient Pu stripping. Backextraction from microemulsion phases has also been a problem in protein separation systems (*15*, *16*). An unusual approach recently reported to be effective in stripping proteins from microemulsion phases involves the direct adsorption of the protein from the microemulsion phase onto silica powder (*36*). In the present study, a microemulsion based sol–gel technique employed by others to synthesize nanoscale ceramic and metalloid particles (*37–40*) was used to backextract metal ions and polymeric Pu(IV) from CMPO/AOT microemulsions.

The Pu polymer and metal ions such as Fe^{3+} and monomeric Pu(IV) were stripped from the organic phase by a procedure that involved encapsulating the metal species in colloidal silica particles that were produced by the acid-catalyzed hydrolysis and polymerization of TEOS (*41*) within the aqueous microdroplets of the organic phase. The SiO_2 capsules were then precipitated from the organic phase by increasing the pH with hydrazine (initial $[N_2H_4]$ was 0.75 *M*). Ammonium hydroxide was equally as effective as N_2H_4 at inducing particle precipitation from the organic phase. However, pH adjustment using NaOH resulted in L/L phase separation, which then significantly reduced the rate of particle agglomeration. The SiO_2 particles were easily recovered by centrifugation and, when dried, produced a free-flowing powder.

The final metal concentration in the organic phase depended on the elapsed time between the TEOS addition and the hydrazine addition. This is illustrated in Table 3 for plutonium stripping from the organic phase with

TABLE 3
Effect of TEOS Polymerization Time on Polymeric Pu(IV)[a] Stripping from 0.2 *M* CMPO/0.2 *M* AOT

Equilibration time, h	Pu recovery, %
0.08	94.2
1.5	97.0
7.5	99.92
18.7	99.994

[a] $[PuO_n]$ = 0.04 m*M*, $[Fe^{3+}]$ = 1 m*M*, [TEOS] = 0.1 *M*, $[N_2H_4]_{initial}$ = 0.75 *M*.

equilibration times ranging from 5 min to overnight. The residual organic phase activity for the longest equilibration time was 1.2 Bq/mL (33 pCi/mL).

Following the addition of TEOS, there was an induction period of about 30–45 s, after which the organic phase became turbid. After 4–5 min, a gel began to appear in the organic phase. This gel was easily condensed to a small volume by mild centrifugation, even after 18 h of polymerization. Initially, the rate of plutonium incorporation within the SiO_2 particles was very high but decreased considerably after the first few minutes, as shown in Table 3. The unincorporated Pu polymer was considered to be that which remained in the supernatant after precipitation of the silica particles with hydrazine.

Under the rather robust reaction conditions used, it is believed that two different types of SiO_2 particles are produced: (a) macroscale silica particles, which are produced from the very rapid hydrolysis of TEOS and are easily recovered by centrifugation; and (b) microscale silica particles, which are responsible for the encapsulation of the extracted plutonium polymer and remain solubilized within the reverse micelles. Attachment of the extracted plutonium species to the microscale silica particles is believed to take place via a condensation reaction between the hydrous plutonium polymer and the alkoxide ligand, as shown by

$$\begin{array}{c} | \\ -Si-OR \\ | \end{array} + HO-Pu- \longrightarrow \begin{array}{c} | \\ -Si-O-Pu- \\ | \end{array} + ROH \qquad (1)$$

When the pH is raised above 2–3, the micelle-solubilized silica particles attain a negative surface charge through the deprotonation of surface hydroxyls. This results in the particles being expelled from the aqueous core of the anionic AOT micelles. The case for covalent attachment of the metal

species to the silica particles rather than physical adsorption is supported by the fact that simply adding collodial silica particles (average particle size of 20 nm) to the loaded organic phase, in place of the TEOS, produced no noticeable reduction in the organic phase plutonium concentration when the silica was subsequently precipitated by the addition of either N_2H_4 or NH_4OH. That the Pu-containing SiO_2 particles are solubilized within the micelle core at acidic pH's is supported by the fact that removal of the macroscale silica particles by centrifuging without first raising the pH produced no detectable change in the organic phase plutonium concentration.

Evidence for the generation of microscale silica particles during metal stripping is presented in Fig. 6. The particles were prepared by a 10-day equilibration of TEOS in the microemulsion system described in Table 3, with the exception that polymeric plutonium was not added (i.e., 0.2 *M* CMPO, 0.2 *M* AOT, 1 m*M* Fe^{3+}, and 0.1 *M* TEOS). The microemulsion was centrifuged for 5 min prior to removing an aliquot of the supernatant for TEM analysis. The particle diameters in Fig. 6 vary between 25 and 75 nm, with a mean diameter of approximately 40 nm. While it is not possible to ascertain the diameter of the unperturbed micelle-core from the size of the silica particles, it is, nevertheless, possible to conclude that the mixed CMPO/AOT micelle is flexible enough to accommodate solutes as large as 40 nm. This would be more than adequate to solubilize an intact plutonium polymer.

In CMPO/AOT microemulsion solutions containing extracted Fe^{3+}, silica precipitation with either N_2H_4 or NH_4OH was accompanied by an immediate organic phase color change from bright yellow to pale orange. The initial yellow color arises from the presence of the Fe–CMPO complex. The subsequent color change to orange indicates the generation of hydrolyzed Fe^{3+} species, which are believed to reside within the aqueous micelle core. After hydrolysis, the encapsulation of iron by SiO_2 could then proceed through a reaction similar to Eq. (1), in which the $Fe(OH)_x$ species react with an alkoxy moiety. When harvested and dried, the Fe-doped silica particles retained a pale brown color which could not be bleached by soaking overnight in 8 *M* HNO_3. This suggests that the hydrolized Fe^{3+} ions are covalently bound to the silica particles rather than physically adsorbed onto the particle surface.

CONCLUSIONS

Winsor II microemulsion systems containing AOT and either CMPO or TBP have been shown to be capable of extracting colloidal Pu(IV) from nitric acid solutions while simultaneously achieving quantitative recovery of Pu between the bulk liquid phases. The CMPO/AOT system exhibited

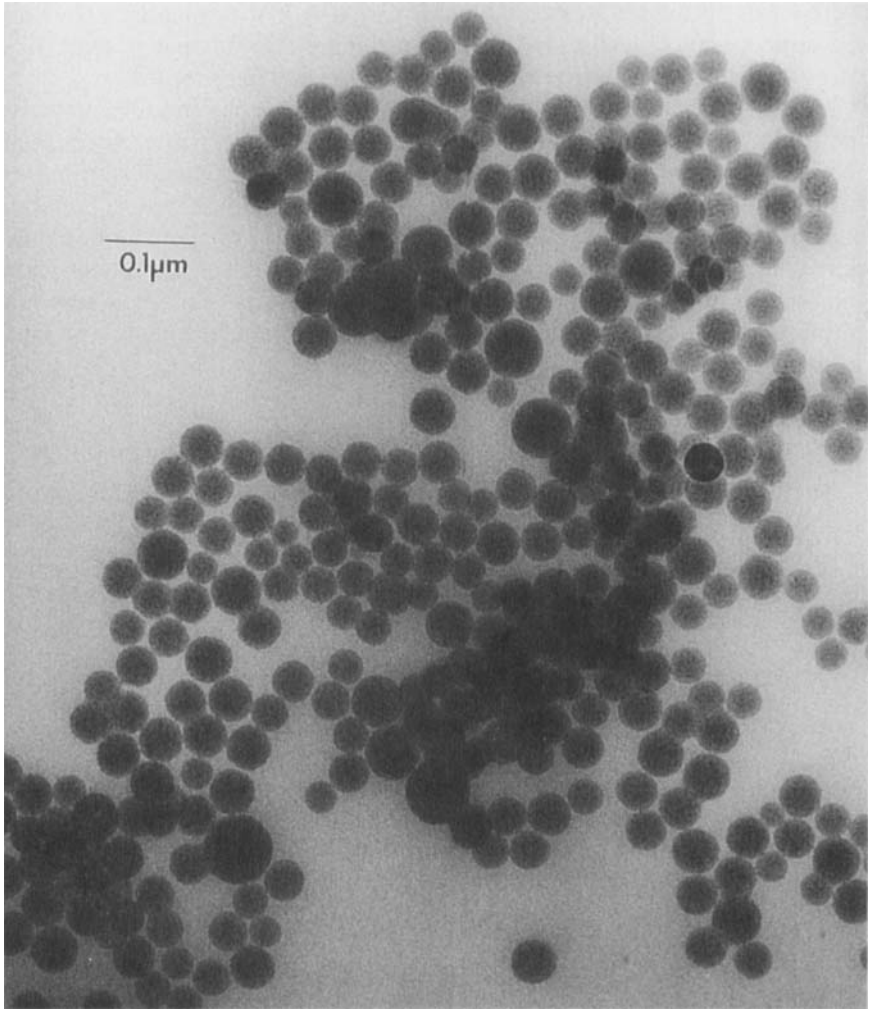

FIG. 6. TEM micrograph of SiO_2 particles obtained by TEOS reaction in the 0.2 *M* CMPO/0.2 *M* AOT microemulsion.

rapid metal extraction kinetics and short phase separation times. The extraction kinetics and phase separation times for the TBP/AOT system were considerably poorer.

Backextraction of polymeric Pu(IV) from microemulsion phases was achieved by encapsulating the plutonium in an SiO_2 network that was generated by the acid-catalyzed hydrolysis of TEOS. The silica particles

were easily recovered from the organic phase by first raising the pH within the aqueous micelle core and then centrifuging the coagulated silica. The recovered silica, when dried, produced a free-flowing powder.

This extraction and stripping sequence offers a potentially attractive method of removing hazardous materials from aqueous waste streams and recovering them directly from the organic solvent in an SiO_2-stabilized form. The use of a microemulsion solvent makes it possible to generate silica particles that have diameters in the nanometer range. The fine powders could then be further treated with phosphate-based binders at room temperatures to produce chemically bonded ceramics (*42*, *43*). These materials possess superior strength and low water permeability, making them well suited to hazardous or radioactive waste disposal.

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REFERENCES

1. J. M. Cleveland, "Solution Chemistry of Plutonium," in *Plutonium Handbook* (O. J. Wick, ed.), Gordon and Breach, New York, 1967, Chap. 13.
2. G. T. Seaborg and W. D. Loveland, *The Elements Beyond Uranium*, Wiley, New York, 1990, p. 90.
3. D. W. Ockenden and G. A. Welch, *J. Chem. Soc.*, p. 3358 (1956).
4. L. M. Toth, H. A. Friedman, and M. M. Osborne, *J. Inorg. Nucl. Chem.*, *43*, 2929 (1981).
5. F. G. R. Gimblett, *Inorganic Polymer Chemistry*, Butterworths, London, 1963, p. 108.
6. A. C. Muscatello, J. D. Navratil, and M. E. Killion, *Sep. Sci. Technol.*, *18*, 1731 (1983).
7. P. Thiyagarajan et al., *Inorg. Chem.*, *29*, 1902 (1990).
8. K. Osseo-Asare, *Sep. Sci. Technol.*, *23*, 1269 (1988).
9. A. G. Gaonkar and R. D. Neuman, *J. Colloid Interface Sci.*, *119*, 251 (1987).
10. C. S. Vijayalakshmi, A. V. Annapragada, and E. Gulari, *Sep. Sci. Technol.*, *25*, 711 (1990).
11. M. A. J. Rodgers and P. C. Lee, *J. Phys. Chem.*, *68*, 3480 (1984).
12. P. L. Luisi, M. Giomini, M. P. Pileni, and B. H. Robinson, *Biochim. Biophys. Acta*, *947*, 209 (1988).
13. J. H. Fendler, F. Nome, and J. Nagyvary, *J. Molec. Evol.*, *6*, 216 (1975).
14. C. A. Boicelli, F. Conti, M. Giomini, and A. M. Giuliani, *Chem. Phys. Lett.*, *89*, 490 (1982).
15. T. A. Hatton, "Reversed Micellar Extraction of Proteins," in *Surfactant-Based Separation Processes* (J. F. Scamehorn, and J. H. Harwell, eds.), Dekker, New York, 1989, p. 55.
16. J. M. Woll, T. A. Hatton, and M. L. Yarmush, *Biotech. Prog.*, *5*, 57 (1989).

17. E. B. Leodidis and T. A. Hatton, "Interphase Transfer for Selective Solubilization of Ions, Amino Acids and Proteins in Reversed Micelles," in *Structure and Reactivity in Reverse Micelles* (M. P. Pileni, ed.), Elsevier, New York, 1989, p. 270.
18. P. D. I. Fletcher and D. Parrott, "Protein Partitioning between Microemulsion Phases and Conjugate Aqueous Phases," in *Structure and Reactivity in Reverse Micelles* (M. P. Pileni, ed.), Elsevier, New York, 1989, p. 303.
19. K. Osseo-Asare and M. E. Keeney, *Proc. ISEC '80,* Assoc. Ing. Sortis Univ. Liege, Liege, Belgium, 1980, p. 80.
20. Y. Zheng and K. Osseo-Asare, *Solvent Extr. Ion Exch., 3,* 825 (1985).
21. H. F. Eicke, J. C. Shepherd, and A. Steinemann, *J. Colloid Interface Sci., 56,* 168 (1976).
22. F. Menger, J. Donahue, and R. Williams, *J. Am. Chem. Soc., 95,* 286 (1973).
23. R. E. Skavdahl and T. D. Chikalla, "Plutonium Refractory Compounds," in *Plutonium Handbook* (O. J. Wick, ed.), Gordon and Breach, New York, 1967, p. 251.
24. A. S. Solovkin, *J. Radioanal. Chem., 21,* 15 (1974).
25. J. L. Woodhead, *J. Inorg. Nucl. Chem., 26,* 1472 (1964).
26. H. A. C. McKay and J. L. Woodhead, *Ibid., 27,* 2247 (1965).
27. H. A. C. McKay and R. J. W. Streeton, *Ibid., 27,* 897 (1965).
28. E. P. Horwitz, D. G. Kalina, H. Diamond, L. Kaplan, G. W. Vandegrift, R. A. Leonard, M. J. Steindler, and W. W. Schulz, "TRU Decontamination of High-Level PUREX Waste by Solvent Extraction Utilizing a Mixed Octyl(Phenyl)-*N,N*-Diisobutylcarbamoylmethylphosphine Oxide/TBP/NPH (TRUEX) Solvent," in *Actinide Lanthanide Separations* (G. R. Choppin, J. D. Navratil, and W. W. Schulz, eds.), World Scientific Publishers, Singapore, 1985, p. 43.
29. W. W. Schulz and E. P. Horwitz, *Sep. Sci. Technol., 23,* 1191 (1988).
30. D. J. Chaiko, Unpublished information.
31. Y. L. Khmelnitsky, A. V. Kabanov, N. L. Klyachko, A. V. Levashov, and K. Martinek, "Enzymatic Catalysis in Reversed Micelles," in *Structure and Reactivity in Reverse Micelles* (M. P. Pileni, ed.), Elsevier, New York, 1989, p. 230.
32. D. J. Chaiko, P.-K. Tse, and G. F. Vandegrift, "Modeling of Aqueous and Organic Phase Speciation for Solvent Extraction Systems," in *Innovations in Materials Processing Using Aqueous, Colloid & Surface Chemistry* (F. M. Doyle, S. Raghavan, P. Somasundaran, and G. W. Warren, eds.), TMS, Warrendale, Pennsylvania, 1988, p. 261.
33. M. Kotlarchyk, J. S. Huang, and S. H. Chen, *J. Phys. Chem., 89,* 4382 (1985).
34. B. Valeur and E. Bardez, "Proton Transfer in Reverse Micelles and Characterization of the Acidity in the Water Pools," in *Structure and Reactivity in Reverse Micelles* (M. P. Pileni, ed.), Elsevier, New York, 1989, p. 103.
35. V. R. Ramakrishnan, A. Darszon, and M. Montal, *J. Biol. Chem., 258,* 4857 (1983).
36. G. Marcozzi, M. Caselli, and P. L. Luisi, *Prog. Colloid Polym. Sci., 81,* 272 (1990).
37. J. P. Wilcoxon and R. L. Williamson, *Mater. Res. Soc. Symp. Proc., 177,* 269 (1990).
38. M. Boutonnet, J. Kizling, and P. Stenius, *Colloids Surfaces, 5,* 209 (1982).
39. K. Osseo-Asare and F. J. Arriagada, *Ibid., 50,* 321 (1990).
40. B. H. Robinson, A. N. Khan-Lodhi, and T. Towey, "Microparticle Synthesis and Characterization in Reverse Micelles," in *Structure and Reactivity in Reverse Micelles* (M. P. Pileni, ed.), Elsevier, New York, 1989, p. 198.
41. K. D. Keefer, *Mater. Res. Soc. Symp. Proc., 32,* 15 (1984).
42. A. K. Sarkar, *Am. Ceram. Soc. Bull., 69,* 234 (1990).
43. D. M. Roy, *Science, 235,* 651 (1987).

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