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Extraction Behavior of Americium and Plutonium with Mixed Solvent Extractants

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ABSTRACT

The mixed solvent extractants, dibutyl N,N-diethylcarbamoylmethylenephosphanate (DBDECMP)-tributyl phosphate (TBP), using carbon tetrachloride diluent, were studied for extracting americium (III) and plutonium (IV) from 0.35 and 7M HNO_3 at 25°C. Synergistic effects were observed in this system as was the case with preliminary results (described herein) using the dihexyl analogue DHDECMP and TBP.

INTRODUCTION

The extraction behavior of americium and plutonium in mixtures of tributyl phosphate (TBP) and the bidentate organophosphorus extractant dihexyl N,N-diethylcarbamoylmethylenephosphonate (DHDECMP) was of interest because of potential problems in cross contamination of the extractants when a Purex process was used in conjunction with a process utilizing a DHDECMP extractant. The latter process has been investigated for the removal of actinides from nuclear fuel reprocessing wastes[1-2] and for the purification of americium[3]. Because DHDECMP has not been available in pure form, its dibutyl analog (DBDECMP) was studied with various amounts of TBP in carbon tetrachloride for the extraction of americium and plutonium from 0.35 and 7M HNO_3 solutions. Some preliminary studies with impure DHDECMP and TBP are also described. No studies have been reported with these mixed extractants[4].

EXPERIMENTAL

Reagents

Reagent grade TBP was supplied by Eastman Kodak Company. The DBDECMP was obtained as reagent grade material (99% purity) from Richmond Organics. The description of the impure (63% purity) DHDECMP is given elsewhere[1]. The TBP was further purified by scrubbing with 1M sodium carbonate and water. DBDECMP and TBP were analyzed (after storage over molecular sieves) and both contained <1% total impurities as determined by gas chromatography - mass spectroscopy methods. The carbon tetrachloride and other chemicals used were reagent grade. The extractant-diluent solutions were pre-equilibrated with 0.35 or 7.0M nitric acid solution prior to use.

The plutonium-239 and americium-241 solutions were prepared prior to each group of experiments by diluting aliquots of stock solutions into nitric acid of 0.35 or 7.0M. The plutonium (14g

Pu/l 0.53M HNO_3) and americium (1.4g Am/l 0.35 or 7.0M HNO_3) stock solutions were purified by anion exchange and oxalate precipitation, respectively, to contain <0.1 and <1% impurity elements. The plutonium (IV) oxidation state was stabilized by addition of stoichiometric amounts of ferrous sulfamate and sodium nitrite as determined from oxidation state analysis of the Pu (VI) and Pu (III).

Procedure

Distribution coefficients (D) were determined by mechanically shaking (for 15 minutes) equal volumes (5 ml) of actinide feed solution and extractant in 15 ml glass vials, at ambient temperatures ($25 \pm 1^\circ C$). (Equilibrium was found to be established within 1 minute.) The phases were found to be effectively separated in 15 minutes, although they were allowed to remain standing over night. Duplicate samples of the aqueous phase were drawn by syringe and each sample analyzed at least twice. The D values (ratio of the total concentration of solute in the organic phase to its total concentration in the aqueous phase) were calculated by using the analysis of the aqueous feed solutions before and after contact with the extractant. The organic phase was difficult to analyze accurately for plutonium and americium and was not performed routinely, but the results of several tests indicated material balances >90%.

Analysis

Nitric acid concentration was determined by acid-base titration (citrate was added to complex the actinide). Plutonium and americium concentrations were determined by radiometric counting methods. Plutonium in the presence of americium was determined by pulse-height radiometric analysis after isotopic dilution and solvent extraction separation. The oxidation state analysis of the plutonium was accomplished by spectrophotometric techniques.

RESULTS AND DISCUSSIONS

Figure 1 shows the results of initial studies using impure DHDECMP in diisopropyl benzene and CCl_4 to extract americium from 0.35, 1.0 and 7.0M HNO_3. The dependency of americium extractions on DHDECMP concentration is approximately three and suggests that americium is extracted by three DHDECMP molecules. This dependency was also found (vida infra) for DBDECMP, and is in agreement with reported values[5,6]. As shown in Figure 1, the addition of TBP to the 30 vol % DHDECMP appears to increase the extraction of americium in both 1 and 7M HNO_3 (distribution ratios for Am in TBP are <0.02). Since pure DHDECMP was not available, further experiments were performed with high purity DBDECMP.

Tables 1 and 2 contain the distribution ratio data for americium and plutonium between DBDECMP, TBP, and mixtures of DBDECMP and TBP in CCl_4 and 0.35 and 7.0M HNO_3 feed solutions. The distribution ratios given are an average of at least duplicate, and in most cases, triplicate measurements. The standard deviations of the measurements are also given.

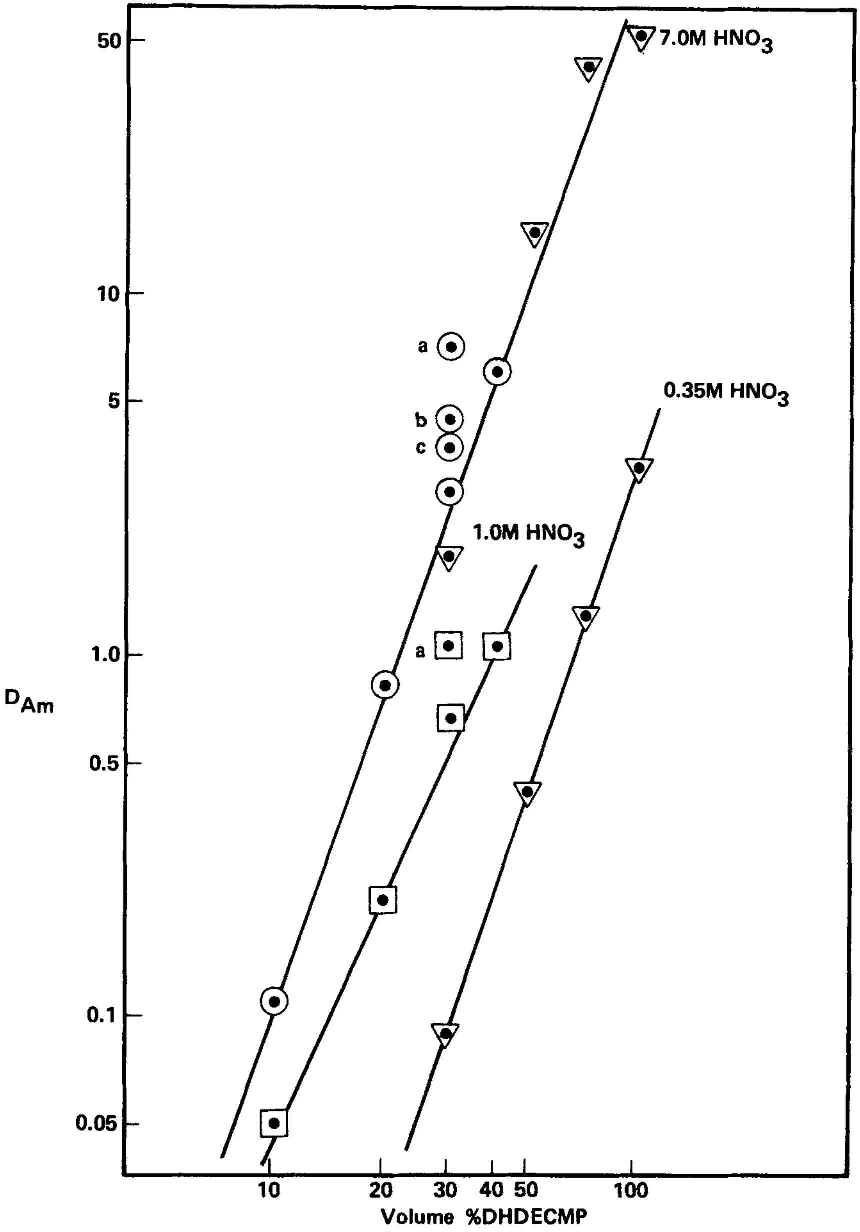

Figure 1. Americium Distribution Ratio versus DHDECMP Concentration for nitric acid feeds (0.0096g/l Am and 0.01g/l Pu) (Extractant contains a) 30% TBP, b) 20%TBP, c) 10%TBP) (▽ CCl_4 diluent; ⊙ and ▣ diisopropyl benzene diluent.)

TABLE 1

AMERICIUM DISTRIBUTION RATIO DATA WITH DBDECMP, TBP, AND DBDECMP-TBP IN CARBON TETRACHLORIDE AND VARIOUS NITRIC ACID FEED SOLUTIONS

Feed Solution	DB - TBP	D_{Am}^{DB}	D_{Am}^{TBP}	D_{Am}^{DB+TBP}	Synerg. Factor
0.0010g/l Am	0 -1.00M	-	0.013±0.004	-	-
7.0M HNO_3	0.25-0.75	0.16±0.01	0.011±0.004	0.36 ±0.01	2.1
	0.50-0.50	1.25±0.05	0.008±0.003	2.04 ±0.02	1.6
	0.75-0.25	5.90±0.49	<0.001	6.13 ±0.02	1.0
	1.0 -0	12.3±0.1	-		-
0.10g/l Pu	0 -1.00M	-	0.018±0.005	-	-
0.00093g/l	0.25-0.75	0.18±0.03	0.009±0.002	0.39 ±0.02	2.1
Am	0.50-0.50	1.65±0.01	0.004±0.002	2.17 ±0.01	1.3
7.0M HNO_3	0.75-0.25	6.10±0.10	0.002±0.002	6.21 ±0.15	1.0
	1.00-0	12.5±0.3	-	-	-
0.00089g/l	0 -1.00M	-	0.007±0.002	-	-
Am	0.25-0.75	0.001±0.002	0.004±0.002	0.007±0.002	1.4
0.35M HNO_3	0.50-0.50	0.012±0.002	<0.001	0.032±0.004	2.7
	0.75-0.25	0.045±0.005	<0.001	0.091±0.005	2.0
	1.00-0	0.12 ±0.01	-	-	-
0.093g/l Pu	0 -1.00M	-	0.011±0.001	-	-
0.00099g/l	0.25-0.75	0.004±0.002	0.007±0.002	0.010±0.005	0.9
Am	0.50-0.50	0.019±0.004	<0.001	0.037±0.009	1.9
0.35M HNO_3	0.75-0.25	0.056±0.009	<0.001	0.102±0.010	1.8
	1.00-0	0.094±0.009	-	-	-

In general the distribution ratios are in agreement with reported values$^{6-8}$. The presence of plutonium in the feeds did not appear to lower D_{Am}. When plotting log D_{Am} against log DBDECMP concentrations, the slope drops from approximately 3 to 2.5 in going from DBDECMP to mixtures of DBDECMP and TBP. The dependency of D_{Am} on TBP concentration is approximately 2. The

TABLE 2

PLUTONIUM DISTRIBUTION RATIO DATA WITH DBDECMP, TBP, AND DBDECMP-TBP IN CCL$_4$ AND VARIOUS NITRIC ACID FEED SOLUTIONS

Feed Solution	DB - TBP	D_{Pu}^{DB}	D_{Pu}^{TBP}	D_{Pu}^{DB+TBP}	Synerg. Factor
0.095g/l Pu	0 -1.00M	-	48.5±6.9	-	-
7.0M HNO$_3$	0.25-0.75	50.4±0.3	29.0±2.6	192±14	2.4
	0.50-0.50	226 ±15	17.0±2.0	540±52	2.2
	0.75-0.25	600 ±53	6.0±0.8	1090±117	1.8
	1.00-0	1120 ±39	-	-	-
0.10g/l Pu	0 -1.00M	-	46.5±6.4	-	-
0.001g/l Am	0.25-0.75	72 ±18	30.8±2.7	179±9	1.7
7.0M HNO$_3$	0.50-0.50	370 ±35	15.0±1.7	504±73	1.3
	0.75-0.25	958 ±140	5.3±0.4	711±29	0.7
	1.00-0	1330 ±75	-	-	-
0.97g/l Pu	0 -1.00M	-	44.6±4.9	-	-
7.0M HNO$_3$	0.25-0.75	58.6±5.4	28.2±0.2	177±9	2.0
	0.50-0.50	211 ±26	15.0±0.2	511±66	2.3
	0.75-0.25	513 ±62	5.1±0.1	833±134	1.6
	1.00-0	1070 ±96	-	-	-
0.010g/l Pu	0 -1.00M	-	0.95±0.09	-	-
0.35M HNO$_3$	0.25-0.75	0.34±0.04	0.58±0.06	1.79±0.04	1.9
	0.50-0.50	1.90±0.32	0.44±0.04	4.12±0.41	1.8
	0.75-0.25	5.00±0.60	0.18±0.04	-	-
	1.00-0	9.44±0.18	-	-	-
0.0010g/l Am	0 -1.00M	-	0.91±0.08	-	-
0.093g/l Pu	0.25-0.75	0.45±0.05	0.40±0.06	5.7 ±0.2	6.7
0.35M HNO$_3$	0.50-0.50	2.34±0.18	0.25±0.06	7.7 ±0.4	3.0
	0.75-0.25	7.10±0.88	0.08±0.04	10.2 ±0.9	1.4
	1.00-0	9.35±0.50	-	-	-
0.90g/l Pu	0 -1.00M	-	0.27±0.09	-	-
0.35M HNO$_3$	0.25-0.75	0.24±0.05	0.18±0.06	0.89±0.07	2.1
	0.50-0.50	1.40±0.10	0.12±0.04	1.95±0.03	1.3
	0.75-0.25	3.50±0.35	0.06±0.02	4.12±0.15	1.1
	1.00-0	7.97±0.26	-	-	-

dependency of D_{Pu} on DBDECMP, DBDECMP-TBP, and TBP concentration is approximately 2.1, 1.6, and 1.5 respectively, for 7M HNO_3. In dilute HNO_3, D_{Pu} is more erratic and less reliable. D_{Am}^{TBP} also has considerable error and is not consistent, but the small numbers do not significantly alter the sums of D_{Am}^{TBP} and D_{Am}^{DB}.

The synergistic factor shown in Tables 1 and 2 is the ratio of the distribution ratio in the mixed extractants to the sum of D^{DB} and D^{TBP}. The synergistic effect appears to increase for americium in 7M HNO_3 when the ratio of TBP to DBDECMP increases, but is the opposite in 0.35M HNO_3 feeds. However, for plutonium increasing the ratio of TBP to DBDECMP gives a larger synergistic factor for both 0.35 and 7.0M HNO_3 feeds.

In conclusion, addition of TBP to DBDECMP increases the distribution ratio of both plutonium and americium. There appears to be a small but significant synergistic effect in both concentrations of nitric acid feed. This is in agreement with the preliminary results using DHDECMP-TBP. The synergism observed indicates that problems could occur when a Purex process is used in conjunction with a process utilizing DBDECMP or DHDECMP extractant. Further work needs to be done to elucidate the extraction mechanism for the mixed extraction system and to explore the advantages of using TBP mixed with DHDECMP.

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