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Chemistry-Separation Processes for
Plutonium and Uranium

EXTRACTION OF PROTACTINIUM WITH DIISOBUTYLCARBINOL

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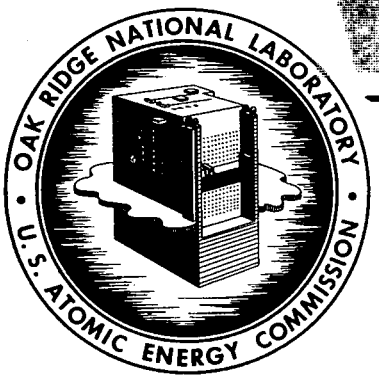

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ABSTRACT

Conditions for extracting protactinium from solutions of irradiated thorium by diisobutylcarbinol (DIBC) (2,6-dimethyl-4-heptanol) were determined in laboratory tracer experiments. Protactinium was extracted from a solution containing 1.0 M thorium, 0.6 M $Al(NO_3)_3$, and 4.0 M HNO_3. Impurities were scrubbed from the organic phase with a solution containing 0.6 M $Al(NO_3)_3$ and 2.0 M HNO_3. Feed/organic/scrub volume ratios were 1/0.4/0.75; there were 4 extraction and 5 scrub stages. Protactinium was stripped from the organic with 1.0 M HNO_3 containing 0.05 M fluoride. The extraction was made at 50°C to decrease emulsion formation. Under these conditions more than 99.5% of the protactinium was extracted. Decontamination factors from uranium, thorium, zirconium-niobium, and the rare earths were 6×10^2, 6×10^4, 5×10^3, 2.5×10^2, and 4×10^3, respectively.

CONTENTS

1.0 INTRODUCTION

Conditions for recovering tracer amounts of protactinium from solutions of irradiated thorium are described.

One of the most promising nuclear power reactor systems utilizes uranium-233 as the fissionable material and thorium as a fertile material. At the present level of knowledge it seems that this is the only thermal reactor system capable of breeding more fissionable material than is consumed. Many processes have been developed for the separation of thorium and uranium-233 from the fission products and from each other. The most completely demonstrated of these separation procedures, the Thorex process, extracts the thorium and uranium with tri-n-butyl phosphate (TBP), leaving the fission products in the aqueous phase.[1,2] Since protactinium is not extracted by this system, the fuel is either stored for 9 months or longer to allow the protactinium to decay to uranium-233 before the fuel is processed[3] or is processed shortly after discharge from the reactor and the aqueous phase is stored to allow decay of the protactinium to the uranium daughter[4] which is then recovered. A process to recover the protactinium prior to the processing of short-decayed fuel would minimize inventory charges of stored fissionable material, separate protactinium which will decay to isotopically pure uranium-233, greatly reduce the volume of radioactive product to be stored, and decrease by as much as 95% the activity of the solutions in the thorium-uranium recovery procedure.

A brief survey of the literature of protactinium recovery and consideration of possible application of the findings to the Thorex process indicated that further study was needed of the extraction of protactinium with DIBC[5] as a head-end process. Laboratory equipment and tracer levels of activity were used in this study. At these protactinium concentrations, traces of impurities in the solvent could account for many of the results reported. Much further study would be required to adapt this process for the isolation of gram quantities of protactinium in engineering-scale equipment. No study was made of the recycle of solvent radiation degradation products, solvent recovery processes, or similar problems. Before such a step could be incorporated as a head-end treatment in the Thorex process, the effect of entrained or dissolved DIBC on the subsequent thorium and uranium recovery by tributyl phosphate would have to be investigated.

Analyses for this investigation were made by G. R. Wilson, J. H. Cooper and E. I. Wyatt of the Analytical Chemistry Division. R. C. Lovelace of the Chemical Technology Division demonstrated laboratory procedures, aided in obtaining materials, and assisted with some of the laboratory experiments.

2.0 EXTRACTION CONDITIONS

Conditions for the extraction of protactinium were determined in a series of batch studies. The effects of the concentration of aluminum nitrate and nitric acid and the percentage of DIBC in Amsco on the separation of protactinium from thorium, uranium, ruthenium, zirconium-niobium, and rare earths were determined. Countercurrent batch extractions were made to determine the possible effect of reflux on the system.

2.1 Batch Extractions

The experimental procedure for the batch extractions was to stir 20 ml of aqueous solution of the desired composition with 20 ml of DIBC in a separatory funnel with an interphase stirrer for 10 min. The phases were then separated and analyzed. The protactinium tracer used was prepared by dissolving thorium nitrate that had been irradiated in the Low Intensity Test Reactor in 6 M HNO_3. In experiments with protactinium not mixed with fission products, protactinium was determined from the gross gamma count of the solution. When solutions contained more than one active ingredient, gamma energy spectrometry was used. For rare earth determinations a lanthanum carrier and beta count method was used.

The acidities of solutions containing protactinium were maintained at at least 1 M to prevent hydrolysis.

Effect of Aluminum Nitrate Concentration. Increasing the aluminum nitrate in 2 M HNO_3 solutions from 0 M to 1.6 M increased the protactinium distribution coefficient to DIBC from 3.7 to 31 (Table 2.1). The extractability of thorium and uranium by DIBC also increased with increasing aluminum nitrate concentration (Table 2.2), but the distribution coefficients remained much less than those of protactinium. From 0.6 M $Al(NO_3)_3$ in 3 M HNO_3 the thorium distribution coefficient was 0.014 and that of uranium was 0.58;[3] the fission product distribution coefficients were: zirconium-niobium 0.011, ruthenium 0.019, and total rare earths 0.0013.

Table 2.1 Distribution of Protactinium to 100% DIBC as a Function of Aluminum Nitrate Concentration

Feed: 2 M HNO_3, 6.72 g Th/liter, 1.5×10^7 Pa γ c/m/ml

$Al(NO_3)_3$ Concentration, M	Distribution Coefficient (o/a)	$Al(NO_3)_3$ Concentration, M	Distribution Coefficient (o/a)
0.0	3.7	0.6	16
0.2	6.0	0.8	15
0.4	6.0	1.0	17
0.5	7.5	1.6	31

Table 2.2 Extraction of Thorium and Uranium by 100% DIBC as a Function of Aluminum Nitrate Concentration

Feed: 232 g Th/liter, 0.5 g U/liter, 3 M HNO_3

$Al(NO_3)_3$ Concentration, M	Distribution Coefficient (o/a)	
	Thorium	Uranium
0.0	0.00099	0.12
0.2	0.0029	0.20
0.4	0.0055	0.21
0.6	0.014	0.58
0.8	0.023	0.67
1.4	0.086	--

Effect of Nitric Acid Concentration. The extraction of protactinium in 0.5 M $Al(NO_3)_3$ by DIBC increased from 6.2 at 1 M HNO_3 to 9.5 at 2.5 M HNO_3 but then decreased to 2.7 at 6 M HNO_3 (Table 2.3). Previous experiments had given nonreproducible data at acidities less than 1 M, and no experiments were made in this range. The thorium distribution coefficient from 0.5 M $Al(NO_3)_3$ solutions increased from 0.00009 when no free acid was present to 0.0006 at 1 M HNO_3 and 0.03 at 5 M acid. The uranium distribution coefficient varied less than 50% between no acid and 6 M HNO_3 (Table 2.4). The extractability of zirconium-niobium and ruthenium increased with increasing acidity but these fission products remained much less extractable than protactinium (Table 2.5).

Table 2.3 Extraction of Protactinium by 100% DIBC as a Function of Nitric Acid Concentration

Feed: 0.5 M $Al(NO_3)_3$, 10 g Th/liter, 1.93×10^7 Pa γ c/m/ml

HNO_3 Concentration, M	Distribution Coefficient (o/a)	HNO_3 Concentration, M	Distribution Coefficient (o/a)
1.0	6.2	3.0	7.3
1.5	9.3	4.0	6.2
2.5	9.5	6.0	2.7

Table 2.4 Extraction of Thorium and Uranium by DIBC as a Function of Nitric Acid Concentration

Feed: 232 g Th/liter, 0.5 g U/liter, 0.5 M $Al(NO_3)_3$

HNO_3 Concentration, M	Distribution Coefficient (o/a)	
	Thorium	Uranium
0.0	0.00009	0.18
1.0	0.0006	0.22
2.0	0.003	0.27
3.0	0.009	0.30
3.5	---	0.29
4.0	0.02	0.28
4.5	---	0.25
5.0	0.03	---
6.0	0.002	0.15

Table 2.5 Extraction of Fission Products by 100% DIBC as a Function of Nitric Acid Concentration

Feed: 0.5 M $Al(NO_3)_3$, 232 g Th/liter, 1.46×10^4 Ru γ c/m/ml, 2.82×10^5 Zr-Nb γ c/m/ml, 5.86×10^5 TRE β c/m/ml, variable acid

HNO_3 Concentration, M	Distribution Coefficient (o/a)		
	Ruthenium	Zirconium-Niobium	Total Rare Earths
0.0	0.07	0.0000	0.000048
1.0	0.07	0.0036	0.000034
2.0	0.08	0.0089	0.000044
3.0	0.12	0.024	0.000063
4.0	0.18	0.044	0.000054
5.0	0.26	0.093	0.000012
6.0	0.02	0.031	0.00064

Effect of DIBC Concentration. The distribution coefficient of protactinium from 0.6 M $Al(NO_3)_3$—2 M HNO_3 increased with increasing DIBC concentration, from 0.026 at 1% DIBC to 3.3 at 20% DIBC and 20 at 100% DIBC (Table 2.6). These high distribution coefficients indicate that solutions containing 20 to 30% DIBC in Amsco could be used if experience should indicate the desirability of decreasing the density or viscosity of the organic phase.

Table 2.6 Extraction of Protactinium by DIBC as a Function of DIBC Concentration

Feed: 0.6 M $Al(NO_3)_3$, 2.0 M HNO_3, 1.58×10^6 Pa γ c/m/ml

DIBC in Amsco, Vol %	Distribution Coefficient (o/a)	DIBC in Amsco, Vol %	Distribution Coefficient (o/a)
1.0	0.026	40.0	7.5
5.0	0.4	60.0	12
10.0	1.3	80.0	14
20.0	3.3	100.0	20

A log-log plot of the distribution of protactinium at low concentrations of DIBC in Amsco has a slope of 1.8 (Fig. 2.1).

2.2 Stripping of Protactinium from DIBC

The addition of fluoride ion to an aqueous 1.0 M HNO_3 stripping solution resulted in the transfer of protactinium to the aqueous phase (Table 2.7). With 0.05 M fluoride, the stripping coefficient (a/o) was maximum, 1500. It is postulated that this high stripping coefficient is caused by the formation of a protactinium fluoride complex that is highly insoluble in DIBC.

Table 2.7 Distribution of Protactinium to Water as a Function of Fluoride Ion Concentration

Initial protactinium activity in DIBC: 1.26×10^6 γ c/m/ml
HNO_3 concentration of the aqueous: 1.0 M

Fluoride Concentration, M	Stripping Coefficient (a/o)	Fluoride Concentration, M	Stripping Coefficient (a/o)
0.0	0.5	0.05	1500
0.01	300	0.07	400
0.03	450	0.1	300

2.3 Emulsion Formation

An emulsion formed when DIBC and thorium-containing feed solutions were contacted. The amount of emulsion formed was dependent on the acid concentration of the feed, the viscosity of the organic phase, and the temperature of the system. As the acid concentration was increased to approximately 2 M, the amount of emulsion formed also increased; further increases in the acid concentration caused a decrease in the amount of emulsion (Fig. 2.2a). When the acid concentration in the feed was 6 M

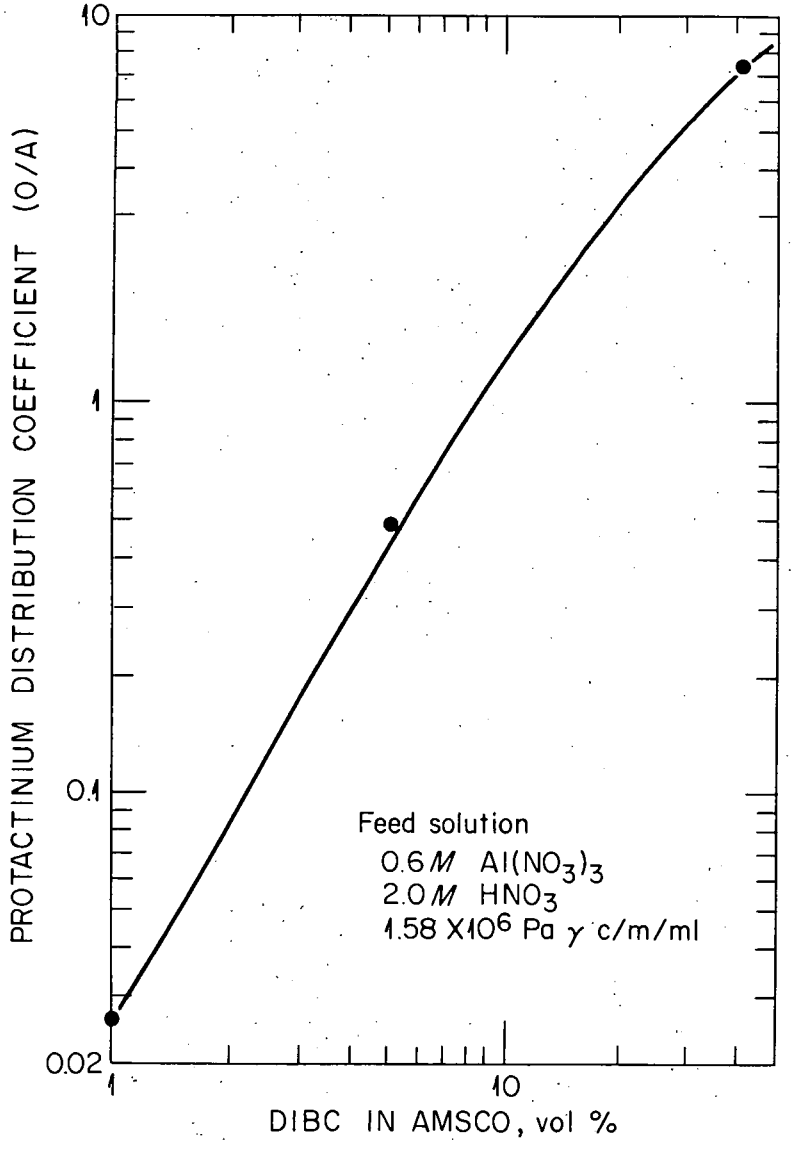

Fig. 2.1. Distribution Coefficient of Protactinium as a Function of Percentage DIBC in Amsco.

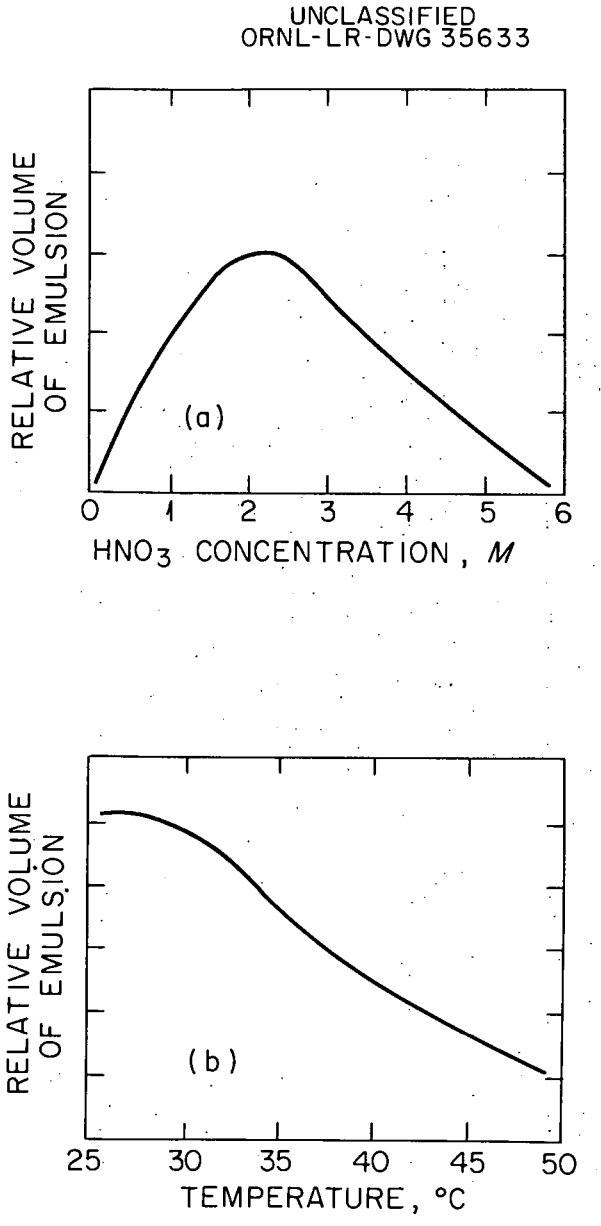

Fig. 2.2. Amount of Emulsion Formed with DIBC [feed: 1 M Th, 0.6 M $Al(NO_3)_3$] as a function of (a) feed acidity at room temperature and (b) temperature at feed acidity of 0.2 N HNO_3.

there was no evidence of emulsion formation, but at this acidity the protactinium was rather poorly extracted (Table 2.3). It was found that as the temperature was increased over the range 25-50°C the amount of emulsion formed became less (Fig. 2.2b). Since the extraction of protactinium remained high at 50°C, this operating temperature was selected for countercurrent batch extractions.

2.4 Countercurrent Batch Extractions

Based on the above batch extractions, the following conditions were selected for laboratory countercurrent batch extractions:

Feed	1 M Th, 0.5 g U/liter, 0.6 M $Al(NO_3)_3$, 4 M HNO_3, tracer protactinium and fission products
Extractant	100% DIBC
Scrub	2 M HNO_3, 0.6 M $Al(NO_3)_3$
Volume ratio	Feed/Extractant/Scrub = 1/0.4/0.75
Stages	4 extraction, 5 scrub
Temperature	50°C

The 3.1 M nitric acid in the extraction section is a compromise between the 1.5 to 2.5 M acid, which is most desirable for protactinium extraction and 6 M acid, which is most desirable to minimize emulsion formation.

In batch extraction experiments, ruthenium was the most extractable fission product. In a single countercurrent batch extraction with fission products present, zirconium-niobium was the most extractable activity, having a separation factor from the protactinium of 250 whereas that from ruthenium was 5×10^3. Other separation factors were uranium 600, thorium 5×10^4, and rare earths 4×10^3. Less than 0.5% of the protactinium remained in the aqueous phase. The protactinium in the second scrub stage built up to about twice the feed concentration because of reflux.

Tracer concentrations of protactinium were used since limited shielding was available. The effects of intense localized irradiation of solutions and possible solvent solubility effects were therefore not encountered.

The operating temperature of 50°C was maintained by using extraction cells with water jackets. Hot water was pumped into the jackets from a constant-temperature bath. The temperature in the bath was set sufficiently above the desired temperature that the heat loss in the system was just sufficient to maintain the 50°C temperature. At this temperature and at an acid strength of approximately 3 M, the disengaging time of the organic and aqueous phases was approximately 1 min, although a very light emulsion remained at the interface. It is believed that this light emulsion, even if it formed, would not interfere with the proper operation of a pulsed column.

3.0 DEGRADATION OF DIBC

3.1 Radiation

DIBC used for extraction of protactinium-233 in full-scale work will be subjected to very intense radiation. Studies at dosages of 0 to 105 watt-hr/liter showed that the extracting ability of DIBC was not impaired by radiation. Samples of 100% DIBC were irradiated in the 10,000-curie cobalt-60 source at levels up to 105 watt-hr/liter. The solvent was then contacted with feed and the distribution coefficients were determined. When thorium irradiated to 4000 g of mass-233 per ton of thorium and decayed 30 days is processed the exposure of the solvent during one process pass is estimated at about 50 watt-hr/liter. An unexplained increase in the distribution coefficient from 17 to 35 occurred with exposures of 14 watt-hr/liter but at 105 watt-hr/liter it decreased to about 30 (Table 3.1).

Table 3.1 Extraction of Protactinium by DIBC as a Function of the Radiation Exposure of the DIBC

Feed: 0.6 M $Al(NO_3)_3$, 2.0 M HNO_3, 2.5×10^6 Pa αc/m/ml

Irradiation Exposure, watt-hr/liter	Distribution Coefficient (o/a)	Irradiation Exposure, watt-hr/liter	Distribution Coefficient (o/a)
0.0	17	14.0	35
3.5	20	105.0	30
10.0	25		

3.2 Heat

DIBC will be heated during processing both as a result of the absorption of the intense radiation and because of operation of the extraction column at an elevated temperature. In order to determine the effect of heat on DIBC, a sample of 100% DIBC was refluxed for 0.5 hr at its boiling point (172 to 175°C). There was no difference in the protactinium distribution coefficient between the heated and unheated DIBC when contacted with the same feed under otherwise identical conditions.

The DIBC was evaporated from a DIBC-protactinium solution that had contacted a nitric acid feed solution. Nitrogen dioxide fumes were emitted, indicating that the dissolved nitric acid attacked the DIBC. However, under the conditions to be used in the extraction process there was no evidence for such attack.

4.0 NIOBIUM INTERFERENCE AND THE PLATING OF PROTACTINIUM ON CONTAINER WALLS

Niobium interference with protactinium adsorption on silica gel was reported in previous studies.[6] No interference with protactinium extraction was noted in these tracer level studies.

In order to test for the plating of protactinium onto the container walls, feed solutions were boiled down to about half volume in both glass and stainless steel containers and then diluted to original conditions. Analyses of the treated samples showed no decrease in protactinium activity over untreated control samples. However, the activity level of the protactinium was much lower than that expected under process conditions. It is anticipated that if the acidity of the feed is kept high the loss of protactinium by this mechanism will be negligible.

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