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Recovery of Plutonium(IV) from Aqueous Solutions Using Emulsion Liquid Membrane Containing 2-Ethylhexyl Phosphonic Acid Mono-2-Ethylhexyl Ester as Ion Transporter

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Abstract: An emulsion liquid membranes (ELMs) containing 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (H_2A_2) was tested for the extraction of plutonium(IV) from aqueous nitrate solutions of different compositions. Span 80 was used as the surface-active agent and a mixture of 0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$ was used as the internal phase. Influence of some important experimental parameters such as exterior phase nitric acid concentration, ionic impurities in the exterior phase, concentration of H_2A_2 in ELM phase, and organic solvents on the ELM permeation process were systematically studied. The maximum efficiency of Pu extraction among group of experiments was 98% with permeability coefficient = 0.508 min^{-1}, and the corresponding concentration factor of Pu in the receiving phase was ca. 10. The stability of the emulsions was tested in the presence of different organic solvents and at different concentrations of Span 80 in LM phase. The extractions of Pu by ELM from actual and simulated waste solutions as well as in presence of some added ionic impurities were investigated. Rate of Pu extraction by ELM was studied at different treatment ratios and under repeat extractions by the same emulsion. The repeat extraction experiments showed that a concentration factor of more than 80 for Pu could be achieved.

Keywords: Emulsion liquid membrane, plutonium, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, Span 80

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INTRODUCTION

Removal of even trace amounts of plutonium which gives out high ionizing alpha radiation with very long half life from the nuclear waste is essential for its safe disposal (1). More specifically, when the amount of plutonium metal component is much less in the large volume of solution and also coexisting with a host of ionic and non-ionic impurities, its removal becomes very difficult. The most commonly used solvent extraction process is not economical under such conditions as it requires a large number of stages in a series of mixer and settler units to achieve desired recovery of extractable metal component. It also requires a large volume of extractant inventory. A liquid membrane (LM) is a single-step extraction and stripping technique that needs very low inventory of complexing agent and a single-stage procedure is enough to obtain desired recovery of the targeted metal component. Also, LM process has been proposed as a clean technology, with useful characteristics such as high specificity, low energy utilization, and capability of removing the contaminant to very low level. Generation of secondary waste is minimum in this technique (2–8). To process a large volume of solutions compared to other LM techniques such as bulk LM and supported LM, application of emulsion liquid membrane (ELM) technique is more practical. ELM allows faster permeation rate of metals due to a large specific interfacial area and thereby minimizes the process time with high throughput (9–14). The equipment designed for the solvent extraction process can also be used for ELM separations without much modifications (15).

The ELM process involves the preparation of an emulsion, contacting the emulsion with the contaminated feed phase by dispersion, and then splitting of the emulsion in the loaded strip phase and the organic phase. The latter is reused to prepare a fresh emulsion. Emulsions are constituted by two immiscible phases (water in oil, w/o) dispersed by mild agitation in a third oil immiscible phase. The dispersed interior phase (IP) is separated from the exterior phase (EP) by a film of oil that operates as an LM between the two aqueous phases. The metal ions are transported from the EP to the IP by diffusion facilitated by the carrier. A conceptual drawing of a liquid membrane globule for the extraction of plutonium is given in Fig. 1. The extraction of Pu by ELM is taking place according to the following chemical equations at LM–EP and LM–IP interfaces, respectively (8).

$$Pu^{4+} + 3NO_3^- + \overline{H_2A_2} \Longleftrightarrow \overline{Pu(NO_3)_3HA_2} + H^+ \quad (1)$$

$$\overline{Pu(NO_3)_3HA_2} + H_2C_2O_4 \Longleftrightarrow Pu(C_2O_4)_2 + 3H^+ + 3NO_3^- + \overline{H_2A_2} \quad (2)$$

Molecular species under line bar are species in membrane phase, and H_2A_2 denotes the dimmer of the carrier molecule. The oil film LM barrier forming the globules of emulsion contains H_2A_2 dissolved in dodecane to facilitate the permeation of hydrophilic plutonium ions across the LM.

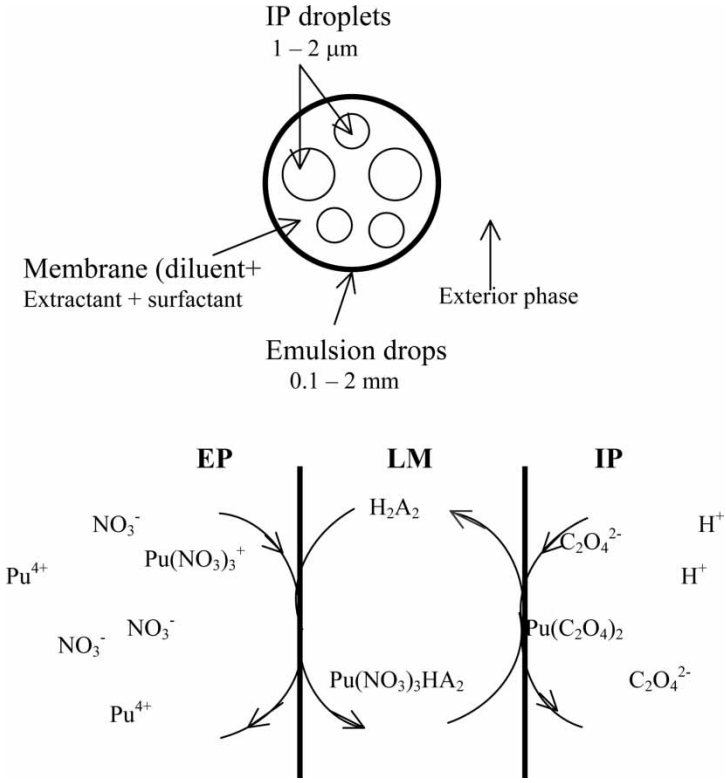

Figure 1. Schematic diagram of ELM globules with simultaneous extraction and stripping mechanism.

These emulsion globules are stabilized using a sorbitate type of surfactant, Span 80. The encapsulated internal aqueous phase inside the emulsion globules contains a mixture of HNO_3 and $H_2C_2O_4$ to trap the plutonium transported across the LM and restrict its reentry into the LM phase.

In the present investigations, an ELM technique is developed to recover/remove plutonium from different aqueous solutions. A2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (H_2A_2) was used as a carrier in LM phase, which is a good extractant for intensive extraction of actinide and lanthanide elements from their dilute solutions (16). Span 80, sorbitan monooleate was chosen as the surface-active agent throughout because of its wide usage in ELM separations. The recovery rates of Pu were investigated by changing the concentration of nitric acid in EP, composition of the IP, the concentration of H_2A_2 and organic solvents in LM phase. The membrane breakage is an important parameter to be investigated in the ELM separations. This includes the rupture of the emulsion and the leakage of IP and extracted solute through the membrane phase to the EP. The membrane breakage

causes a decrease of driving force for mass transfer and slow decrease of the metal concentration in the raffinate, thereby lowering the extraction efficiency (17). In this study, stability of ELM was tested in different organic solvents and at different concentrations of Span 80 in the ELM phase. To determine the applicability of this ELM system for the recovery of Pu, the extractions of Pu were studied from EP containing simulated and actual active waste solutions and solution spiked with different ionic impurities.

EXPERIMENTAL

Reagents

Reagent grade n-dodecane, kerosene, and Span 80 were obtained from Fluka, Germany. 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (trade name PC-88A) procured from Daihachi Chemicals Industry, Japan, as commercial grade reagent. Reagent grade n-hexane, benzene taken were obtained from Merk Ltd. These all reagents were used without further purification.

Tracer Solution

Plutonium-239, being the major constituent in the Pu sample was used to study its permeation characteristics. Plutonium was purified by anion exchange method (18). The tetravalency of Pu was adjusted by the addition of sodium nitrite (ca. 0.03 mol dm^{-3}) (19). Analytical waste solutions usually accumulated during process control, and research activities in radiochemical laboratories were studied for removal of Pu from them using ELM. The compositions of these waste solutions are similar to that reported in our earlier communication (8). Simulated active waste solution which is usually obtained as high active liquid waste concentrate in fuel reprocessing operations was prepared by dissolving some metal nitrates in 3 mol dm^{-3} HNO_3. The metal ions taken for this purpose are Ca^{+2}(10 mg dm^{-3}), Ce^{3+} (30 mg dm^{-3}), Cs^{+} (10 mg dm^{-3}), Fe^{3+} (200 mg dm^{-3}), Na^{+} (1 g dm^{-3}), Ni^{2+} (30 mg dm^{-3}), Ru^{3+} (0.05 mg dm^{-3}), and Zr^{4+} (0.05 mg dm^{-3}). In this solution, a known quantity of $Pu(NO_3)_4$ (final concentration of Pu = 10.8 mg dm^{-3}) was added. This simulated active waste solution was taken as EP to observe the Pu recovery by ELM. Selective permeation of Pu in the presence of various ionic impurities was studied using EP containing mixture of ions as described in Table 1.

ELM Batch Tests

The w/o Emulsion was prepared from equal volumes of organic (0.3 mol dm^{-3} H_2A_2 + 112 mmol dm^{-3} Span-80 in dodecane) and aqueous

Table 1. Composition of the cationic mixtures before and after contact with ELM[a]

Solution A: concentration[b] mg dm^{-3}			Solution B: concentration[b] mg dm^{-3}		
Cation	A_1	A_2	Cation	B_1	B_2
Al	5.0	5.0	Ce	5.0	4.5
B	2.0	2.0	Dy	5.0	5.0
Be	2.0	2.0	Eu	5.0	5.0
Ca	5.0	5.2	Gd	2.0	2.0
Cd	2.0	2.0	Sm	5.0	5.0
Cr	5.0	4.8			
Cu	5.0	5.0			
Fe	5.0	5.3			
Mg	5.0	5.1			
Mn	5.0	5.0			
Mo	5.0	<0.1			
Ni	5.0	5.1			
Pb	5.0	5.0			
Si	5.0	5.3			
Zr	5.0	<0.1			

[a]$[HNO_3] = 0.5$ mol dm^{-3} in both of these solution A and solution B.

[b]A_1 and B_1 are the initial concentrations and A_2 and B_2 are the concentrations of the same after 1 h contact with ELM.

stripping solution (0.05 mol dm^{-3} $HNO_3 + 0.3$ mol dm^{-3} $H_2C_2O_4$). The mixture was stirred (using Omni mixer of Du pont instruments) at high speed (ca. 8000 rpm) to form emulsion. Then 5 cm^3 of emulsion was dispersed into 50 cm^3 of aqueous solution, which was under low agitation. During agitation, samples were drawn out from EP at intervals. Finally, the mixture solution was allowed to settle to separate emulsion from the external solution. About 4 mL of emulsion at the end of the run was chemically demulsified.

Stability Test for the ELM

As described earlier, during the preparation of the emulsion ca. 560 ppm of K^+ in the form of KNO_3 was added to the IP of the emulsion. From this 5 mL emulsion was dispersed in 50 mL of 0.5 mol dm^{-3} HNO_3. Such solutions were agitated for different durations of time and EP was analysed for K content.

Analytical

Analysis of Pu was carried out radiometricaly using argon gas flow 2π geometry proportional counter. An inductively coupled plasma emission spectrophotometer (ICP, Jobin Yvon JY-48 spectrometer) was used for the

analysis of metal ions other than Pu. Reproducibility of the results for the repeated experiments was within $\pm 5\%$, and material balance of Pu was $>95\%$.

RESULTS AND DISCUSSION

In the study of membrane transport process it is convenient to use the parameter "Flux" (J) to describe the complete process of permeation of solute through membrane. For the process of ELM, in measurable terms, it is best to express flux as the decrease in the initial concentration of solute in the feed solution with time (t)

$$J = (-dC/dt) \cdot (V_{EP}/A) \tag{3}$$

where C is the concentration of transportable solute, V_{EP} is the volume of feed solution, and A is the membrane area.

The integration of Eq. (3) and substitution of permeability coefficient P as flux per unit concentration leads to

$$\ln C/C_0 = -(A/V_{EP}) \cdot P \cdot t \tag{4}$$

In case of ELM, A is proportional to the volume of emulsion (V_E). Hence, Eq. (4) is modified as following:

$$\ln C/C_0 = -(V_E/V_{EP}) \cdot P \cdot t \tag{5}$$

where C_0, C_t are the initial and final concentrations of Pu in the EP solution, V_E/V_{EP} is the treatment ratio (volume of emulsion/volume of EP solution) and t is the contact time. Equation (5) was used for the calculation of P with following assumptions: stripping reaction at LM–IP interface is very fast and no accumulation of solute in the membrane phase, uniform size of emulsion globules produced under similar conditions of preparation of emulsion and same rate of coalescence under different experimental conditions. From the mass balance of metals in interior and exterior phases, the percentage extraction, %E was determined as follows:

$$\%E = [1 - (C_t/C_0)] \times 100 \tag{6}$$

The enrichment (E_n) of Pu is given as

$$E_n = [Pu]_{IP,t}/[Pu]_{EP,0} \tag{7}$$

where $[Pu]_{IP,t}$, and $[Pu]_{EP,0}$ are the concentrations of Pu in IP at time t and in EP at time 0, respectively.

Effect of the Speed of Stirring in the External Phase

A significant effect of the stirring of the EP solution (0–200 rpm) on the Pu flux across the ELM was observed in the preliminary experiments. The % E of Pu increases with speed of stirring and reaches to saturation at around 150 rpm. In Fig. 2 results are given for the percentage extraction of Pu by ELM in 1 h of equilibration time. The treatment ratio is also a deciding factor to optimize the stirring speed for obtaining the maximum permeability. The stirring speed was restricted upto 200 rpm to avoid hydrodynamic breakage of the ELM (20).

Effect of Carrier Concentration

Permeability coefficients of Pu were determined by taking a fairly wide range of $[H_2A_2]$ in the ELM phase and keeping other experimental parameters constant. In Fig. 3 experimental results are given describing the changes in the permeability of Pu by varying the concentration of H_2A_2 in LM phase while keeping the $[HNO_3]$ in EP; 0.5 mol dm^{-3} and in IP; 0.3 mol dm^{-3} $H_2C_2O_4 + 0.05$ mol dm^{-3} HNO_3. The permeability coefficient of Pu increases with increase in the concentration of H_2A_2 in LM phase and reaches to a maximum at around $[H_2A_2] = 0.3$ mol dm^{-3} (Fig. 4). The increasing concentrations of H_2A_2 in the LM phase favor more extraction of Pu at LM–EP interface. This condition generates increasing concentration gradient in the LM phase between LM–EP and LM–IP interfaces and hence more flux of Pu across the LM barrier. There was no more improvement

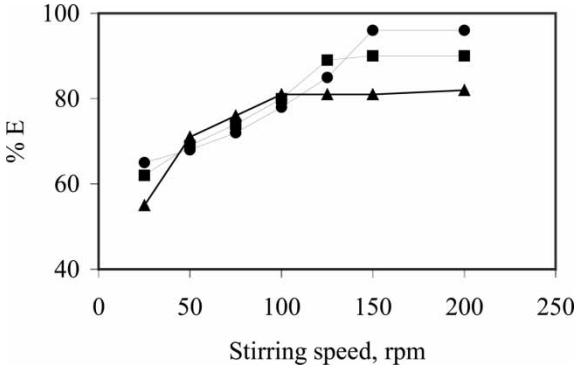

Figure 2. Effect of stirring speed of EP on the extraction of Pu by ELM (treatment ratio; —▲— 0.5 : 10, —■— 1 : 10, —●— 2 : 10). LM—0.3 mol dm^{-3} $H_2A_2 + 5\%$ Span 80 in dodecane; EP—0.5 mol dm^{-3} HNO_3 containing 25 mg dm^{-3} Pu(IV); IP—0.05 mol dm^{-3} $HNO_3 + 0.3$ mol dm^{-3} $H_2C_2O_4$. Equilibrium time 1 h and stirring speed 150 rpm.

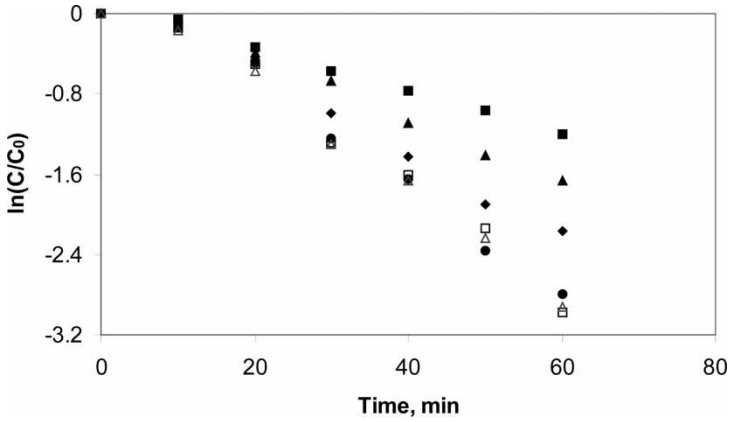

Figure 3. Permeation of Pu(IV) across ELM as function of time at different concentrations of H_2A_2 ([H_2A_2]: ■, 0.078 mol dm^{-3}; ▲, 0.16 mol dm^{-3}; ◆, 0.24 mol dm^{-3}; ●, 0.32 mol dm^{-3}; □, 0.47 mol dm^{-3}; △, 0.55 mol dm^{-3}). LM—H_2A_2 + 5% Span 80 in dodecane; EP—0.5 mol dm^{-3} HNO_3 containing 25 mg dm^{-3} Pu(IV); IP—0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$. Equilibrium time 1 h and stirring speed 150 rpm.

in the permeation of Pu beyond 0.3 mol dm^{-3} of H_2A_2. At higher concentrations of H_2A_2 the increase of viscosity of the membrane phase and unfavorable conditions at the stripping (IP) interface of the membrane (Eq. (2)) generates more resistance for the transport of Pu across the LM. For all further experiments 0.3 mol dm^{-3} of H_2A_2 was used in LM phase.

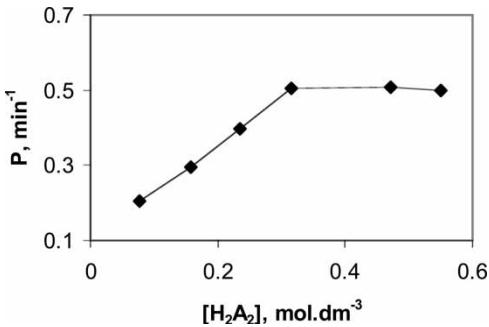

Figure 4. Effect of [H_2A_2] on the permeability coefficient of Pu across the ELM. LM—H_2A_2 + 5% Span 80 in dodecane. EP—0.5 mol dm^{-3} HNO_3 containing 25 mg dm^{-3} Pu(IV). IP—0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$. Equilibrium time 1 h and stirring speed 150 rpm.

Effect of [HNO_3] in Exterior Phase

Figure 5 describes the effect of nitric acid concentration on permeation of Pu across the ELM. The permeation of Pu is almost similar for the concentration of HNO_3 between 1–3 mol dm^{-3} in EP and above this, the permeation decreases. Almost quantitative recovery of Pu (>90%) could be obtained from the aqueous feed solutions containing [HNO_3] in the range of 0.5–5 mol dm^{-3} using extractions with ELM. H_2A_2 is cationic type of extractant and extract metal species from basic as well as acidic solutions with good efficiency. The mechanism for the extraction of metal ions from more acidic solutions by H_2A_2 is of complex nature (exchange—solvate mechanism (21). The initial increase in the permeation of Pu with increase in the concentration of HNO_3 in the EP could be attributed to the increase of the driving force for transport process as described by Eq. (1) (a salting out process). The higher acidity in the aqueous feed solutions lowers the cationic dissociation of H_2A_2 and hence decrease in the permeation of Pu across the ELM is observed.

Effect of Interior Phase Composition

Different reagents (such as EDTA, citric acid, and hydroxylamine hydrochloride) were tested for the effective entrapment of Pu in the IP of the ELM. The maximum %E obtained for 1 h ELM transport process when stripping solutions were; EDTA (0.05–0.2 mol dm^{-3}) = 58%, citric acid (0.05–0.2 mol dm^{-3}) = 55%, and hydroxylamine hydrochloride (0.05–0.2 mol dm^{-3}) = 57%. Oxalic acid and HNO_3 was found to be most suitable stripping mixture. The chemical reaction at LM–IP interface responsible for the stripping of Pu from LM phase is described in Eq. (2). The

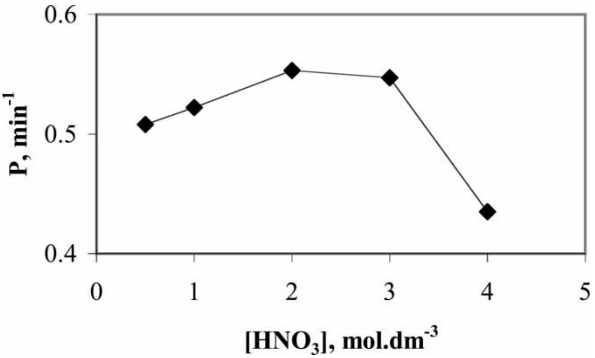

Figure 5. Effect of [HNO_3] in the EP on the permeation of Pu across ELM. LM—0.3 mol dm^{-3} H_2A_2 + 5% Span 80 in dodecane. EP—25 mg dm^{-3} Pu(IV) in HNO_3. IP—0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$. Equilibrium time 1 h and stirring speed 150 rpm.

optimum concentration of oxalic acid and HNO_3 to obtain maximum permeability were $0.3\,mol\,dm^{-3}$ and $0.05\,mol\,dm^{-3}$, respectively. The results described in Table 2 suggest that the stripping of Pu takes place in two stages. First nitric acid releases Pu ion from the LM phase by proton exchange and then complexes it with $C_2O_4^{2-}$.

Stability of Emulsion and Effect of the Organic Solvents

The stability of emulsion under the experimental conditions imparts significant influence on the overall separation process by ELM. The stability of emulsion was investigated in terms of the break-up rate constant, K_b, defined by Eq. (9)

$$\ln(1-\varepsilon) = -K_b t \tag{8}$$

$$\varepsilon = \frac{V_{EP}C}{V_{IP}C_{i,0}} \tag{9}$$

where ε is the break-up ratio of emulsion, V_{EP} and V_{IP} are the initial volumes of aqueous EP and IP, respectively, C and $C_{i,0}$ are the tracer concentrations in the EP and in IP at time t and 0, respectively. The tracer in this case was potassium ions preloaded into the interior phase of the emulsion at the preparation stage. The amount of tracer in the EP indicates the degree of break-up.

Figure 6 shows the leaching of K^+ from emulsion globules into EP with respect to time. The emulsion is made by mixing equal volume of $0.3\,mol\,dm^{-3}$ H_2A_2 and $112\,mmol\,dm^{-3}$ Span 80 dissolved in organic solvent and $0.3\,mol\,dm^{-3}$ $H_2C_2O_4 + 0.05\,mol\,dm^{-3}$ HNO_3 containing known amount of KNO_3. The organic solvents tested are benzene,

Table 2. Extraction of Pu(IV) by ELM at varying concentration of oxalic acid and nitric acid in IP

$[H_2C_2O_4]$ mol dm^{-3}	$[HNO_3]$ mol dm^{-3}	%E	P min^{-1}
0.075	0.05	72	0.295
0.150	0.05	85	0.316
0.200	0.05	90	0.509
0.300	0.05	90	0.508
0.200	0.00	58	0.145
0.200	0.10	50	0.116

EP: $0.5\,mol\,dm^{-3}$ HNO_3 containing ca. $25\,mg\,dm^{-3}$ of Pu(IV), LM phase: $0.3\,mol\,dm^{-3}$ $H_2A_2 + 5\%$ Span 80 in dodecane. %E was calculated after 1 h of emulsion—EP equilibration. Stirring speed of EP—150 rpm.

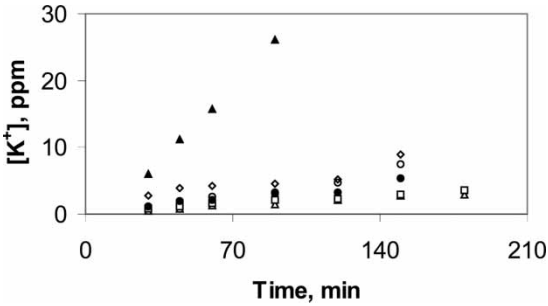

Figure 6. Leaching of K from IP of emulsion with respect to time. LM medium; △ dodecane, □ kerosene, ▲ hexane, ◇ benzene, ○ toluene, ● xylene. LM—0.3 mol dm^{-3} H_2A_2 + 5% Span 80 in respective diluent. EP—0.5 mol dm^{-3} HNO_3. IP—0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$ + 560 ppm K^+. Stirring speed 150 rpm

dodecane, n-hexane, toluene, and xylene. The leaching of K^+ in the EP was more from the emulsion made by n-hexane as an organic solvent. Varying the surfactant concentration in the LM phase, batch-wise stability tests were performed. The stability profiles in different organic solvents are illustrated in Fig. 7. The stability of emulsion in different organic solvents are in the order; dodecane > kerosene > xylene > toluene > benzene > n-hexane. The least viscous hexane makes the emulsion more fragile. Along with viscosity and density, the hydrophobicity of the diluent is also a deciding factor towards emulsion stability. The aliphatic hydrocarbons are less hydrophobic than aromatics. The hydrophilic nature of organic solvent allows more

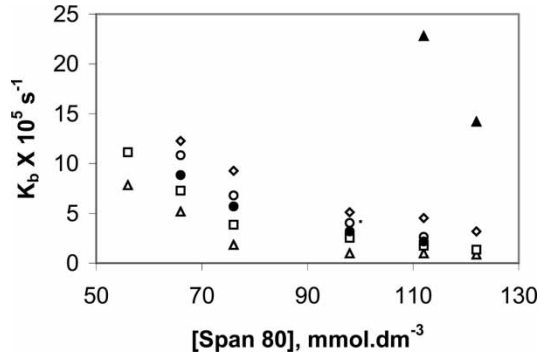

Figure 7. Effect of the concentration of Span 80 on the break up rate constant of emulsion. LM medium; △ dodecane, □ kerosene, ▲ hexane, ◇ benzene, ○ toluene, ● xylene. LM—0.3 mol dm^{-3} H_2A_2 + Span 80 in dodecane. EP—0.5 mol dm^{-3} HNO_3. IP—0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$ + 560 ppm K^+. Stirring speed 150 rpm.

transport of water inside the emulsion globules resulting excessive swelling of the emulsion and breaking. This factor reflected in the less stable emulsion formed with aromatic solvents such as benzene, xylene, and toluene compare to that with dodecane and kerosene. In case of dodecane as an organic solvent the break-up at about 10% was observed when the surfactant concentration in the range of 98–122 mmol dm^{-3}. This percentage is equivalent to potassium concentration of 2.8 mg dm^{-3} in the external phase after a contact time of 3 h. The initial concentration of potassium in the interior solution was 560 mg dm^{-3}.

The break-up rates of emulsion were also determined by varying concentration of H_2A_2 in the LM phase (studied only for dodecane as an organic solvent). For the selective concentration range of H_2A_2, i.e., 0.05 to 0.4 mol dm^{-3} at optimized surfactant concentration (112 mmol dm^{-3}), the break-up rate remained constant between 10–11%.

Figure 8 shows the effect of organic solvents on the transport of Pu(IV) across ELM. In solvent extraction process, usually the influence of diluent on the extraction of metal component is correlated with some physicochemical parameters of the solvent. In present nonequilibrium systems of ELM the effect of organic solvents on the extraction of Pu(IV) is more or less decided by the stability of the emulsion with the respective organic solvent. The order of the extraction of Pu(IV) by ELM in different organic solvents system can be given as dodecane > kerosene > xylene > toluene > benzene > n-hexane.

Effect of Treatment Ratio and Repeated Extractions

For the treatment of high volume of waste solutions, it is desirable to maintain a high-treatment ratio, i.e., V_{EP}/V_E. The effect of treatment ratio on the extraction of Pu is shown in Fig. 9. The increase of treatment ratio lowers

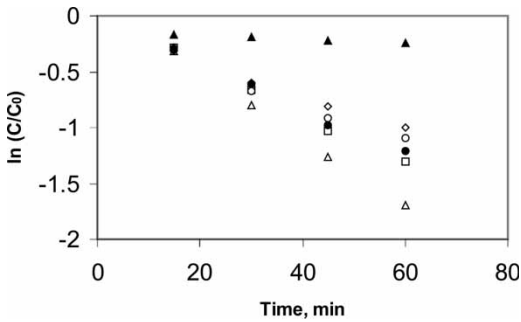

Figure 8. Effect of diluent on the extraction of Pu by ELMLM medium; △ dodecane, □ kerosene, ▲ hexane, ◇ benzene, ○ toluene, ● xylene. LM—0.3 mol dm^{-3} H_2A_2 + 5% Span 80 in respective diluent. EP—0.5 mol dm^{-3} HNO_3 containing 25 mg dm^{-3} Pu(IV). IP—0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$. Equilibrium time 1 h and stirring speed 150 rpm

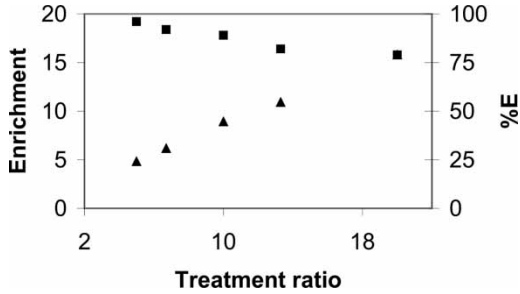

Figure 9. Extraction recovery of Pu by ELM at different treatment ratios. ■: %E, ▲: enrichment. LM—0.3 mol dm^{-3} H_2A_2 + 5%; Span 80 in dodecane. EP—0.5 mol dm^{-3} HNO_3 containing 25 mg dm^{-3} Pu(IV). IP—0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$. Equilibrium time 1 h and stirring speed 150 rpm.

the rate of extraction of Pu in the emulsion phase. Besides the lowering of extraction, 80% of Pu could be extracted by keeping the treatment ratio 20. The high treatment ratio yields more concentrated Pu product. To operate the system with highest efficiency, it is desirable to load the IP of ELM to the greatest extent possible. As reported earlier by Frankenfeld et al. (10) an important feature of liquid membranes is that in many instances, extremely high loading can be attained.

The experiments of ELM extractions were carried out by taking fresh feed solutions and keeping the emulsion the same. The permeability coefficients explaining the rate of the extraction of Pu by ELM and the enrichment of Pu in the IP of emulsion are given in Fig. 10. During first three stages, the permeability coefficient remains the same and then decreases. The decrease in Pu permeability after the third stage may be due to breaking of emulsion (probably because of the excessive swelling of emulsion). In these experiments, loading of Pu up to 1.72 g dm^{-3} in the IP of ELM from EP containing

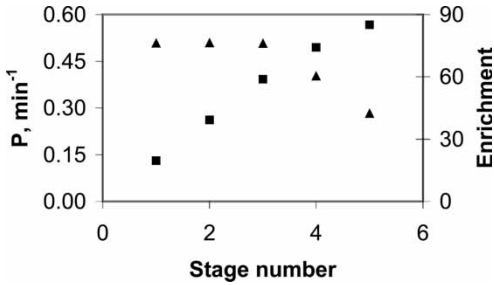

Figure 10. Effect of repeat extractions by same emulsion on the permeability of Pu across ELM. ▲: P, ■: enrichment. LM—0.3 mol dm^{-3} H_2A_2 + 5% Span 80 in dodecane. EP—0.5 mol dm^{-3} HNO_3 containing 19.57 mg dm^{-3} Pu(IV). IP—0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$. Equilibrium time 1 h and stirring speed 150 rpm.

19.57 mg dm^{-3} of Pu was noted. In this concentration factor greater than 80 is demonstrated. These data are useful in the designing of a continuous process system.

Extraction of Pu in the Presence of Ionic Impurities and from Waste Solutions

The influences of ionic impurities in the EP on the extraction of Pu by the ELM are described in Table 3. The permeability of Pu across ELM was determined when EP contains different concentrations of sodium salts of different anionic compositions. The presence of SO_4^{2-} and PO_4^{3-} showed prominent lowering of the extraction of Pu into the ELM phase. With the addition of 0.5 mol dm^{-3} of SO_4^{2-} the rate of Pu extraction was decreased by 35% and in the presence of 0.2 mol dm^{-3} of PO_4^{3-} the same was decreased by 43%. These results are consistent with the solvent extraction behavior of HA. The presence of more complexing SO_4^{2-} and PO_4^{3-} anions lowers the extraction of Pu into the LM phase.

Table 3. Effect of ionic impurities in ep on the rate of transport of Pu(IV) across ELM

Salt	Concentration mol dm^{-3}	P min^{-1}	%E
NIL	—	0.509	90
NaCl	2	0.353	88
	3	0.212	72
$NaNO_3$	3	0.340	87
	4	0.201	70
Na_2SO_4	0.25	0.353	88
	0.50	0.149	59
	1.00	0.085	40
Na_3PO_4	0.10	0.201	70
	0.20	0.122	52
U(VI)	1[a]	0.306	84
	2[a]	0.231	75
	4[a]	0.122	52

[a]U(VI) was added as $UO_2(NO_3)_2$ and concentrations of U(VI) are given in g dm^{-3}.

EP: 0.5 mol dm^{-3} HNO_3 containing ca. 25 mg dm^{-3} of Pu(IV).

IP: 0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$.

LM phase 0.3 mol dm^{-3} H_2A_2 + 5% Span 80 in dodecane.

%E was calculated after 1 h of emulsion–EP equilibration.

The selectivity in the extraction of Pu was determined from two types of cationic mixtures such as some lanthanide and some general type of cations. For analytical simplicity (better resolution in ICP-AES analysis of metal ions), the cations were grouped into two solutions, i.e., solution A and solution B. With this procedure of extraction, Pu could be decontaminated from many metallic impurities (Table 1). For the given experimental conditions, Mo, Zr, and little quantity of Ce got extracted into the membrane phase. The effect of uranium concentration in the EP on the permeation of Pu was determined (Table 3). The increase in the concentration of uranium in EP lowers the permeability of Pu across ELM. For the given conditions of EP uranium forms complex with H_2A_2 and also decomplexing of uranium from H_2A_2 are difficult to achieve. The irreversible extraction of uranium by H_2A_2 lowers the facilitated transport of Pu across the ELM. In Table 4 results are given for the transport recovery of Pu from two types of nuclear waste solutions. Perchloric acid waste is an analytical waste generated during the coulometric analysis of Pu. These solutions generally contain Pu (200–500 mg dm^{-3}), Fe (ca. 70 mg dm^{-3}), NO_3^- (ca. 0.2 mol dm^{-3}), ClO_4^- (ca. 1 mol dm^{-3}), and SO_4^{2-} (ca. 0.5 mol dm^{-3}). More than 90% Pu was extracted from this waste solution in 60 min contact with ELM. The enrichment

Table 4. Recovery of Pu from waste solutions

Waste solution	Time of equilibration min	Concentration of Pu in EP mg dm^{-3}	Permeability P, min^{-1}	%E	Enrichment
Analytical	0	480.0	—	—	—
	15	210.5	ND	56.1	5.6
	30	111.4	0.508	76.8	7.7
	60	42.65	ND	91.1	9.1
	90	22.82	0.511	95.2	9.5
HLLW[1]	0	10.95	—	—	—
	15	4.870	ND	55.1	11.0
	30	1.610	0.505	85.2	17.0
	45	0.500	ND	95.4	19.1
	60	0.190	0.507	98.2	19.7
HLLW[2]	0	10.85	—	—	—
	15	6.910	ND	36.3	7.3
	30	4.780	0.410	55.9	11.2
	45	2.630	ND	77.8	15.2
	60	1.770	0.402	83.7	16.7

ND, Not determined.
LM—0.3 mol dm^{-3} H_2A_2 + 5% Span 80 in dodecane.
IP—0.05 mol dm^{-3} HNO_3 + 0.3 mol dm^{-3} $H_2C_2O_4$.
Equilibrium time 1 h and stirring speed 150 rpm.

more than 9 of Pu in the IP was obtained in this experiment. After 1 h treatment, concentration of Pu in the EP came down from 480 mg dm^{-3} to 23 mg dm^{-3}. The another nuclear waste studied was simulated HLLW. In this HLLW were prepared of two types: HLLW(1) contained no U and HLLW(2) contained 1 g dm^{-3} of U. From HLLW(1) 85% of Pu was extracted by the ELM in 30 min while for the same from HLLW(2) it required more than 60 min. Also to investigate co-extraction of fission products with Pu, a mixture of radiotracers containing Cs-137, Ce-144, and Ru-103, 106 were added to HLLW (1). The (Y-sepctra of EP before and after 1 h contact with ELM were recorded. In this no significant extraction of Cs-137 while 10% of Ce-144 and 9% of Ru-103, 106 extraction were observed. Maximum 98% recovery of Pu with its enrichment more than 19 in IP was obtained.

Demulsification

Demulsification of w/o emulsion is the final step of the process of ELM separations. Methods such as centrifugation, heating, filtration, chemical addition, and electrical are most common in use (22–24). In present investigations, the demulsification was carried out by the addition of acetone or 2-ethylhexanol to the emulsion solution. In 4 mL of emulsion solution, about 2 mL of chemical additive was added to obtain clear phase separation and the recovery of Pu in the IP was determined. More than 95% of material balance of Pu extracted by ELM was obtained when 2-ethylhexanol was used for demulsification. In case of acetone, the material balance of Pu was very poor. This is because in the presence of acetone, the entrapped Pu in IP was getting re-extracted into the separated organic phase. This extraction characteristic was practically confirmed by solvent extraction experiments.

CONCLUSION

An efficient method for the recovery/removal of Pu(IV) from various aqueous solutions using ELM is demonstrated. For the given optimized conditions (EP–2 mol dm^{-3} HNO_3 containing 25 mg dm^{-3} Pu(IV), IP—0.3 mol dm^{-3} $H_2C_2O_4 + 0.05$ mol dm^{-3} HNO_3, LM—0.3 mol dm^{-3} $H_2A_2 + 112$ mol dm^{-3} Span 80 in dodecane) 98% recovery of Pu could be obtained in 1 h equilibration time. The stability of emulsion in different organic solvents was in the order dodecane > kerosene > xylene > toluene > benzene > n-hexane. Greater efficiency of Pu recovery could be obtained by taking high treatment ratio as well as by performing repeat extractions by the same emulsion. The concentration factor of more than 80 was experimentally obtained by repeat extractions method. A selective extraction of Pu is described when EP contains various cationic impurities with the exception

of Zr and Mo, which are co-extracted with Pu. The utility of this method for the recovery of Pu from some waste solutions is demonstrated.

NOMENCLATURE

C_0	Concentration of Pu in EP at time 0 (mg dm^{-3})
C	Concentration of Pu in EP at time t (mg dm^{-3})
%E	Percentage extraction of Pu
ELM	Emulsion liquid membrane
E_n	Enrichment of [Pu] in IP
EP	External phase
IP	Internal phase
K_b	Break-up rate constant of emulsion (s^{-1})
LM	Liquid membrane
P	Permeability coefficient (min^{-1})
$[Pu]_{EP,0}$	Concentration of Pu in EP at time 0 (mg dm^{-3})
$[Pu]_{EP,t}$	Concentration of Pu in EP at time t (mg dm^{-3})
$[Pu]_{IP,t}$	Concentration of Pu in IP at time t (mg dm^{-3})
t	Contact time of EP and emulsion (min)
V_E	Volume of emulsion (cm^3)
V_{EP}	Volume of EP (cm^3)
w/o	Water in oil
ε	Degree of break up of emulsion

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REFERENCES

1. Tani, S., Ozawa, M., and Wakabayashi, T. (1993) Proceedings of the IAEA Technical Committee Meeting on Safety and Environmental Aspects of Partitioning and Transmutation Actinides and Fission Products, Vienna, November 29–December 2.
2. Frankenfeld, J.W. and Li, N.N. (1987) Recent advances in liquid membrane technology. In *Handbook of Separation Process Technology*; Rousseau, R.W., ed.; Wiley: New York, 845–856, Chapter 19.
3. Noble, R.D. and Way, J.D., (eds.) (1987) *Liquid Membranes, Theory and Applications*; American Chemical Society: Washington DCACS Symp. Ser. 347, Chapter 1.
4. Danesi, P.R. (1984) Separation of metal species by supported liquid membranes. *Sep. Sci. Technol.*, 19: 857–894.

5. Separation of Hydrocarbons with Liquid Membrane. U. S. Patent, 3, 410, 794.
6. Kakoi, T., Nishiyori, T., Oshima, T., Kubota, F., Goto, M., Shinkai, S., and Nakashio, F. (1997) Extraction of rare earth metals by liquid surfactant membranes containing a novel cyclic carrier. *J. Membr. Sci.*, 136: 261–271.
7. Kedari, C.S., Pandit, S.S., and Ramanujam, A. (1999) Studies on the in situ electro-oxidation and selective permeation of cerium(iv) across a bulk liquid membrane containing tributyl phosphate as the ion transporter. *Sep. Sci. Technol.*, 34 (9): 1907–1923.
8. Kedari, C.S., Pandit, S.S., and Ramanujam, A. (1999) Selective permeation of plutonium(iv) through supported liquid membrane containing 2-ethylhexyl 2-ethylhexyl phosphonic acid as ion carrier. *J. Membr. Sci.*, 156: 187–196.
9. Kasaini, H., Nakashio, F., and Goto, M. (1998) Application of emulsion liquid membranes to recover cobalt ions from a dual—component sulphate solution containing nickel ions. *J. Membr. Sci.*, 146: 159–168.
10. Frankenfeld, J.W., Cahn, R.P., and Li, N.N. (1981) Extraction of copper by liquid membranes. *Sep. Sci. Technol.*, 16: 385–402.
11. Cahn, R., Li, N.N., and Calo, J.M., (eds.) (1992) *Commercial Application of Emulsion Liquid Membranes*; Marcel Dekker: New York, NY.
12. Hayworth, H.C., Ho, W.S., Burns, W.A., and Li, N.N. (1983) Extraction of uranium from wet process phosphoric acid by liquid membranes. *Sep. Sci. Technol.*, 18 (6): 493–521.
13. Zhang, X.J., Liu, J.H., and Lu, T.S. (1987) Industrial application of liquid membrane separation for phenolic waste water treatment. *Water Treatment*, 2: 127.
14. Draxler, J., Furst, W., and Marr, R.J. (1988) Separation of metal species by emulsion liquid membranes J. *Membr. Sci.*, 38: 281–293.
15. Breembroek, G.R.M., Witkamp, G.J., and Van Rosmalen, G.M. (2000) Design and testing of an emulsion liquid membrane pilot plant. *Sep. Sci. Technol.*, 35: 1539–1571.
16. Kedari, C.S., Pandit, S.S., and Ramanujam, A. (1997) In situ electro-oxidation and liquid-liquid extraction of cerium(IV) from nitric acid medium using tributyl phosphate and 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate. *J. Radioanal. Nucl. Chem.*, 222: 141–147.
17. Wan, Y. and Zhang, X. (2002) Swelling determination of W/O/W emulsion liquid membranes. *J. Membr. Sci.*, 196: 185–201.
18. Ryan, E. and Wheelwright, E.J. (1959) The recovery, purification and concentration of plutonium by anion exchange in nitric acid. USAEC Rept. HW-55893.
19. Cleveland, J.M. (1970) *The Chemistry of Plutonium*; Gordon and Breach: New York, 76.
20. Kulkarni, P.S., Tiwari, K.K., and Mahajani, V.V. (2001) Recovery of nickel via liquid emulsion membrane process using methane sulfonic acid as a strippant. *Sep. Sci. Technol.*, 36: 639–656.
21. Rozen, A.M. and Kruprov, B.V. (1996) Dependence of the extraction ability of organic compounds on their structure. *Russ. Chem. Rev.*, 65 (11): 973–1000.
22. Goto, M., Irie, J., Kondo, K., and Nakashio, F. (1989) Electrical demulsification of w/o emulsion by continuous tubular coalescer. *J. Chem. Eng. Jpn.*, 22 (4): 401–406.
23. Kim, B.-Y., Moon, J.H., Sung, T.-H., Yang, S.-M., and Kim, J.-D. (2002) Demulsification of water-in-crude oil emulsion by a continuous electrostatic dehydrator. *Sep. Sci. Technol.*, 37 (6): 1307–1320.
24. Abou-nemeh, I., Moors, M., and Van Peteghem, A.P. (1992) Electrostatic splitting of the emulsion used in lquid surfactant membrane process for metals separation. *Sep. Sci. Technol.*, 27 (10): 1319–1335.