Equilibrium and Kinetic Studies on the Separation of Uranium and Thorium from Nitric Acid Medium by Liquid Emulsion Membrane Based on Trioctylphosphine Oxide Extractant

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It was found that the extraction percent (*E*%) values of U(VI), Th, Zr and Fe(III) from 0.1 mol dm⁻³ (M) HNO₃ solution by 0.1 M TOPO in cyclohexane solution are 98, 78, 85 and 85%, respectively. Among these elements, only U(VI) and Th were found to be stripped from their organic phase by 0.1 M sodium citrate solution. Cerium, copper and cadmium were not extracted by trioctylphosphine oxide (TOPO) under similar conditions. Based on these equilibrium results, a liquid emulsion membrane (LEM) was prepared from TOPO/Span 80/sodium citrate and the factors affecting its stability were studied. Permeation of U(VI) into this membrane was kinetically studied in detail. Its forward permeation rate was found to be mainly dependent on TOPO concentration and slightly dependent on U(VI) and HNO₃ concentration of the external phase. Permeation results showed that it is possible to recover 98% of U(VI) and 82% of Th from 0.1 M HNO₃ solution containing Ce, Zr, Fe(III), Cd, and Cu by the membrane. The recovered U(VI) and Th were contaminated with less than 2% of Fe(III).

Keywords Liquid emulsion membrane, uranium(VI) and thorium separation, trioctylphosphine oxide, nitric acid, membrane stability, permeation kinetics

Since Li in 1968¹ invented the use of liquid emulsion membrane (LEM) as a new separation technique, many investigators have studied the separation of metals by LEM with special reference to the separation of uranium. In this respect, Macasek *et al.*² presented various emulsion systems with liquid membranes containing different extractants (carriers), such as trioctylphosphine oxide (TOPO), tributyl phosphate (TBP), Kelex-100 and di-2-ethylhexyl phosphoric acid (HDEHP) for U(VI) permeation from sodium sulfate solutions. They reported that the use of HDEHP as a membrane carrier encapsulated in the membrane with a solution of H₂SO₄ or H₃PO₄ is the most effective system. Yoo *et al.*³ studied the separation of U from a solution of H₃PO₄ by LEM containing a combined extractant of HDEHP and TOPO. They found that the mass transfer rate of U increased with temperature. The complexation of U by HDEHP/TOPO was favored at low temperatures, whereas stripping was favored at high temperatures. Both the diffusion of uranyl complex and stripping were considered as the simultaneous rate controlling steps. An improved emulsion extraction process was studied for recovery of U from a wet process phosphoric acid (WPPA) by adding excess oxidizing agent to the WPPA feed using an LEM composed of HDEHP and TOPO.^{4,5} High levels of U extraction and concentration were obtained.

In previous publications^{6,7}, the permeation of Th from a dilute HCl medium by LEM containing HDEHP in cyclohexane as a carrier, polyethylene glycol dioleate as a surfactant, and HCl as a stripping agent was investigated. Based on this system, a method for separation of trace Th-234 from its parent U in macroamounts was developed using a batch technique.⁶ Comparative studies between column and batch LEM techniques for recovery of Th-234 from natural uranium were carried out.⁷

The present work is directed mainly to investigate the possible recovery of U(VI) and Th from Zr, Ce, Fe(III), Cu, and Cd in a nitrate medium using TOPO as a carrier in LEM. Detailed investigations on the stability of the membrane system were performed.

Experimental

Chemicals and reagents

The extractant trioctylphosphine oxide (TOPO) and the cyclohexane were purchased from Aldrich. The surfactants were Sorbitan monooleate (Span 80), Sorbitan monolaurate (Span 20), polyoxyethylene trioleate (Tween 85) and Arlacel A* (Biochemical reagent) which were supplied from Fluka AG. The other chemicals and reagents used were of A.R. grade.

Membrane preparation

Unless otherwise stated the LEM used was prepared by

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mixing 25 cm³ of 0.1 M TOPO in cyclohexane with 4% by volume of Span 80. To this mixture, 25 cm³ of 0.1 M sodium citrate solution was added. The emulsification was performed with an ultra high speed motor equipped with a specially designed bladed impeller stirrer. A stirring speed of 7000 rpm for 3–5 min was used and the mixture was cooled during emulsification.

Procedures

Batch liquid-liquid extraction experiments were carried out by mixing equal volumes of the organic phase and the aqueous phase (5 cm³ each) containing the metal ions, U(VI), Th, Zr, Ce, Fe(III), Cu or Cd of concentration of 0.02 M, unless otherwise stated. Equilibrium was attained by shaking the two phases for 30 min using a mechanical shaker. Known sample portions from the aqueous phase were taken for metal ion determination before and after equilibration to determine the extraction percent in the organic phase. The distribution ratio, *D*, was calculated from the ratio of metal ion concentration in the organic phase to that in the aqueous phase.

In permeation experiments, a known volume of the prepared membrane was dispersed in a thermostated vessel containing a known volume of the external phase, HNO₃, containing the metal ions under investigation. The mixture was agitated and samples were drawn from the external phase after known time intervals for determining the element concentration. Uranium(VI), Ce and Zr were determined in different samples spectrophotometrically using Arsenazo-III and Th with Thoron-I. Cadmium, Cu and Fe(III) were determined by atomic absorption spectrometry.

Results and Discussion

Liquid-liquid extraction

Extraction equilibrium was first examined to identify the extraction behavior and the suitable conditions for U(VI) and Th extraction from HNO₃ medium containing other elements with a solution of TOPO in cyclohexane.

The effect of HNO₃ concentration of the range 0.2–11.0 M on the extraction of 0.02 M of both U(VI) and Th with 0.05 M TOPO was studied. The results obtained showed that the extraction percent (*E*%) increases with the increase in HNO₃ concentration to reach a maximum value of approx. 98% for U(VI) at 0.1 M HNO₃ and approx. 78% for Th at 1.0 M HNO₃. This is followed by a gradual decrease for both elements with further increase in HNO₃ concentration up to 11 M (Fig. 1).

The effect of TOPO concentration on the extraction of 0.02 M of both U(VI) and Th from two different HNO₃ concentrations (0.1 and 5.0 M) is given in Fig. 2 as a log-log relation between the distribution ratio, *D*, and [TOPO]. Straight lines were obtained with slopes equal to one for U(VI) and equal to 3 for Th, from the two HNO₃ concentrations.

Since TOPO is known to extract metal species as ion association complexes and from the slopes obtained, the

Fig. 1 Effect of nitric acid molarities on the extraction % of 0.02 M of U(VI) and Th by 0.05 M TOPO in cyclohexane.

Fig. 2 Effect of TOPO concentration on the distribution of 0.02 M of U(VI) and Th from 0.1 and 5 M HNO₃ solutions.

following extraction equilibria are suggested:

for U(VI) extraction, and

for Th extraction, where a bar above indicates the organic phase.

Among these main extracted species $\text{UO}_2(\text{NO}_3)_2$, TOPO and $\text{Th}(\text{NO}_3)_4$, TOPO were further verified by loading experiments which gave maximum loading of

Table 1 Effect of different reagents on stripping of U(VI), Th, Fe(III) and Zr from 0.1 M TOPO in cyclohexane^a

Stripping reagent	% Stripped			
	U(VI)	Th	Fe(III)	Zr
0.1 M Na acetate	0.0	15	0.0	0.0
0.1 M Na oxalate	0.0	15	0.0	0.0
0.1 M Na citrate	82.0	55	0.0	0.0
0.5 M HCl	35.0	80	44	0.0
0.5 H ₂ SO ₄	64.0	80	86	0.0

a. Organic to aqueous phase volume ratio of 1.0.

U(VI) from HNO₃ solutions when the ratio of U(VI) to TOPO was 1 : 1, and maximum loading of Th when the ratio was 1 : 3.

The effect of temperature on the extraction of both U(VI) and Th was also studied in the temperature range 30–60°C. The results obtained showed that the temperature has only a slight effect on the extraction of both elements.

The extraction of Ce, Zr, Fe(III), Cu, and Cd from 0.1 M HNO₃ solution by 0.1 M TOPO in cyclohexane was investigated. It was found that Ce, Cu and Cd were not extracted, while *ca.* 85% of both Zr and Fe(III) were extracted.

Aqueous solutions of HCl, H₂SO₄, sodium oxalate, sodium acetate and sodium citrate were examined as stripping agents for U(VI), Th, Zr and Fe(III) recovery from their organic phases (Table 1). From this table, it is clear that Zr was not stripped by any of the reagents used. When 0.5 M HCl or H₂SO₄ solution was used, U(VI), Th and Fe(III) were stripped to different extents. On the other hand, 0.1 M sodium citrate solution stripped only 82.0% of U(VI) and 55% of Th. This suggests the use of 0.1 M sodium citrate as an internal phase in the LEM investigations to separate U(VI) and Th from other metal ions.

Stability of LEMs

LEM s are stabilized by surfactant molecules which line up at the interfaces between the membrane and the aqueous phases by appropriate hydrophilic–lipophilic balance value. Stability of an emulsion is greatly influenced by the structure of the surfactant and affects the degree of transport of metal ions through the emulsion membrane. Therefore, the stability of the prepared LEM was studied in terms of the degree of its break-up (leakage), given by the following expression.⁹

$$\text{Leakage \%} = ([C_{\text{ex}}]/[C_{\text{in}}]_{\text{max}}) \times 100$$

where $[C_{\text{ex}}]$ denotes the concentration of the tracer in the continuous external phase and $[C_{\text{in}}]_{\text{max}}$ stands for the maximum possible tracer concentration in the internal phase. Since Cd was not extracted by the investigated system, it was chosen as a tracer in the internal aqueous phase (0.1 M sodium citrate) for stability measurements.

Fig. 3 Effect of the type of surfactant on the leakage % of LEM.

Fig. 4 Effect of Span 80 concentration on the leakage % of LEM.

In all stability measurements, the external phase was 100 cm³ of 0.1 M HNO₃, the LEM volume was 6 cm³ and the temperature used was 30°C.

The effect of the type of surfactant on the stability of the emulsion globules was studied. Using a constant surfactant concentration (4%), the leakage % as a function of time is given in Fig. 3 for the four different surfactants. Tween 85 showed the highest stability for the emulsion globules, followed by Span 80 and Span 20, whereas Arlacel A* showed the lowest stability. However, it was found that Tween 85 has a disadvantage of forming agglomerates, followed by coagulation of the emulsion. Therefore, Span 80 was taken as a surfactant

Fig. 5 Effect of temperature on the leakage % of LEM.

and the effect of its concentration on the emulsion stability was examined. Increasing the concentration of Span 80 from 2 to 6% in the preparation of the membrane showed an increase in its stability (Fig. 4). Higher surfactant concentration was not tested, since it was reported that high surfactant concentration forms a highly viscous W/O emulsion which decreases the rate of metal ions transport through the membrane.⁹

The effect of temperature on the stability of the emulsion globules was studied. The result obtained is given in Fig. 5. It is clear that the stability of the emulsion membrane increases with the decrease in temperature.

The effect of the carrier concentration on the stability of the emulsion was also studied. A carrier concentrations which varied from 0.01 to 0.2 M TOPO in cyclohexane were used. It was found that the emulsion became unstable with increasing the carrier concentration higher than 0.1 M TOPO.

Uranium permeation and kinetics

Based on the results obtained from the studies on both the liquid-liquid extraction and the stability of the emulsion globules, the general conditions for the permeation of U(VI) by LEM in this study were as follows unless otherwise stated: a 100 cm³ of an aqueous external solution of 0.1 M HNO₃, 6.0 cm³ of an LEM prepared from 0.1 M TOPO and 4% Span 80 in cyclohexane together with 0.1 M sodium citrate aqueous solution (pH=8.5). All experiments were carried out at 30°C.

The permeation percent of U(VI) at equilibrium is given in Tables 2a and 2b together with the time at which equilibrium was reached. Each parameter was studied separately by keeping the others constant. From this table it is clear that the permeation percent of U(VI)

Table 2a Effect of [HNO₃] and [U(VI)] in the external phase solution on the permeation % of U(VI) at constant [TOPO]=0.1 M and [Na citrate]=0.1 M

[HNO ₃]/ M	[U(VI)]/ M	Time _{equ} / min	Permeation, %	k/s ⁻¹
0.001	5.00×10 ⁻⁴	15	58.0	0.059
0.001	5.00×10 ⁻⁴	11	79.0	0.090
0.100	5.00×10 ⁻⁴	11	80.0	0.142
1.00	5.00×10 ⁻⁴	11	96.0	0.190
3.00	5.00×10 ⁻⁴	11	87.0	0.154
5.00	5.00×10 ⁻⁴	11	85.0	0.139
0.10	2.50×10 ⁻⁴	11	90.0	0.214
0.10	5.00×10 ⁻⁴	11	80.0	0.143
0.10	7.50×10 ⁻⁴	11	76.0	0.126
0.10	1.25×10 ⁻³	13	74.0	0.090
0.10	1.75×10 ⁻³	13	44.0	0.070

Table 2b Effect of [TOPO] and [Na citrate] in the internal phase on the permeation % of U(VI) at constant [HNO₃]=0.1 M and [U(VI)]=5×10⁻⁴ M

[TOPO]/ M	[Na citrate]/ M	Time _{equ} / min	Permea- tion, %	k/s ⁻¹
1×10 ⁻³	1×10 ⁻¹	9	5.8	0.002
1×10 ⁻²	1×10 ⁻¹	11	15.0	0.015
5×10 ⁻²	1×10 ⁻¹	11	37.0	0.075
1×10 ⁻¹	1×10 ⁻¹	11	80.0	0.140
2×10 ⁻¹	1×10 ⁻¹	13	96.0	0.280
1×10 ⁻¹	1×10 ⁻²	7	75.0	0.123
1×10 ⁻¹	1×10 ⁻¹	11	70.0	0.142
1×10 ⁻¹	1.0	13	93.0	0.141

increased with the increase of HNO₃ concentration from 0.001 to 1 M in the external solution and that it decreases with the increase of HNO₃ concentration from 1 to 5 M. On the other hand, the permeation percent decreases with the increase of U(VI) concentration in the external solution. Increasing the carrier or strippant concentration shows a regular increase in the permeation percent.

In order to get a quantitative measure of the kinetics of uranyl ion complexation and permeation, the following simple first order rate equation was applied:¹⁰

$$[M]/[M_0] = e^{-kt} \quad (1)$$

and

$$\ln([M]/[M_0]) = -kt \quad (2)$$

where [M] is the time dependent concentration of U in the external phase solution, [M₀] is the initial concentration, *t* is the resident time and *k* is the rate constant which characterizes the complexation kinetics.

Plotting ln([M]/[M₀]) against *t* for the different parameters produced straight lines. The values of the rate constant *k* were determined from the slopes in each

Fig. 6 The log-log relation between k and $[\text{HNO}_3]$, $[\text{U(VI)}]$, $[\text{TOPO}]$, and $[\text{Na citrate}]$.

Fig. 7 Plot of permeation % of U(VI), Th and Fe(III) against time using 10:100 (v/v) of LEM: external phase ratio.

case, and are given in Tables 2a and 2b.

Plotting $\log k$ versus the logarithm of the variable under investigation gives its power dependency (Fig. 6). From this figure, it is clear that the rate constant slightly depends on U(VI) and HNO_3 concentrations in the external phase where slopes of -0.6 and 0.3 were obtained, respectively. Concerning the LEM composition, the rate constant was found to be independent of the strippant concentration while a slope of unity is obtained for the carrier concentration. From these data, the rate of U(VI) permeation, at 30°C and at the ratio of membrane to external phase volume of 6:100, can be represented by the following relation:

$$d[\text{M}]/dt = K[\text{HNO}_3]^{0.3}[\text{U(VI)}]^{-0.6}[\text{TOPO}]^1$$

Separation of U and Th from other metal ions

In a trial to increase the permeation of U(VI) more than 80% which was obtained using the above-mentioned conditions, the ratio of membrane to external phase volume was increased to 10:100. Thus, to 100 cm^3 solution of 0.1 M HNO_3 , containing $120\text{ }\mu\text{g}/\text{cm}^3$ of U(VI), and $1000\text{ }\mu\text{g}/\text{cm}^3$ of Th together with $120\text{ }\mu\text{g}/\text{cm}^3$ of each of the metal ions Zr, Ce, Fe(III), Cu, and Cd, a 10 cm^3 portion of the membrane prepared (as given in the experimental section) was added. Under such conditions, the permeation of the investigated metal ions was studied. The data obtained are illustrated in Fig. 7. It was found that approx. 98% U(VI) is permeated together with 82% of Th after 9 min, while less than 2% of Fe(III) is permeated. Concerning the other metal ions, no detectable permeation was observed.

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