MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0134131 5

ORNL-3496
UC-10 – Chemical Separations Processes
for Plutonium and Uranium
TID-4500 (22nd ed.)

CHEMICAL TECHNOLOGY DIVISION
CHEMICAL DEVELOPMENT SECTION C
PROGRESS REPORT ON SEPARATIONS PROCESS RESEARCH FOR JANUARY-JUNE, 1963

K. B. Brown

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price: $2.50 Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-3496

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION, CHEMICAL DEVELOPMENT SECTION C, PROGRESS REPORT ON SEPARATIONS CHEMISTRY AND SEPARATIONS PROCESS RESEARCH FOR JANUARY-JUNE, 1963

K. B. Brown

Date Issued

OCT 18 1963

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0134131 5

CONTENTS

Page

Abstract 1

1. Separations Process Development 6

1.1 Cesium Recovery from Ores 6

1.1.1 Separation of Cesium from Pollucite Ore 6

1.1.2 Cesium Recovery with BAMBP 8

1.1.3 Cesium Recovery with Santophen-1 10

1.2 Separation of Alkali Metals 16

1.3 Acid Recovery by Amine Extraction 21

1.4 Final Cycle Plutonium Recovery by Amine Extraction . . 23

1.4.1 Batch Tests with Aged 1BP Solution 24

1.4.2 Batch Tests with Fresh 1BP Solution 27

1.5 Extraction of Lanthanides and Transplutonium Elements by Dialkylphosphoric Acids 30

1.5.1 Extraction by Di(2-ethylhexyl)phosphoric Acid from Citric Acid 32

1.5.2 Extraction by Di(2-ethylhexyl)phosphoric Acid from Glycolic Acid 33

1.5.3 Extraction by Di(2-ethylhexyl)phosphoric Acid from Oxydiacetic Acid 33

1.5.4 Extraction by Di(2-ethylhexyl)phosphoric Acid from Glycine 34

1.5.5 Modification of Di(2-ethylhexyl)phosphoric Acid by a Phenol 34

1.5.6 Extraction by Ditridecylphosphoric Acid 36

1.5.7 Extraction by Di(2-ethylhexyl)dithiophosphoric Acid 37

1.6 Extraction of Nitric Acid, Lanthanides, and Transplutonium Elements by Amines 37

1.6.1 Extraction of Nitric Acid from Nitrates 37

1.6.2 Extraction of Lanthanides and Transplutonium Elements 39

1.7 Extraction of Lanthanides and Transplutonium Elements from Carbonate Solutions 41

Page

1.8 Summary of Differences Between the Extractabilities of Americium and Cerium and Europium 41

1.9 Extraction of Californium and Einsteinium 44

1.10 Extraction of Americium(VI) 44

1.10.1 Preparation of Americium(VI) 45

1.10.2 Procedure 45

1.10.3 Extraction by Tri-n-octylphosphine Oxide . . 46

1.10.4 Extraction by Tributyl Phosphate 48

1.10.5 Extraction by Di(2-ethylhexyl)phosphoric Acid. 48

1.10.6 Extraction by a Tertiary Amine 50

1.11 Separation of Transplutonium Elements from Iron . . . 51

1.11.1 Precipitation Methods 52

1.11.2 Solvent Extraction 52

2. Fundamental and Descriptive Chemistry of Solvent Extraction Systems 62

2.1 Extraction of Metals from Chloride Solutions with Amines 62

2.1.1 Procedures 62

2.1.2 Germanium(IV) 62

2.1.3 Selenium(IV) 64

2.1.4 Rubidium 64

2.1.5 Strontium 64

2.1.6 Yttrium 64

2.1.7 Niobium(V) 67

2.1.8 Molybdenum(VI) 67

2.2 N,N-Dialkyl Amides as Extractants 70

2.2.1 Uranium and Thorium Extraction from Nitric Acid 72

2.2.2 Extraction of Nitric Acid 79

2.2.3 Zirconium, Hafnium, and Europium Extraction from Nitric Acid 79

2.2.4 Extractions from Solutions High in Nitrate and Low in Acidity (Lanthanides, Transplutonium Elements, Cesium, Strontium) 82

2.2.5 Uranium and Thorium Extraction from Chloride and Sulfate Solutions 83

Page

2.2.6 Compatibility of Diluents and Phase Separation . 84

2.2.7 Uranium Stripping 85

2.2.8 Description of Reagents 86

2.2.9 Reagent Stability 86

2.3 Distribution Coefficients and Separation Factors as Functions of Diluent Type: Tributyl Phosphate Diluted by Aromatics vs Tributyl Phosphate Diluted by Aliphatics 88

2.4 Improved Stability of Amsco 125-82 90

2.5 Diluent Effect on Strontium Extraction by Di(2-ethylhexyl)phosphoric Acid 92

2.5.1 pH Shift 93

2.5.2 Synergism and Antagonism 100

2.6 The Equilibrium Between Tri-n-octylamine and Sulfuric Acid in Various Diluents of Low Volatility 102

2.6.1 Screening Tests 103

2.6.2 Sulfuric Acid Distribution 103

References 109

CHEMICAL TECHNOLOGY DIVISION, CHEMICAL DEVELOPMENT SECTION C, PROGRESS REPORT ON SEPARATIONS CHEMISTRY AND SEPARATIONS PROCESS RESEARCH FOR JANUARY-JUNE, 1963

K. B. Brown

ABSTRACT

Cesium Recovery from Ores

Adaptation of the phenol extraction (Phenex) process to the recovery of cesium from ore leach liquors continued to show promise. In roast-leach tests, 98 to 99% of the cesium was dissolved from pollucite ore by roasting the ore at 800°C with 1.8 parts of Na_2CO_3 plus 1.2 parts of NaCl and leaching with water. More than 99% of the cesium was recovered from the leach liquor and separated from other alkali metals by extracting with 4-*sec*-butyl-2-(α-methylbenzyl)phenol (BAMBP) in diisopropylbenzene and stripping with hydrochloric acid. Santophen-1 also extracted cesium effectively, but, because of the limited solubility of the cesium-Santophen-1 complex in the diluent, the utility of this phenol in ore processing is questionable.

Separation of Alkali Metals

The extraction and separation of alkali metals from nitrate solutions was studied with several different types of extractants, including substituted phenols, alkylphosphoric acids, sulfonic acids, carboxylic acids, and mixtures of some of these. With all of these reagents, cesium was extracted more strongly than rubidium, which in turn was extracted more strongly than the other alkali metals. Separation factors were higher with the phenols than with the other extractants.

Acid Recovery by Amine Extraction

Preliminary tests showed the potential usefulness of tertiary amines for recovering and purifying phosphoric acid from the highly contaminated wet-process acid produced in the fertilizer industry. Water stripping of the amine solvent yielded a product that was more than 1.5 *M* in H_3PO_4 and was almost free of iron and aluminum.

Final-Cycle Plutonium Recovery by Amine Extraction

Batch equilibration tests with both aged and fresh samples of Purex-plant 1BP solution showed that the aged but not the fresh samples contained a considerable quantity of zirconium-niobium species highly extractable by the hydrocarbon diluents used with amines and other extractants. The amounts of zirconium-niobium extractable from the aged solution were sufficient to account for the low decontamination previously obtained when aged plant 1BP solution was used in continuous countercurrent testing of the plutonium-recovery flowsheet. Individual and batch cascade tests with the fresh plant solution showed separation and decontamination factors high enough for use in the projected process.

Extraction of Lanthanides and Transplutoniums by Dialkylphosphoric Acids

The behavior of americium and curium relative to the lanthanides in extraction by di(2-ethylhexyl)phosphoric acid (HDEHP) from carboxylic acids was shifted from the behavior in extractions from mineral acids, where americium is similar to promethium. The shift was greatest in extractions from oxydiacetic acid, where cerium was 4 times as extractable as americium, while differences within the element groups were very small. Extractions from nitric acid were increased by adding glycine (aminoacetic acid). Extractions were greatly reduced by adding a phenol to HDEHP. Ditridecylphosphoric acid (HDTDP) was a stronger extractant than HDEHP and gave smaller differences between the lanthanides. Di(2-ethylhexyl)-di-thio-phosphoric acid was a much weaker extractant than HDEHP and gave only small differences between the elements.

Extraction of Nitric Acid, Lanthanides, and Transplutonium Elements by Amines

A tertiary amine (Alamine 336) nitrate extracted nitric acid from 6 N $LiNO_3$ until the apparent composition was $R_3N \cdot 1.5\ HNO_3$. A quaternary ammonium (Aliquat 336) nitrate extracted nitric acid from 6 N $LiNO_3$ until the apparent composition was $R_4NNO_3 \cdot HNO_3$. Alamine 336 extracted europium and americium about 3 times as well as cerium from carboxylic acids, while preference was in the reverse order from concentrated $Al(NO_3)_3$. Aliquat 336 extracted cerium, europium, and americium strongly and about equally from dilute $KHCO_3$ solutions.

Extraction of Americium(VI)

In several extraction systems Am(III) was more extractable than Am(VI). Maximum preference factors were higher than 10^4 for extraction by di(2-ethylhexyl)phosphoric acid, higher than 100 by tri-n-octylphosphine oxide, and about 30 by tributyl phosphate. In extractions by amines, the differences were smaller and under some conditions in the reverse direction. Some of the systems appear suitable for the separation of americium from curium.

Separation of Transplutonium Elements from Iron

Separation of transplutonium elements from large amounts of iron may be possible by precipitation with fluoride. Very high separation of americium and iron was obtained by multistage countercurrent extraction of americium with di(2-ethylhexyl)phosphoric acid in diisopropylbenzene from dilute nitrate solutions containing 0.04 M citric acid at pH 4.5, followed by stripping with dilute nitric acid containing 0.04 N citric acid at pH 0.5.

Extraction of Metals from Chloride Solutions with Amines

In further studies on the extraction of metal ions from HCl and LiCl—0.2 M HCl (0.5 to 10 M Σ Cl^-) with representative primary, secondary, tertiary, and quaternary amines in diethylbenzene, maximum extraction coefficients obtained (0.1 M amine) were about 70 for Ge(IV), 70 for Se(IV), 6×10^{-4} for Rb, 4×10^{-3} for Sr, 0.03 for Y, 200 for Nb(V), and 1700 for Mo(VI). In general, extraction coefficients increased with increasing chloride concentration and were higher with Aliquat 336 (quaternary amine) than with the other amines.

N,N-Dialkyl Amides as Extractants

Fourteen amides were tested for their ability to extract uranium and thorium, and several of them to extract zirconium, hafnium, europium, cerium, americium, and nitric acid, from aqueous solutions. The extractions varied widely with structure of the amides, suggesting that, with suitable choice of structure and aqueous nitric acid concentration, thorium and uranium can be recovered either separately or simultaneously. None of the amides gave uranium extraction as high as did tributyl phosphate (TBP),

but all indicated uranium-thorium separations that were at least as good as those obtained with TBP. Calculated uranium-fission product separation factors with some branched amides were two- to tenfold better than those obtainable with TBP, and there was evidence that it may be possible to separate transplutonium elements from lanthanides. The amides alone were ineffective extractants for uranium or thorium from sulfuric acid and hydrochloric acid solutions, but their combinations with di(2-ethylhexyl)phosphoric acid gave synergistic uranium extraction about as high as that with di(2-ethylhexyl)phosphoric acid and TBP. The amides tested extracted nitric acid readily. A number of conditions were encountered where poor phase separations occurred. Phase separations were usually better when the amide was dissolved in an aromatic rather than an aliphatic diluent. Uranium stripping was accomplished by water or by dilute nitric acid. The stability of the amides to hydrolysis by acids increases with increasing molecular weight. After severe treatment with boiling 2 M HNO_3, two high-molecular-weight amides showed 20 to 40% hydrolysis.

Distribution Coefficients and Separation Factors as Functions of Diluent Type: Tributyl Phosphate - Aromatics vs Tributyl Phosphate - Aliphatics

Solutions of tributyl phosphate (TBP) in some simple alkylbenzenes, for example, diethylbenzene, butylbenzene, and trimethylbenzene, gave uranium extraction coefficients from 2 M HNO_3 which were about 1.5 times higher than those shown by the same concentration of TBP in Amsco 125-82. Calculated separation factors of uranium from hafnium were about 2 times higher.

Improved Stability of Amsco 125-82

The stability of Amsco 125-82 (an aliphatic hydrocarbon) toward nitric acid was improved in two ways: (1) by treatment with concentrated sulfuric acid to destroy the sites otherwise reactive to nitric acid, probably by sulfonation to sulfuric acid-soluble by-products or by rearrangement of the molecule to a more stable configuration; and (2) by preliminary nitric acid degradation followed by scrubbing with sulfuric acid, in which the important nitration products are soluble. After treatment, the Amsco could be degraded with nitric acid but at a consistently low rate, very similar to that of the relatively stable n-dodecane.

Diluent Effect on Strontium Extraction by Di(2-ethylhexyl)phosphoric Acid

With n-nonane as diluent, strontium extraction by di(2-ethylhexyl)-phosphoric acid (HDEHP) was synergized by the addition of tributyl phosphate and depressed by the addition of dodecyl alcohol. The maximum enhancement observed was a doubling, and it occurred when the mole ratio TBP/DEHP was near 2. With benzene and some other diluents, in contrast, the E_{Sr} remained nearly constant at each given value of the mole ratio NaDEHP/ΣDEHP. Both NaDEHP/ΣDEHP and E_{Sr} shifted vs pH with additives to benzene and with substitution of other diluents: to lower pH with benzene + TBP and with dibutyl ether; to higher pH with benzene + dodecyl alcohol and with chloroform.

The Equilibria Between Tri-n-octylamine and Sulfuric Acid in Various Diluents of Low Volatility

A diluent of low volatility suitable for use with tri-n-octylamine (TOA) and its sulfate salts (TOAS and TOAHS) is desired in order to permit the determination of water activities in the extractant phase by isopiestic osmotic balancing. Several low-vapor-pressure liquids that showed sufficient miscibility with TOA and TOAS were tested as diluents in the equilibrium extraction of sulfuric acid. While their equilibrium curves differed noticeably from each other and from that obtained with benzene, they were sufficiently like the latter to be considered for tests to be compared with tests in benzene. Two of these, phenylcyclohexane (vapor pressure, 60 μ at 25°C) and n-hexadecane modified with 5 vol % dodecanol (vapor pressure of mixture, less than 5 μ) were chosen for first use in the projected isopiestic tests.

1. SEPARATIONS PROCESS DEVELOPMENT

1.1 Cesium Recovery from Ores

(D. J. Crouse, W. D. Arnold)

Studies of a process[1] for recovering cesium from ore leach liquors by extracting with substituted phenols continued to show considerable promise. In roast-leach tests, cesium was dissolved efficiently from pollucite ore by roasting the ore with alkaline fluxes and leaching with water. Highest recoveries (98 to 99%) were obtained with Na_2CO_3-NaCl flux. In batch countercurrent tests, more than 99% of the cesium was recovered from the leach liquor and separated from other alkali metals by extracting with 4-sec-butyl-2-(α-methylbenzyl)phenol (BAMBP) in diisopropylbenzene and stripping with hydrochloric acid. Good recoveries were also obtained with Santophen-1, but physical difficulties were encountered.

1.1.1 Separation of Cesium from Pollucite Ore

In earlier tests,[1] cesium was dissolved from pollucite ore by roasting the ore with $Ca(OH)_2$-$CaCl_2$ and leaching with water. However, the presence of $CaCl_2$ in the leach liquor complicated processing, since calcium hydroxide precipitated upon addition of the caustic which was necessary for adjusting the pH to the level required for solvent extraction. A suitable feed was prepared only after precipitating essentially all the calcium from the liquor.

In more recent tests, this complication has been avoided by simply roasting the ore with alkali metal salts. As shown in Table 1.1.1, a major fraction of the cesium was dissolved by roasting the pollucite ore at 600 to 900°C with a number of different alkaline fluxes and leaching with water. Grinding the ore to -200 mesh considerably increased recoveries over those obtained with ore ground to -50 mesh. Recoveries were highest with Na_2CO_3-NaCl flux. With pulverized ore and a Na_2CO_3/NaCl/ore ratio of 1.8/1.2/1.0, 99% of the cesium was dissolved with water after roasting for 2 hr at 800°C. Cesium recovery was somewhat less (96%) when the temperature was lowered to 600°C. Also, less cesium was dissolved when smaller amounts of flux were used. Fluxes of NaOH-NaCl, NaOH-Na_2CO_3,

Table 1.1.1. Roast-Leach Tests with Pollucite Ore

Procedure: pollucite ore (22.9% Cs, 0.64% Rb, 0.98% K, 1.45% Na, 0.21% Li, 17.5% Al_2O_3, and 48.5% SiO_2) was mixed with indicated flux and roasted for 2 hr; cooled mass leached with water for 1 hr using ~15 ml water/g of pollucite ore

Fusion Mixture (grams per gram of ore)	Ore Mesh Size	Roast Temp. (°C)	Cesium Recovery[a] (%)
1.8 Na_2CO_3-1.2 NaCl	-50	800	90[b]
1.8 Na_2CO_3-1.2 NaCl	-200	800	99
1.8 Na_2CO_3-1.2 NaCl	-50	600	58
1.8 Na_2CO_3-1.2 NaCl	-200	600	96
1.0 Na_2CO_3-0.7 NaCl	-200	800	89
0.5 Na_2CO_3-0.3 NaCl	-200	800	75
3.0 NaOH-1.0 NaCl	-50	800	70[b]
0.7 NaOH-2.3 NaCl	-50	800	90[b]
0.7 NaOH-2.3 NaCl	-50	900	95[b]
2.3 NaOH-0.7 Na_2CO_3	-50	600	89
1.7 NaOH-1.3 KOH	-50	600	55[b]
1.7 NaOH-1.3 KOH	-200	600	70
1.7 NaOH-1.3 KOH	-50	800	50[b]
3.0 KOH-1.0 KCl	-50	800	70[b]
3.0 LiOH-1.0 LiCl	-50	800	80[b]
3.0 $Ca(OH)_2$-1.0 $CaCl_2$	-50	800	70[b]
1.3 $Ca(OH)_2$-1.7 NaCl	-50	900	20[b]
3.0 Na_2CO_3	-50	800	25[b]
3.0 K_2CO_3	-50	800	85[b]
3.0 $CaCO_3$	-50	800	<1[b]

[a]Based on leach liquor and residue analyses. Material balances (based on total cesium found compared to cesium in the head ore) were in the range 85-110%.

[b]Based on head ore and leach liquor analyses. Since material balances were not obtained, the numbers should be considered only as crude estimates of the effectiveness of the treatment.

or K_2CO_3 were about as effective as Na_2CO_3-NaCl, but NaOH-KOH, KOH-KCl, LiOH-LiCl, and $Ca(OH)_2$-$CaCl_2$ gave poorer results. The fluxes containing hydroxides were difficult to handle in that they fused into a hard mass that stuck to the sides of the porcelain crucible. In the water-leaching step, these fused materials were slow to soften and disintegrate. This behavior could account for failure to obtain higher recoveries in many tests with the hydroxide fluxing agents.

1.1.2 Cesium Recovery with BAMBP

The recovery of cesium from a pollucite ore leach solution was successfully demonstrated in a batch countercurrent test with 1 M BAMBP in diisopropylbenzene. The liquor was prepared by roasting the pollucite ore with Na_2CO_3-NaCl flux (Na_2CO_3/NaCl/ore ratios of 1.8/1.2/1.0) for 2 hr at 800°C and leaching with water. The filtered liquor had a pH of 12.9 and contained 9.2 g of cesium per liter. Cesium recovery in the roast-leach operation was 98%. After adjustment of the pH to 13.1 with sodium hydroxide, more than 99.4% of the cesium was recovered in five extraction and two scrub stages (Table 1.1.2). Relative flows of organic/aqueous feed/scrub (0.02 M NaOH) were 1/1.5/0.2. The scrubbed extract, which contained about 13 g of cesium per liter, was 96% stripped in a single contact with 0.08 N HCl at an organic/aqueous phase ratio of 8/1 to give a solution containing about 100 g of cesium per liter. Evaporation of this solution to dryness gave a cesium chloride product containing a total of less than 0.2% of the other alkali metals and silicon:

	Product Analysis (%)	Decontamination Factor,[a] Cs/metal
Cs	82.1	--
Rb	0.011	230
K	0.137	610
Na	0.021	16,000
Li	<0.01	>10
Si	<0.02	>3000

[a]From feed liquor to product.

Table 1.1.2. Recovery of Cesium from Pollucite Liquor with BAMBP

Organic phase: 1 M BAMBP in diisopropylbenzene
Aqueous phase: liquor prepared by roasting pollucite ore with Na_2CO_3-NaCl and leaching with water; liquor adjusted to pH 13.1 with caustic; constituents in grams per liter: 9.0 Cs, 0.28 Rb, 9.1 K, 37.5 Na, 0.01 Li, 0.01 Fe, 0.05 Al, 7.2 Si, 27 Cl, and 22 CO_3; traced with Cs^{134}
Scrub: 0.02 M NaOH
Contact: batch countercurrent; 5-min contacts
Relative flows: organic/feed/scrub = 1/1.5/0.2

Stage	pH	Cs Concentration (g/liter)		E_a^o
		Organic	Aqueous	
Scrub-2	12.8	13.5	9.3	1.4
Scrub-1	12.8	15.0	12.1	1.2
Aqueous feed	13.1	--	9.0	--
Extraction-1	13.1	15.3	8.5	1.8
Extraction-2	13.1	13.9	5.9	2.3
Extraction-3	13.1	9.3	2.1	4.5
Extraction-4	13.1	3.3	0.36	9.3
Extraction-5	13.1	0.49	0.04	11.4

The potassium content of the product was higher than expected in practice since the feed liquor for this test was accidentally contaminated with potassium, bringing the concentration to about 20 times the usual.

Cesium can be extracted more efficiently with BAMBP in aliphatic diluents than in diisopropylbenzene, which was used in the above experiment. In batch tests with a pollucite liquor (9.4 g of cesium per liter, pH 13.1) at a phase ratio of 1/1, cesium extraction coefficients were 34, 24, and 26 in 1 M BAMBP in Amsco 125-82, Amsco 123-15, and ordinary kerosene diluents, respectively, compared with 7.6 with diisopropylbenzene (Table 1.1.3). Phase separation was rapid with all of these diluents.

Table 1.1.3. Effect of Diluent on Cesium Extraction with BAMBP

Organic phase: 1 M BAMBP in indicated diluent
Aqueous phase: pollucite ore leach solution containing 9.4 g of cesium per liter at pH 13.1; traced with Cs^{134}
Phase ratio: 1/1
Contact time: 5 min

Diluent	Phase Separation Time (min)	pH	Cs Concentration (g/liter)		Cesium E_a^o
			Organic	Aqueous	
Diisopropylbenzene	1.1	13.1	8.35	1.10	7.6
Kerosene	1.2	13.1	9.00	0.35	26
Amsco 123-15[a]	1.2	13.1	8.95	0.37	24
Amsco 125-82[b]	1.2	13.1	9.04	0.27	34

[a]A refined kerosene.

[b]Aviation naphtha.

1.1.3 Cesium Recovery with Santophen-1

Santophen-1 is a commercial phenol that showed high cesium extraction power in fission product recovery tests.[1] Its selectivity for cesium over other alkali metals is about the same as that of BAMBP (Sec 1.2). Comparative isotherms for the extraction of cesium from a pollucite liquor (pH 13.1) with 1 M solutions of BAMBP and Santophen-1 in diisopropylbenzene are shown in Fig. 1.1.1. Santophen-1 extracted cesium more efficiently than BAMBP at the dilute end of the isotherm, but the latter loaded higher with cesium. The lower loading with Santophen-1 was probably due to the loss of an appreciable fraction of this phenol to the aqueous phase that occurs at high pH's.

Effect of Different Diluents. — Santophen-1 is soluble to 1 M concentration at room temperature in aromatic diluents, such as diisopropylbenzene and Solvesso 100, but not in aliphatic diluents such as kerosene. However, 1 M solutions were prepared in kerosene modified with 50 vol % Solvesso 100 or 10 vol % tridecanol. The extraction of cesium as a function of pH with 1 M Santophen-1 in the latter two diluents and in

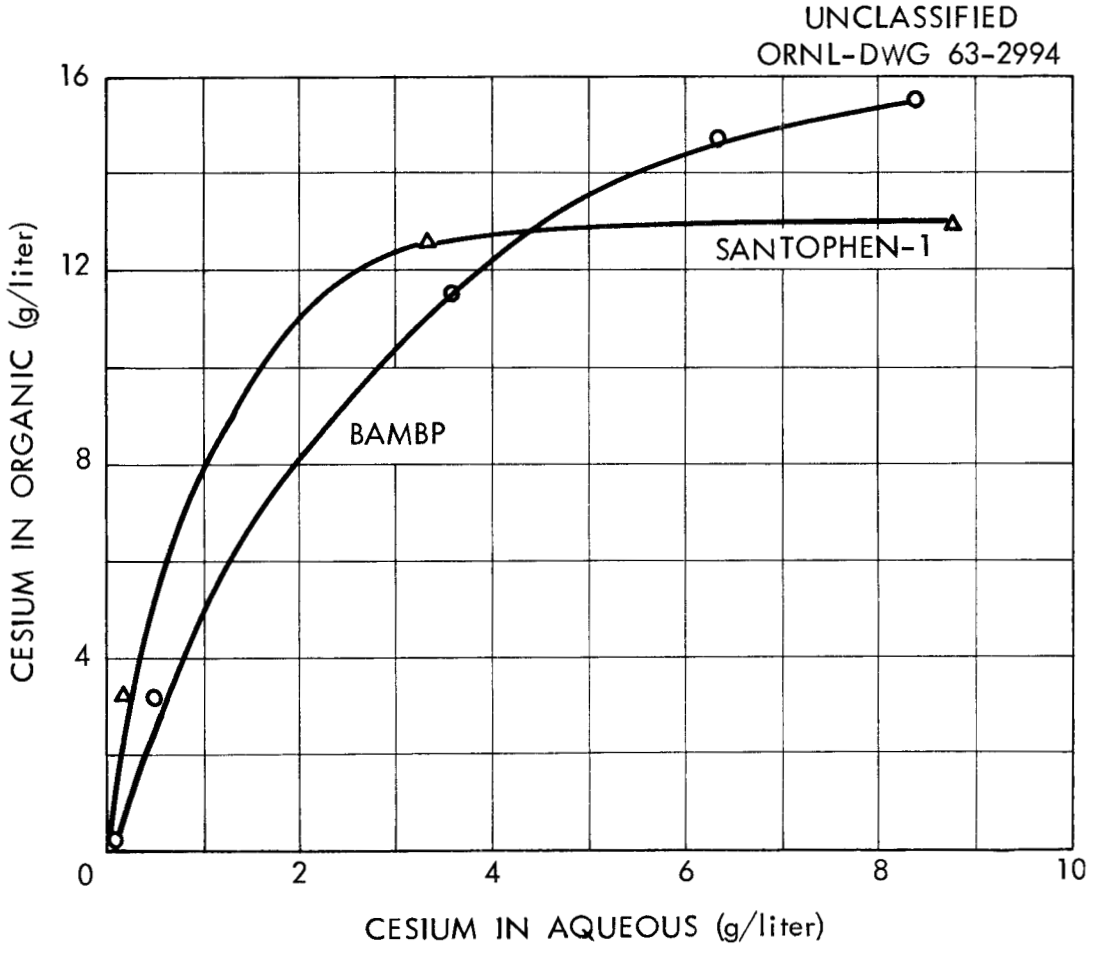


Fig. 1.1.1. Cesium Extraction Isotherms. Organic phase: 1 M phenol in diisopropylbenzene. Aqueous phase: pollucite ore leach solution containing 9.0 g of cesium per liter at pH 13.1.

diisopropylbenzene and Solvesso 100 is shown in Fig. 1.1.2. As expected from earlier tests, the extraction coefficient increased with increase in pH to 12 to 12.5 and then decreased because of loss of phenol to the aqueous phase. Extraction coefficients were highest with 50% kerosene—50% Solvesso 100 diluent and lowest with Solvesso 100 diluent. Phase separation was good with all the diluents except kerosene-tridecanol.

Batch Countercurrent Tests. — Attempts to use Santophen-1 in batch countercurrent extractions of cesium from pollucite liquors have thus far been unsuccessful because of the formation of a white crystalline precipitate in the system, which caused severe emulsions. The precipitate, formed primarily in the aqueous-feed end of the system (first extraction stage and scrub stages), was shown to contain both cesium and phenol. Apparently the cesium—Santophen-1 complex has very limited solubility in the diisopropylbenzene and 50% kerosene-50% Solvesso 100 diluents used in the test runs. However, the precipitate is slow to form under some conditions and in simple batch equilibrations was not observed even at cesium loadings up to 13 g/liter.

In one batch countercurrent test with 1 M Santophen-1 in diisopropylbenzene and a pollucite liquor containing 9 g of cesium per liter, the precipitate formed almost immediately in the feed stage, where the loading of the solvent with cesium was 10 to 12 g/liter. The feed-liquor pH in this run was about 13, and acid was added to the last extraction stage to minimize the loss of Santophen-1 to the raffinate, which is high when treating liquors at this pH level. Since the high reflux of Santophen-1 occurring under these conditions may have contributed to the precipitation problem, another run was made (this time with 1 M Santophen-1 in 50% kerosene-50% Solvesso 100) with liquor adjusted to pH 12 with CO_2. (About 20% of the cesium and 30% of the silica in the liquor were precipitated in the feed adjustment step.) Acid was not added to the last extraction stage in this run, since the pH of the raffinate was 11.0, and Santophen-1 loss to the raffinate under these conditions is relatively low (less than 1 g/liter). The extraction system contained five stages, and the extract was scrubbed in two stages with water. Physical operation of the circuit was satisfactory throughout 26 contacts, that is, addition of 26 increments each of organic, feed liquor, and scrub, which was considerably more than

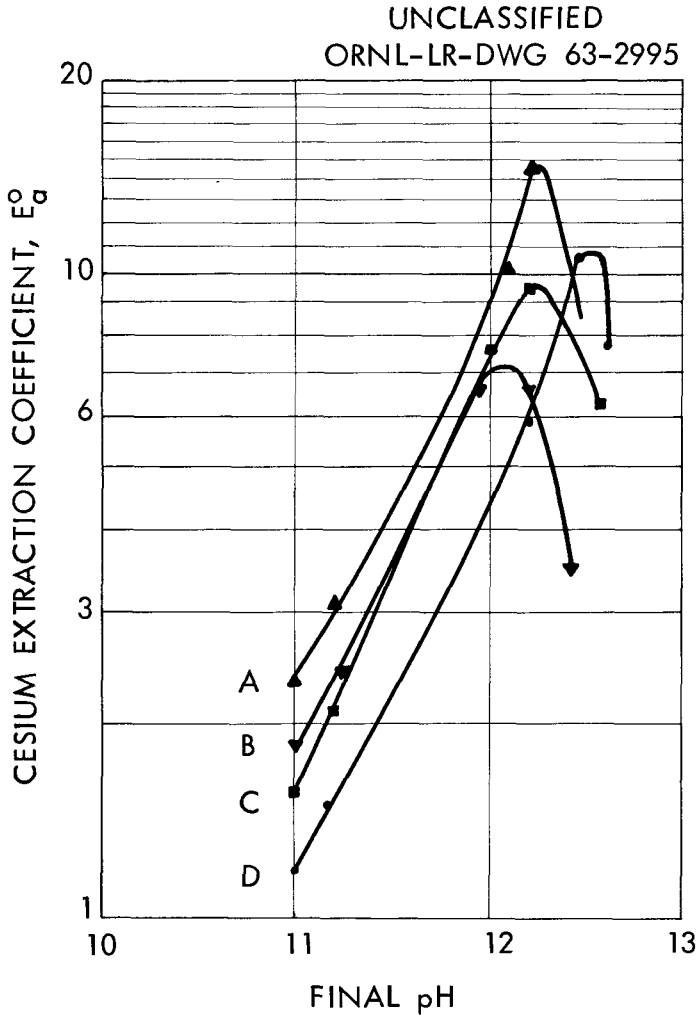


Fig. 1.1.2. Effect of Diluent on Cesium Extraction with Santophen-1. Organic phase: 1 M Santophen-1 in (A) 50% kerosene—50% Solvesso 100, (B) 90% kerosene—10% tridecanol, (C) diisopropylbenzene, or (D) Solvesso 100. Aqueous phase: pollucite ore leach liquor adjusted in pH with NaOH or HCl (initial Cs concentration = 8.7 to 9.6 g/liter). Phase ratio: 1/1.

necessary to achieve steady-state conditions. A profile of the system taken after 21 contacts showed that 99.6% of the cesium had been recovered (Table 1.1.4). Extraction coefficients in the extraction and scrub stages ranged from 3 to 4.5. On the 27th contact, a precipitate formed in the top extraction stage and the two scrub stages, causing gel-like emulsions. This terminated the run.

Table 1.1.4. Recovery of Cesium from Pollucite Liquor with Santophen-1

Organic phase: 1 M Santophen-1 in 50% kerosene-50% Solvesso 100
Aqueous phase: liquor prepared by roasting pollucite ore with Na_2CO_3-NaCl and leaching with water; liquor adjusted to pH 12 with CO_2; constituents in g/liter, 7.60 Cs, 0.25 Rb, 0.36 K, 42.5 Na, 0.017 Li, 5.5 Si, 28 Cl, and 15 CO_3
Scrub: H_2O
Contact: batch countercurrent; 5-min contacts
Relative flows: organic/feed/scrub = 1/1.2/0.2

Stage	pH	Cs Concentration (g/liter)		Cesium
		Organic	Aqueous	E_a^o
Scrub-2	11.3	10.0	2.79	3.6
Scrub-1	11.4	10.4	2.93	3.6
Aqueous feed	12.0	--	7.59	-
Extraction-1	11.3	10.5	3.54	3.0
Extraction-2	11.1	5.05	1.29	3.9
Extraction-3	11.1	1.87	0.41	4.5
Extraction-4	11.0	0.50	0.104	4.8
Extraction-5	11.0	0.114	0.026	4.4

The scrubbed extract collected during the run (before precipitation occurred) was stable for seven days and then precipitated after it was moved. The cesium concentration in the solvent dropped from 9.6 to 1.9 g/liter, and the phenol concentration dropped from its original value of about 1 M to 0.8 M. Heating under the hot-water tap dissolved most of the precipitate, indicating that precipitation might be avoided by operating at higher temperature. However, because of a strong adverse

effect of an increase in temperature on the cesium extraction coefficient, this is not an attractive solution to the problem. The precipitate was also redissolved by adding ketones, TBP, diamylamylphosphonate (DAAP), or di(2-ethylhexyl)phosphoric acid (D2EHPA) to the solvent. Adding TBP (and presumably DAAP) depresses the cesium extraction coefficient (Table 1.1.5). Modification with D2EHPA synergizes cesium extraction at relatively low pH's (Sec 1.2) and use of this reagent combination may be practicable. However, this mixture is more difficult to strip and less selective for cesium than the phenol alone.

Table 1.1.5. Effect of TBP on Cesium Extraction with Santophen-1

Organic phase: 1 M Santophen-1 with indicated concentration of TBP in Solvesso 100 or 50% kerosene-50% Solvesso 100
Aqueous phase: pollucite leach liquor containing 7.6 g of cesium per liter at pH 12.0
Contact: 5 min at 1/1 phase ratio

Diluent	TBP Concentration (M)	Phase Separation Time (min)	pH	Cesium E_a^o
Solvesso 100	0.0	1.5	11.1	1.51
	0.1	1.0	11.2	1.06
	0.3	1.6	11.3	0.46
	0.5	3.0	11.4	0.16
50% Kerosene-50% Solvesso 100	0.0	0.7	11.0	3.10
	0.1	0.8	11.1	1.96
	0.3	0.8	11.4	0.70
	0.5	3.0	11.5	0.21

1.2 Separation of Alkali Metals

(D. J. Crouse, W. D. Arnold)

The extraction and separation of alkali metals from nitrate solutions was studied with several different types of reagents including substituted phenols, alkylphosphoric acids, sulfonic acids, carboxylic acids, and mixtures of some of these. Separation factors between the alkali metals were higher with the phenols than with the other extractants.

In all tests, the organic phase was contacted with an equal volume of an aqueous phase containing 0.1 M $CsNO_3$, 0.2 M $RbNO_3$, 0.4 M KNO_3, 0.4 M $NaNO_3$, and 0.4 M $LiNO_3$. The pH was adjusted by adding concentrated solutions of either nitric acid or caustic to the mixed phases. Mixing was continued for at least 5 min after reagent addition before the phases were sampled for flame spectrometric analysis.* It should be emphasized that the magnitude of many of the extraction coefficients shown in Figs. 1.2.1-3 is limited by the loading of the extractant with alkali metals. Also, for tests with Santophen-1, dodecylphosphoric acid (DDPA) and neo-tridecanoic acid, extraction coefficients at high pH levels are undoubtedly significantly depressed by large loss of extractant (as the alkali metal salt) to the aqueous phase. For uniformity, diisopropylbenzene was used as diluent for all the extractants. This is not necessarily the optimum diluent choice, and with certain extractants (for example BAMBP; see Sec 1.1.2) higher extraction coefficients might be obtained with, for example, an aliphatic diluent.

The favorable separations attainable with phenols[2-5] are shown in Figs. 1.2.1a and 1.2.1c for 4-sec-butyl-2-(α-methylbenzyl)phenol (BAMBP) and Santophen-1 (4-chloro-2-benzylphenol). At pH 12 to 13, where extraction coefficients with these reagents are relatively large, the order of extractability was Cs > Rb > K > Na > Li. In this pH region, separation factors were 15 to 20 for both cesium/rubidium and rubidium/potassium. At pH values less than 8, sodium and potassium were extracted more strongly than cesium and rubidium, but this was not of practical importance since extractions of all of the alkali metals were too small to be of interest.

---

*Analyses were performed by T. C. Rains of the ORNL Analytical Division.

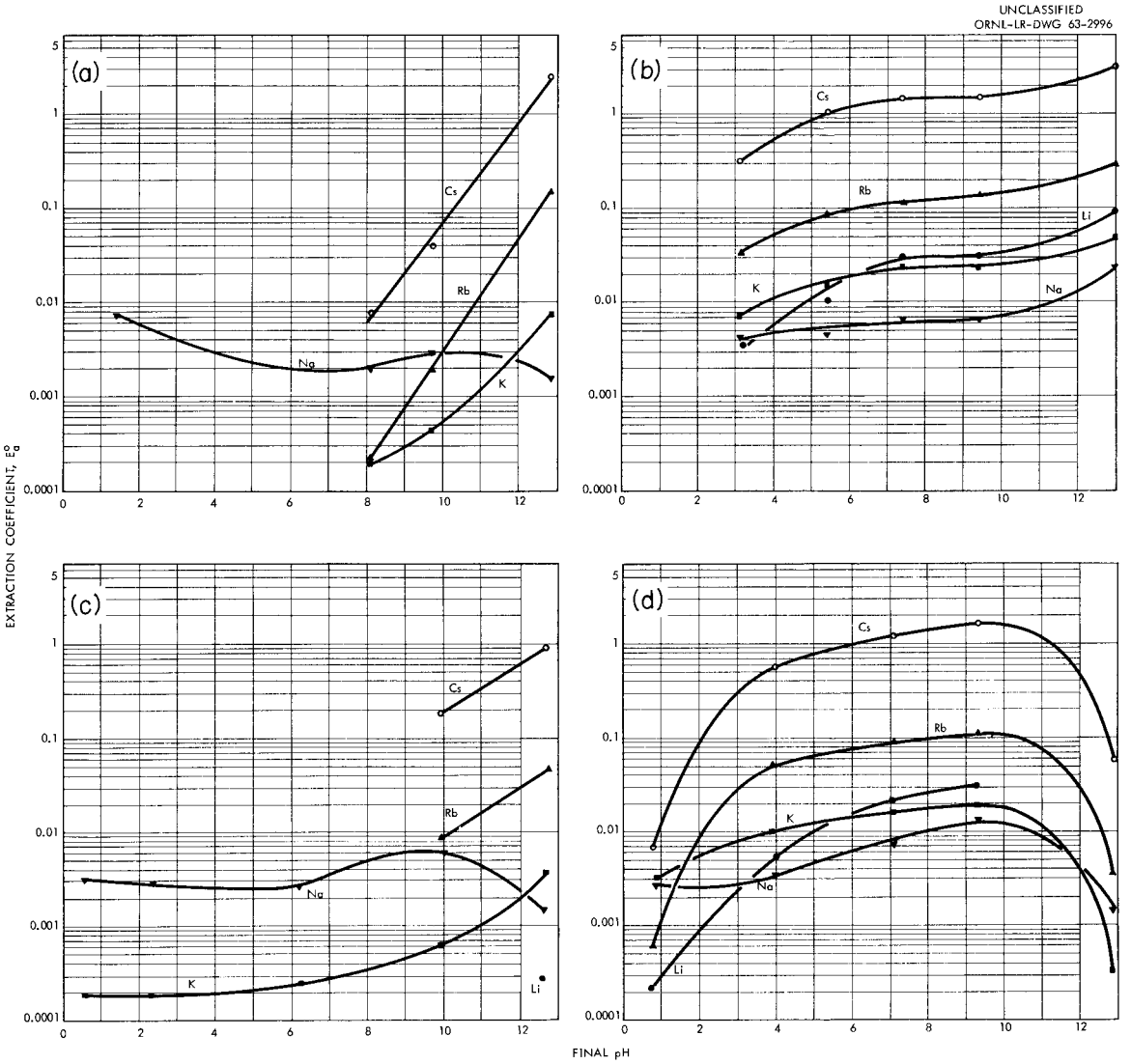


Fig. 1.2.1. Extraction of Alkali Metals. Organic phase: (a) 1 M BAMBP, (b) 1 M BAMBP—0.1 M D2EHPA, (c) 1 M Santophen-1, and (d) 1 M Santophen-1—0.1 M D2EHPA; diisopropylbenzene diluent. Aqueous phase: mixed alkali metal nitrate solution containing 0.1 M Cs, 0.2 M Rb, 0.4 M K, 0.4 M Na, and 0.4 M Li. Phase ratio: 1/1. Procedure: pH was adjusted by adding concentrated nitric acid or 50% caustic solution to the phases during contact. (For pH values where coefficients are shown for some but not all alkali metals, coefficients for the missing metals were less than 0.0001.)

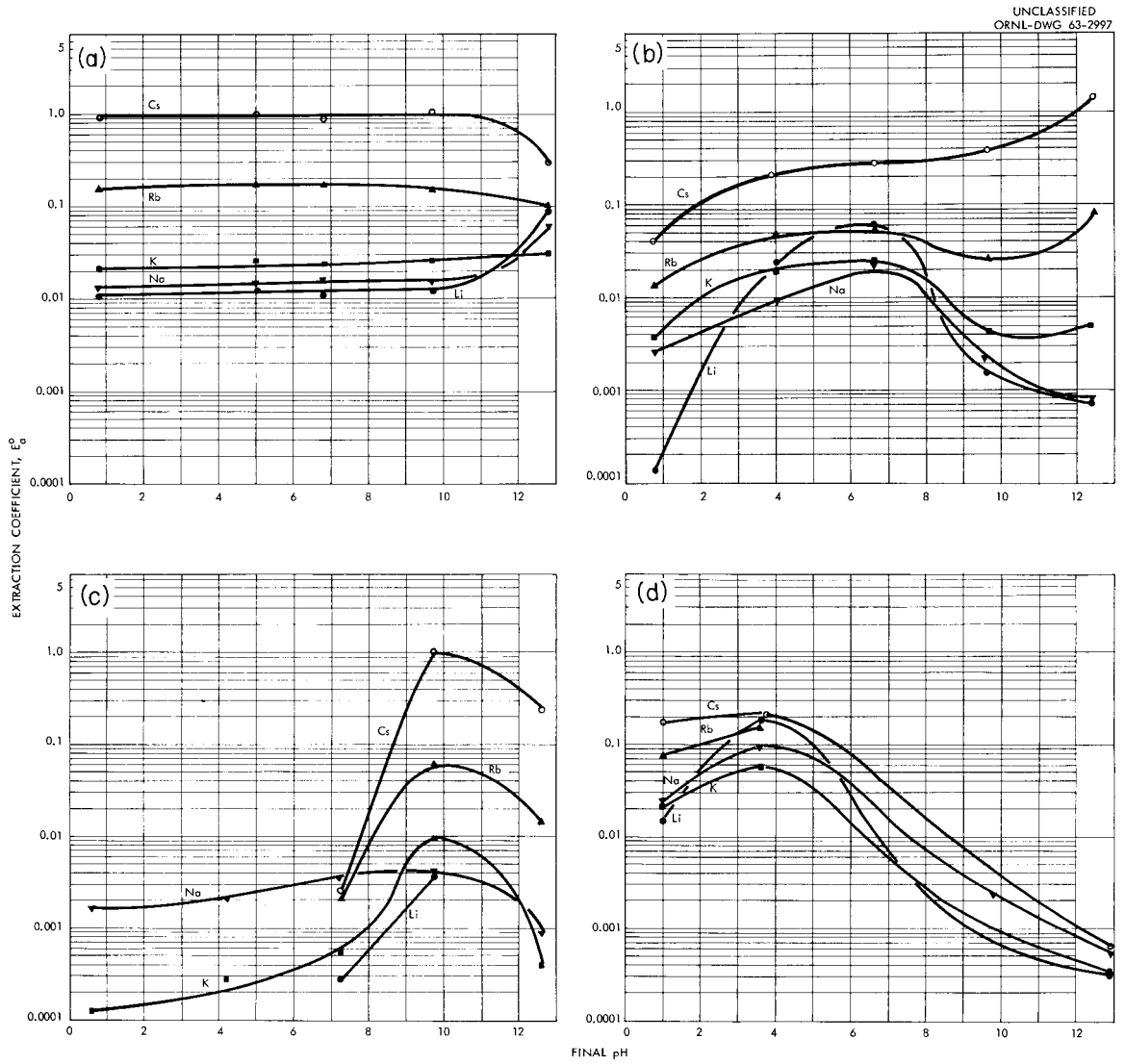


Fig. 1.2.2. Extraction of Alkali Metals. Organic phase: (a) 1 M Santophen-1—0.1 M DNNSA, (b) 1 M Santophen-1—0.1 M DDPA, (c) 1 M Santophen-1—0.1 M neo-tridecanoic acid, (d) 0.5 M DDPA; diisopropylbenzene diluent. Aqueous phase: mixed alkali metal nitrate solution containing 0.1 M Cs, 0.2 M Rb, 0.4 M K, 0.4 M Na, and 0.4 M Li. Phase ratio: 1/1. Procedure: pH adjusted by adding concentrated nitric acid or 50% caustic to phases during contact. (For pH values where coefficients are shown for some but not all alkali metals, coefficients for the missing metals were less than 0.0001.)

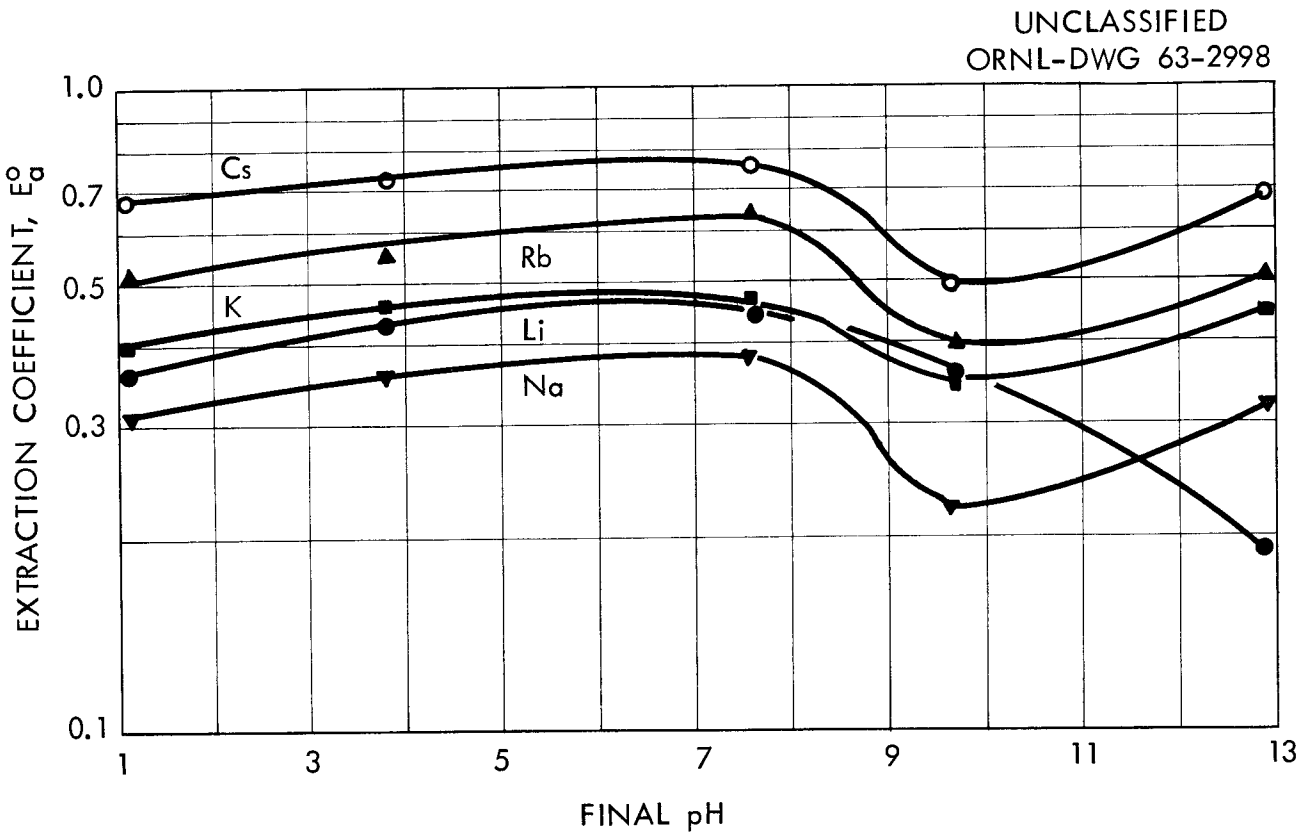


Fig. 1.2.3. Extraction of Alkali Metals with 0.5 M DNNSA in Diisopropylbenzene. Aqueous phase: mixed alkali metal nitrate solution containing 0.1 M Cs, 0.2 M Rb, 0.4 M K, 0.4 M Na, and 0.4 M Li. Phase ratio: 1/1. Procedure: pH adjusted by adding concentrated HNO_3 or 50% caustic to the phases during contact.

Hanford workers discovered[5] that combining a small concentration of di(2-ethylhexyl)phosphoric acid (D2EHPA) with BAMBP greatly enhances cesium extraction from relatively acidic liquors where extractions with BAMBP or D2EHPA alone are inappreciable. In tests studying this synergistic effect, cesium and rubidium extraction coefficients in the pH range 3 to 8 were 100 to 10,000 times higher for 1 M BAMBP—0.1 M D2EHPA (Fig. 1.2.1b) and 1 M Santophen-1—0.1 M D2EHPA (Fig. 1.2.1d) than for 1 M BAMBP (Fig. 1.2.1a) or 1 M Santophen-1 (Fig. 1.2.1b). Extraction results for BAMBP and Santophen-1, when used in combination with D2EHPA (Figs. 1.2.1c and 1.2.1d), were almost identical in the pH range 2 to 8. At pH about 13, coefficients dropped drastically for the Santophen-1—D2EHPA combination because of the high loss of Santophen-1 to the aqueous phase. The cesium/rubidium and rubidium/potassium separation factors for the synergistic combinations were about 10 and about 5, respectively, over the total pH range. The addition of D2EHPA to the solvent considerably increased the extraction of lithium since this reagent extracts lithium preferentially[3] to the other alkali metals.

The combination of a sulfonic acid such as dinonylnapththalene-sulfonic acid (DNNSA) with a phenol also synergized extractions of alkali metals. With 1 M Santophen-1—0.1 M DNNSA (Fig. 1.2.2a) the extraction coefficients showed little dependence on pH in the pH range 1 to 10. The separation factors for cesium/rubidium and rubidium/potassium were in the range 5 to 7, whereas there was little difference in extraction coefficients for potassium, lithium, and sodium.

Combination of 0.1 M DDPA (Fig. 1.2.2b) or 0.1 M neo-tridecanoic acid (Fig. 1.2.2c) with 1 M Santophen-1 gave synergized extractions, but the effect was less pronounced than with D2EHPA or DNNSA.

With 0.5 M DDPA alone (Fig. 1.2.2d) the extraction order was Cs > Rb > Na > K, but separation factors between adjacent elements in the series were less than 2. Extractions of lithium were slightly weaker than for sodium and potassium except at pH 4, where the coefficient for lithium was approximately equivalent to that for cesium. The large loss of extraction power at higher pH's is attributed to the large loss of DDPA to the aqueous phase.

The extraction order with 0.5 M DNNSA alone was Cs > Rb > K > Li > Na, but, as with DDPA, the separation factors between adjacent elements in the series were less than 2 (Fig. 1.2.3). Extraction coefficients with this reagent showed a very weak dependence on pH.

1.3 Acid Recovery by Amine Extraction
(D. J. Crouse, W. B. Howerton)

Studies of sulfuric acid recovery by amine extraction from simulated Sulfex process waste solutions were reported previously.[4] The relatively weak-base sterically hindered tertiary amines, for example, N-benzyl-di(2-ethylhexyl)amine, were preferred for this use since they could be stripped to the free-base form with water and yield, at the same time, a relatively concentrated acid product solution. Recent tests showed the potential utility of tertiary amines for the recovery and purification of phosphoric acid from the highly contaminated wet-process acid produced in the fertilizer industry. For this application, stronger-base amines are required for extraction.

The distributions of phosphoric acid between pure phosphoric acid solutions and 0.25 M solutions of several amines in 84% Amsco 125-82—16% isodecanol diluent are shown in Fig. 1.3.1. The extraction isotherms show that more than 90% acid recovery and a 1.5 M H_3PO_4 concentration in a water-strip product could be obtained from 5 M H_3PO_4 in four ideal extraction and four ideal stripping stages with Alamine 336* (tertiary amine with mixed n-octyl and n-decyl alkyls) or with benzyl-dilaurylamine. Maximum indicated solvent loadings were 45 to 50 g of phosphoric acid per liter. Extraction was less efficient with benzyl-dilaurylamine than with Alamine 336, but stripping would be easier. With the more weakly basic di(2-ethylhexyl)hexylamine, only about 50% of the phosphoric acid would be recovered in four ideal extraction stages. However, with this amine, water stripping would produce a 3 to 4 M H_3PO_4 product.

---

*Extraction of phosphoric acid with Alamine 336 (and other amines) in combination with organic phosphates and phosphonates has been reported by Agers, et al.[6]

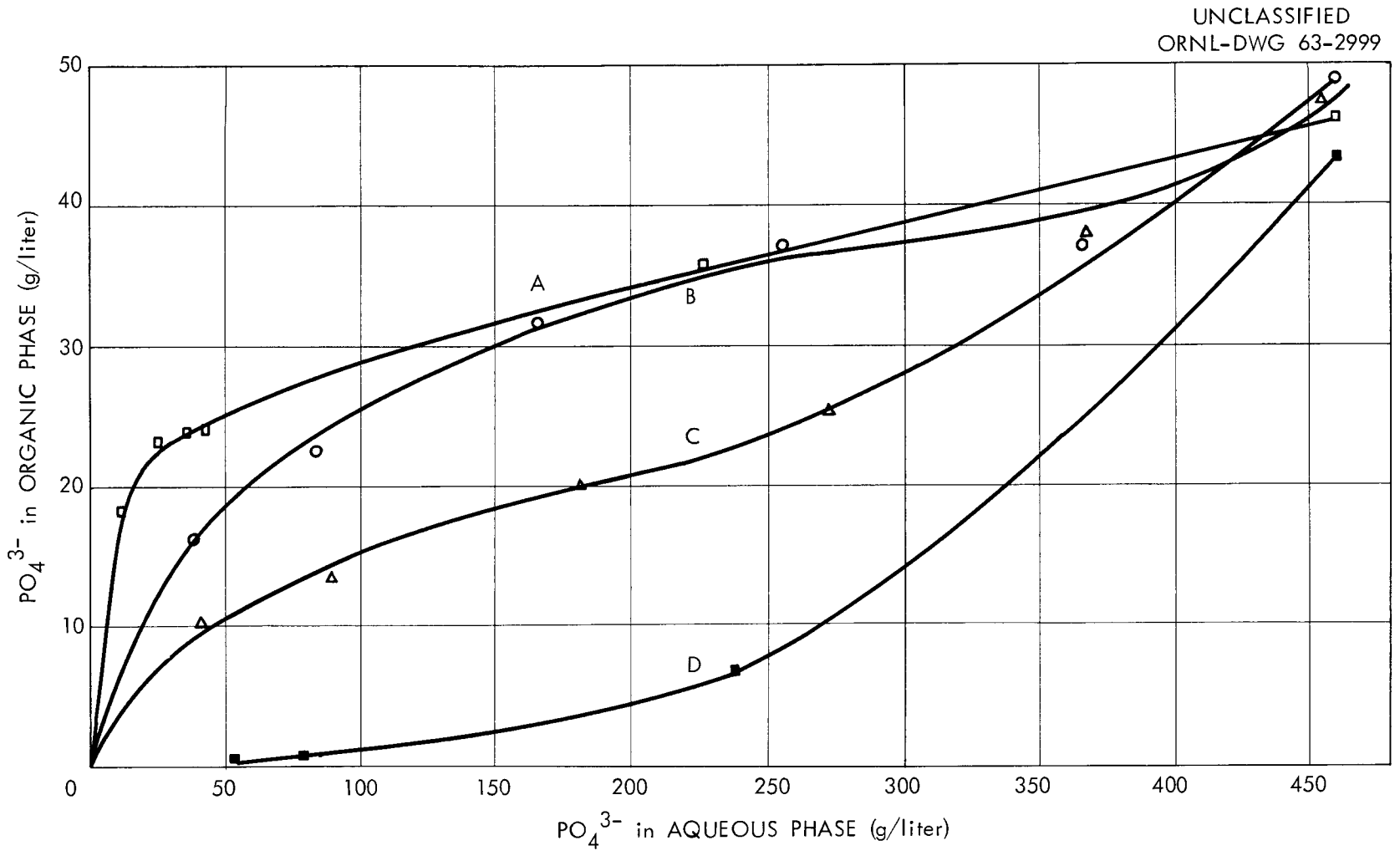


Fig. 1.3.1. Extraction of Phosphoric Acid with Tertiary Amines. Aqueous phase: 0.5 to 5 M H_3PO_4. Organic phase: 84% Amsco 125-82—16% isodecanol diluent containing (A) 0.25 M Alamine 336, (B) 0.25 M benzyldilaurylamine, (C) 0.15 M di(2-ethylhexyl)hexylamine—0.10 M Alamine 336, and (D) 0.25 M di(2-ethylhexyl)hexylamine. Phase ratio, aqueous/organic: 2/1.

Mixtures of amines of different basicities can be used to give the desired balance between extraction and water stripping. An extraction isotherm for a 3/2 mixture of di(2-ethylhexyl)hexylamine and Alamine 336 fell, as expected, between isotherms for these amines used alone.

Coefficients for the extraction of Fe(III), Fe(II), and aluminum from 5 M H_3PO_4 with Alamine 336 and with the mixture of di(2-ethylhexyl)-hexylamine and Alamine 336 were less than 0.003, indicating a high degree of purification of the phosphoric acid. Some contamination with sulfuric acid would be expected, but the extent has not yet been determined.

If desired, ammonium phosphate rather than phosphoric acid can be obtained as a product by stripping the amine with ammonium hydroxide. The preparation of both products by a two-step strip (water followed by ammonium hydroxide) may also be attractive. Such a procedure would allow higher recovery of phosphate values in the extraction cycle, with the simultaneous production of a more concentrated phosphoric acid product solution.

1.4 Final Cycle Plutonium Recovery by Amine Extraction
(C. F. Coleman, F. A. Kappelmann, J. P. Eubanks)

In previous reports, an amine extraction flowsheet was proposed for final-cycle purification and concentration of plutonium from Purex-plant 1BP solution. Batch countercurrent tests demonstrated its satisfactory chemical and physical operation with simulated feeds,[2,3,7] but continuous countercurrent testing with actual but aged Purex-plant 1BP solution gave poor decontamination from gross gamma.[3] As then described:

> "While the physical operation [in hot-cell tests] was excellent and the plutonium distribution appeared entirely consistent with the expected profiles, the gamma decontamination factors were only ~100-500, much lower than needed for the plutonium purification, and than expected from previously reported separations from tracer Zr-Nb and from dissolver solution mixed fission products. These results suggest that the 1BP solutions used contained a higher proportion of amine-extractable Zr-Nb species than do dissolver solutions or chemically separated tracer solutions, either because of concentration of such species already existent, or because of their formation through aging or interaction with

> organic degradation products, etc. Aging, if involved, might apply only to the conditions of these particular tests, but the other possibilities could be general...[3]"

Subsequent batch tests with an additional sample of Purex-plant 1BP solution, similarly aged, showed that that solution did indeed contain a high proportion of zirconium-niobium species extractable by several of the hydrocarbons used as diluents, and in fact more extractable by the hydrocarbon when alone than when containing amine and alcohol.

Finally, arrangements were made to obtain a new sample of 1BP solution, with rapid handling and transportation. Tests completed within 70 hr after it was withdrawn from the plant stream showed little or no such diluent-extractable gamma activity, as was found in the aged sample. Separation factors for plutonium over gross gamma emitters were $\geq 10^4$ in single extractions from the fresh solution, and the decontamination factor for plutonium over zirconium-niobium was 2×10^4 in a batch cascade extraction-scrub-strip test, high enough for the projected purification process to be feasible.

Special thanks are due to J. W. Ullmann of ORNL and to H. C. Rathvon and co-workers at Hanford who cooperated in obtaining and shipping all the 1BP samples, most especially the last, rapidly handled sample. The tests were carried out in the Chemical Isolation Laboratory with the cooperation of R. E. Leuze and co-workers.

1.4.1 Batch Tests with Aged 1BP Solution

The 1BP sample was 3.3 M in nitric acid and contained 2×10^6 gross gamma counts min^{-1} ml^{-1}, mostly zirconium-niobium. It contained some solids, and about 10% of the gamma activity was removed by filtration. Reproducibility of gamma analyses was poor, probably in part because of the solids (even after filtration), but comparative tests with and without filtration of both 1BP and organic extracts failed to show any definite association of extractable gamma activity with the solids. At the time that the tests were started, the sample had been kept in a stainless steel container for about four months after having been withdrawn from the plant stream, and some comparative tests were continued at intervals over an additional four months. Although there was considerable variation in detailed results from nominally similar tests,

the general magnitudes of extractability were consistent, and the results shown in Fig. 1.4.1 were typical. Several conclusions can be drawn from the extraction patterns shown in the figure, as follows:

1. A large proportion of the gamma activity in the aqueous feed, 10% and more, was extractable by the hydrocarbon diluents alone.

2. Fractions of similar magnitude were extracted in the first contact by diethylbenzene, Amsco 125-82, and n-dodecane, although the drop-off in subsequent contacts varied more.

3. In the first contact, less was extracted by amine or tributyl phosphate solution than by the diluent alone. This was even more noticeable when a high-molecular-weight alcohol was also present.)

4. The widely varying extraction patterns with and without extractant in the diluent, and with different diluents, suggest fractionation of a range of gamma-containing species of differing extractabilities. (This seems reasonable in view of the probability that the aged 1BP solution contained a range of zirconium complexers, for example, di- and monobutyl phosphoric acids plus nitro compounds and their derivatives.)

5. Although extractabilities by the three different diluents had diverged greatly by the fourth contact, extractabilities by amine solutions in those three diluents were fairly close together again in a fifth contact.

6. The extractability appeared perceptibly higher after eight months than after four months aging.

7. None of the combinations of extractions tried indicated any possibility of effectively removing the extractable gamma activity with a diluent before extracting plutonium with an amine solution.

More important, taken together, these indications showed with increasing conclusiveness that the high gamma extraction was a property of the aging of the 1BP sample and probably would not be encountered in normal processing.

Several other lines of testing and some possible treatments were scouted but were dropped as it became evident that the high gamma extractability was not pertinent to normal processing. The preliminary results indicated that (1) the extracted gamma activity was not readily scrubbed out of either amine solution or diluent with aqueous nitric acid; (2) pretreatments of the aged 1BP with chromate and with oxalate had perceptible

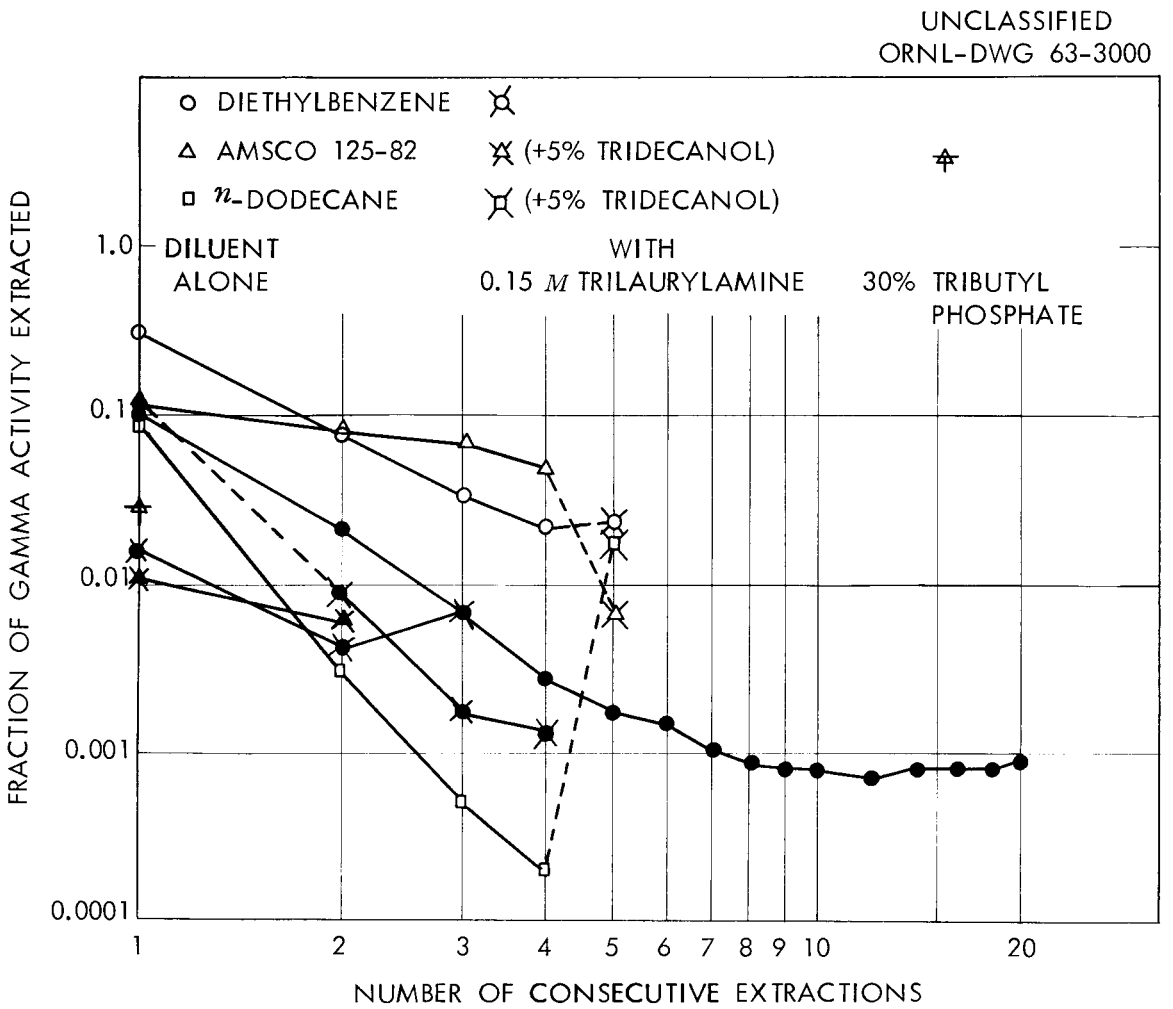


Fig. 1.4.1. Gamma Extraction from Aged 1BP Solution by Diluents and Diluent-Extractant Combinations. Phase ratio: 1/1. Black points: 1BP aged about four months; open points: about eight months.

but not important effects on the extraction; (3) heat treatments, presence or absence of nitrite, and age (up to several days) after adding nitrite had little or no effect; and (4) there was not great difference among different batches of diethylbenzene, successive distillation fractions from a batch of diethylbenzene, and diethylbenzene samples scrubbed with oxidant, base, and acid.

1.4.2 Batch Tests with Fresh 1BP Solution

After obtaining the convincing but still indirect evidence described above (that the excessive gamma extraction should not be encountered if the solution were not allowed to age), a sample of fresh 1BP solution was obtained and tested for direct confirmation. This was a much smaller sample than the preceding ones, in order to be shipped by air, and only a few tests were planned. The following tests were completed within 70 hr after the sample was withdrawn from the plant stream.

1. The sample was 3.1 M in nitric acid and contained 1.6×10^7 gross gamma counts min^{-1} ml^{-1}, again most of this being from zirconium-niobium. As before, there was considerable experimental or analytical scatter, but this time it was expected because the small samples and rather low activity levels came close to analytical limits. Fractions of the gross gamma activity extracted by diethylbenzene and by amine solutions were in the range 0.01 to 0.001, and separation factors for plutonium over gross gamma were 10^4 and higher (Fig. 1.4.2). The results appear to indicate some increase in gamma extraction, but less than the corresponding increase in plutonium extraction, with increasing amine concentration. However, the experimental scatter may well be as great as these detailed apparent variations.

2. A batch cascade (cross-current) extraction-scrub-strip test was run as indicated in Fig. 1.4.3. Each 2-ml volume of the nitrite-treated 1BP feed contacted the same three 3-ml volumes of 0.15 M trilaurylamine/diethylbenzene in succession. The raffinates varied randomly in the range 0.01 to 0.1% of the feed plutonium concentration for the first 15 volumes of feed, then increased to 0.2% at the 20th. Each organic was scrubbed separately with seven 3-ml volumes of 5 M HNO_3 and three of 0.5 M HNO_3, then stripped with five 3-ml volumes of 4 M acetic acid. The stripped organics retained 0.02, 0.02, and 0.07% of the feed plutonium concentration. The decontamination of plutonium from zirconium-niobium

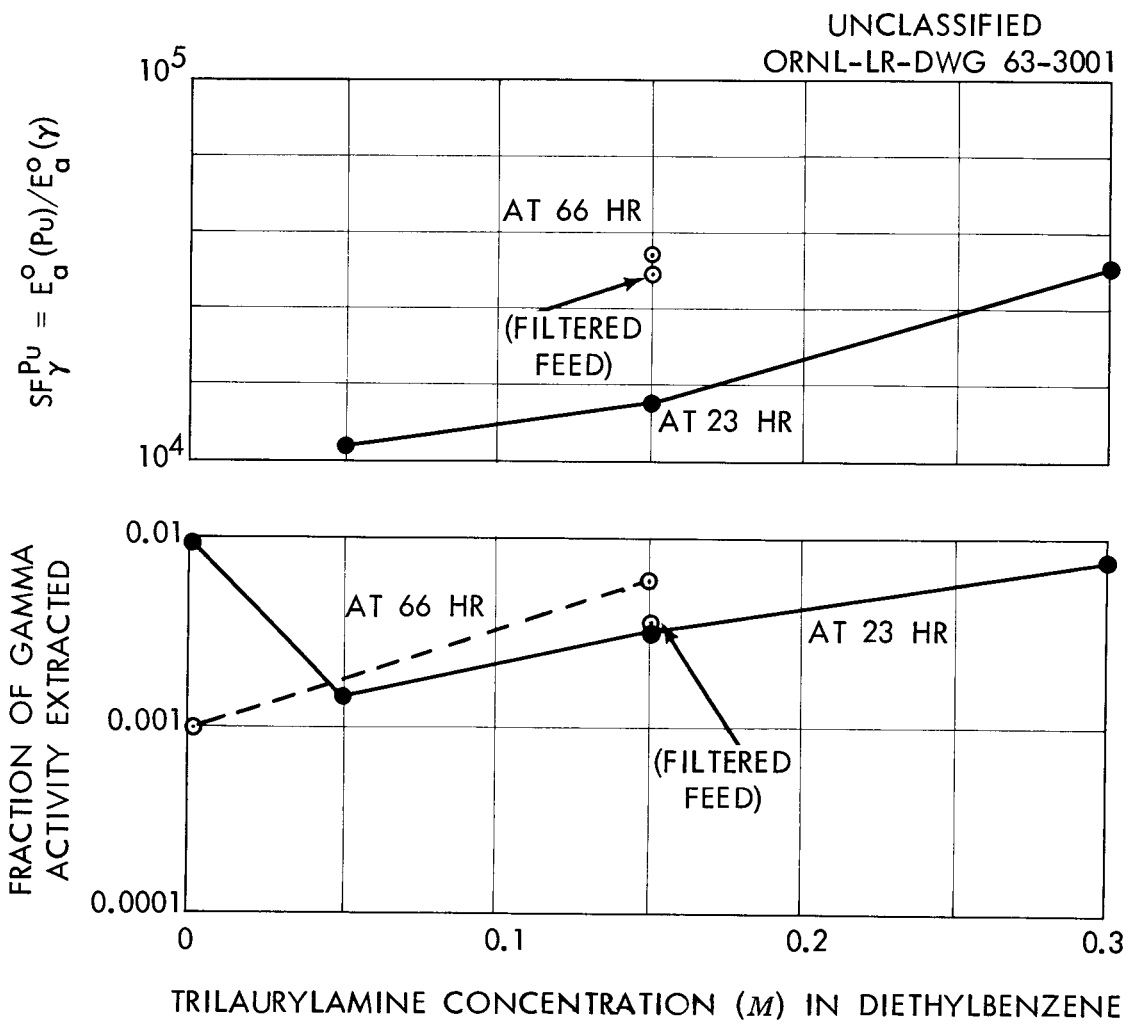


Fig. 1.4.2. Gamma Extraction from Fresh 1BP Solutions, and Corresponding Plutonium/Gamma Separation Factors. Phase Ratio: 1/1.

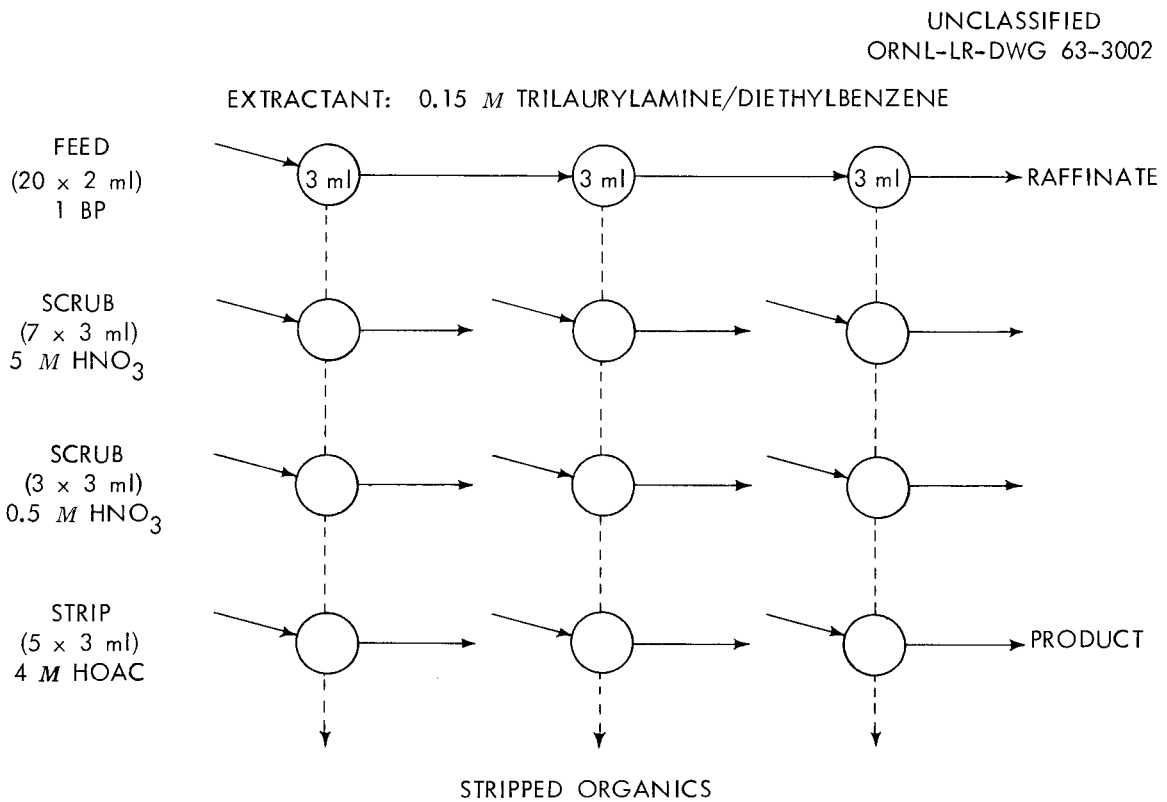


Fig. 1.4.3. Diagram of Batch Cascade Extraction-Scrub-Strip Test with Purex-Plant 1BP Solution.

(radiochemical analyses), from feed to first strip solution, was 2×10^4, and was approximately the same for plutonium from gross gamma.

Gross gamma activity picked up by the successive scrub solutions decreased as shown in Fig. 1.4.4. It is not possible to distinguish, in the gamma activity thus scrubbed out, between the portion that had actually been extracted and the portion that accompanied the extract as entrained feed. It is certain that entrainment was a larger-than-ordinary factor in separating the phases at these small volumes without the benefit of filtering or centrifuging.

Several tests somewhat more complex than those described above were attempted, in hope of obtaining more detailed information on the scrubbing of the gamma activity, especially. The results were consistent with the foregoing but failed to provide any more detailed information because the uncertainty due to entrainment and consequent carryover could not be eliminated.

1.5 Extraction of Lanthanides and Transplutonium Elements by Dialkylphosphoric Acids

(B. Weaver, F. A. Kappelmann, J. R. Collins)

The chemistry of the lanthanides and transplutoniums is being studied in an effort to find differences that may be useful in separating the two groups and in separating individual elements, with present emphasis on solvent extraction methods. This and the following sections present the results of recent work on the extraction of the trivalent elements by various solvents from various aqueous solutions and on the extraction of americium oxidized to the hexavalent state.

Preliminary studies on the extraction of lanthanides[1] and transplutoniums from aqueous solutions of carboxylic acids by dialkylphosphoric acids were extended to a greater number of carboxylic acids. Also, some data on extraction by ditridecylphosphoric acid (HDTDP) and di(2-ethylhexyl)di-thio-phosphoric acid (HDEHSSP) were obtained for comparison with data for di(2-ethylhexyl)phosphoric acid (HDEHP). In these tests, the lanthanide group was represented by cerium and europium. The transplutonium elements were represented by americium and sometimes by curium.

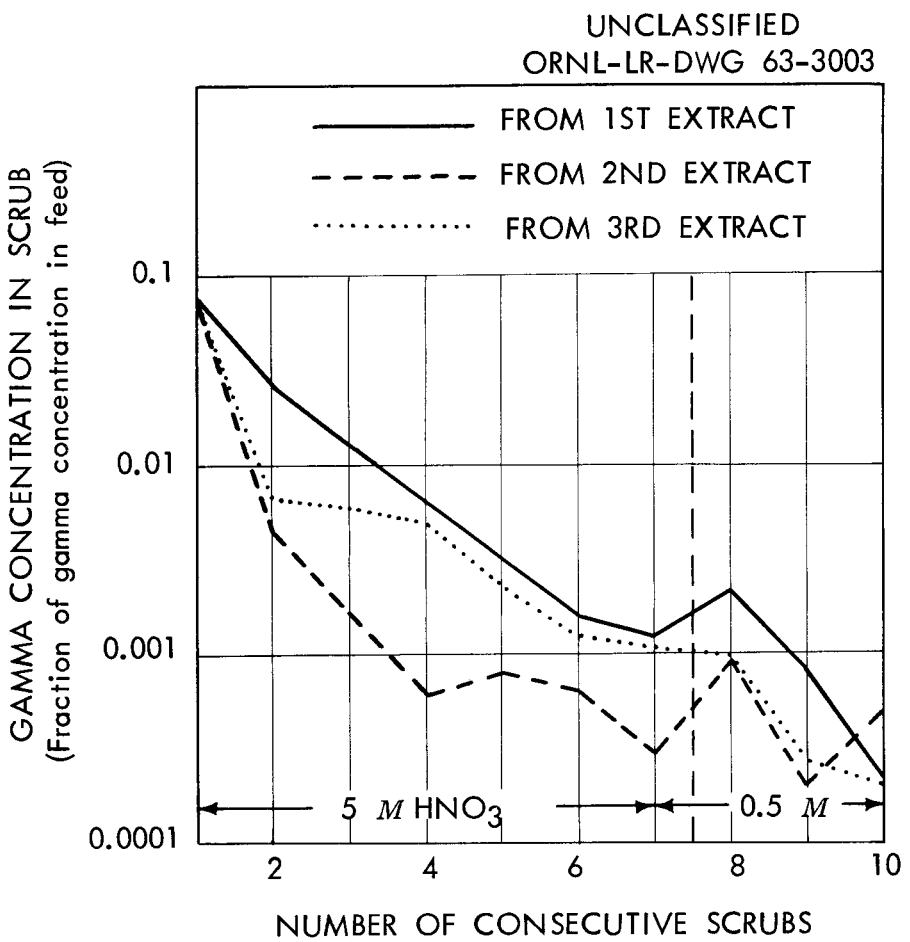


Fig. 1.4.4. Gamma Contents of Successive Scrub Solutions from Batch Cascade Test (Fig. 1.4.3 shows the extraction scheme).

Carboxylic acids are being explored because of their effect on americium extraction. For example, americium is similar to praseodymium in extraction from mineral acids, whereas from carboxylic acids it shifts to a behavior similar to cerium or even lanthanum. A still greater shift could make this extraction system a likely basis for a group separation process.

1.5.1 Extraction by Di(2-ethylhexyl)phosphoric Acid from Citric Acid

In extractions by di(2-ethylhexyl)phosphoric acid in diisopropylbenzene (DIPB) from citric acid of various concentrations, the europium/cerium separation factor was 15 to 20. The separation factor for cerium/americium was 2 or more (Table 1.5.1). Making the aqueous phase 0.1 N in HNO_3 decreased the extraction of all the metals and also seemed to have an effect on the relative position of americium. The presence of 1 g of samarium per liter had only a small effect on the extraction of tracer quantities of the other elements.

Table 1.5.1. Extraction by Di(2-ethylhexyl)phosphoric Acid from Citric Acid

Organic phase: 0.5 M HDEHP in DIPB

Aqueous Phase	Distribution Coefficient, E_a^o		
	Ce	Eu	Am
0.1 N HNO_3	--	163	3.8
0.1 M Citric acid	424	>5000	196
0.5 M Citric acid	23	390	10
2.0 M Citric acid	0.56	9.5	0.23
3.4 M Citric acid	0.10	1.6	0.04
2.5 M Citric acid, 1 g Sm/liter	0.27	5.3	0.14
2.5 M Citric acid, 1 g Sm/liter, 0.1 N HNO_3	0.11	2.8	0.08
3.4 M Citric acid, 1 g Sm/liter	0.12	2.7	0.06
3.4 M Citric acid, 1 g Sm/liter, 0.1 N HNO_3	0.04	0.9	0.03

1.5.2 Extraction by Di(2-ethylhexyl)phosphoric Acid from Glycolic Acid

Glycolic (hydroxyacetic) acid was superior to formic, acetic, tartaric, and citric acids with respect to phase separation and reproducibility of experimental results. In extractions from glycolic acid, separation factors between europium and cerium and between cerium and americium were about the same as those with citric acid (Table 1.5.2). Extractions with Amsco 125-82 as diluent were about 50 times as high as with DIPB; so, DIPB is suitable for the operation of a partitioning system.

Table 1.5.2. Extraction by Di(2-ethylhexyl)phosphoric Acid from Glycolic Acid

HDEHP (M)	Diluent	Glycolic Acid (M)	Distribution Coefficient, E_a^o		
			Ce	Eu	Am
0.1	DIPB	0.75	0.66	15	0.33
0.1	DIPB	1.0	0.58	13	0.26
0.1	DIPB	1.5	0.17	2.1	0.05
0.1	DIPB	3.75	0.022	0.28	0.008
0.1	Amsco 125-82	1.0	23	330	11
0.25	DIPB	0.5	18	173	6.2
0.25	DIPB	1.0	3.8	66	1.6
0.25	DIPB	3.0	0.32	4.6	0.13
0.25	DIPB	5.0	0.09	1.0	0.035
0.3	DIPB	1.5	4.4	75	1.9
0.3	DIPB	3.75	0.56	8.3	0.28

1.5.3 Extraction by Di(2-ethylhexyl)phosphoric Acid from Oxydiacetic Acid

Extraction coefficients from oxydiacetic acid were much lower than those from glycolic acid (Table 1.5.3). The separation factor between europium and cerium was reduced to less than 3. However, americium and curium apparently remained less extractable than any of the lanthanides.

Table 1.5.3. Extraction by Di(2-ethylhexyl)phosphoric Acid from Oxydiacetic Acid

Organic phase: 0.3 M HDEHP in Amsco 125-82

Concentration of Oxydiacetic Acid in Aqueous Phase (M)	Distribution Coefficient, E_a^o			
	Ce	Eu	Am	Cm
0.25	0.51	1.2	0.11	0.14
0.5	0.18	0.43	0.04	
1.0	0.064	0.16	0.018	

1.5.4 Extraction by Di(2-ethylhexyl)phosphoric Acid from Glycine

Glycine (aminoacetic acid) showed comparatively unusual properties. Extraction increased rather than decreased with increase in glycine concentration (Table 1.5.4). Also, extractions were higher from mixtures of glycine and nitric acid than from nitric acid alone. Since the extraction coefficients of cerium, europium, and americum are inversely proportional to the cube of the hydrogen ion concentration, the effect of the glycine was probably at least partially due to its ionization as a base in the nitric acid solution. Extraction by HDEHP in unmodified diluents gave separation factors of about 40 between europium and cerium, but americium behaved like cerium. Use of DIPB instead of Amsco 125-82 reduced all extractions by a factor of about 50. Modification of the Amsco diluent with 10% tridecanol (TDA) greatly decreased extractions and halved the separation factor between europium and cerium. Substitution of 0.15 M TBP for the TDA increased extraction of all elements eight- or tenfold. The data showed some shift of the relative extractabilities of americium and cerium under various conditions.

1.5.5 Modification of Di(2-ethylhexyl)phosphoric Acid by a Phenol

Modification of a DIPB solution of HDEHP with a high concentration of 4-sec-butyl-2(α-methylbenzyl)phenol (BAMBP), which does not extract lanthanides nor transplutonium elements by itself, reduced the extraction

Table 1.5.4. Extractions by Di(2-ethylhexyl)phosphoric Acid from Glycine-Nitric Acid Mixtures

Concentration of Extractant in the Diluent	Composition of Aqueous Phase	Distribution Coefficient, E_a^o			
		Ce	Eu	Am	Cm
0.1 M in Amsco 125-82	1 M HNO_3 only	<0.001	0.025	<0.001	
	1 M HNO_3, 1 M glycine	0.60	26	0.58	
0.1 M in DIPB	1 M HNO_3, 1 M glycine	0.011	0.44	0.013	
0.3 M in Amsco 125-82 + 10% TDA	0.5 M HNO_3, 0.5 M glycine	2.9	50	2.8	
	0.5 M HNO_3, 1.0 M glycine	600	7000	330	
	1.0 M HNO_3, 0.5 M glycine	0.007	0.049	0.011	
	1.0 M HNO_3, 1.0 M glycine	0.54	11	0.56	0.63
0.3 M plus 0.15 M TBP in Amsco	1.0 M HNO_3, 1.0 M glycine	6.4	93	5.6	

of cerium and americium by factors up to about 10 and europium by factors up to about 50 (Table 1.5.5). Thus, the separation between lanthanides typical of extractions by HDEHP was greatly reduced.

Table 1.5.5. Effect of a Phenol on Extraction by Di(2-ethylhexyl)phosphoric Acid

	E_a^o					
	0.1 M HDEHP-DIPB			0.1 M HDEHP, 1 M BAMBP-DIPB		
Aqueous Phase	Ce	Eu	Am	Ce	Eu	Am
0.01 N HNO_3	140	≥5000	120	13	140	16
0.03 N HNO_3	2.3	180	3.4	0.44	5.3	0.49
0.1 N HNO_3	0.09	2.6	0.25	0.006	0.06	0.007
1 M Glycolic acid	0.58	13	0.26	0.07	0.42	0.046
1 N HNO_3, 1 M glycine	0.038	2.0	0.038	0.010	0.058	0.005

1.5.6 Extraction by Ditridecylphosphoric Acid

Ditridecylphosphoric acid was tested as an extractant from several carboxylic acid solutions (Table 1.5.6). In all cases the separation factor between europium and cerium was much lower than obtained previously with HDEHP, but the separation between cerium and americium was about the same. This reagent would apparently not be as useful as HDEHP for separating americium from the heavy lanthanides in this system.

Table 1.5.6. Extraction by Ditridecylphosphoric Acid (HDTDP)

Organic phase: 0.1 M HDTDP in DIPB

	Distribution Coefficient, E_a^o		
Aqueous Phase	Ce	Eu	Am
0.5 M Tartaric acid	7.3	24	2.6
2.0 M Tartaric acid	0.14	0.46	0.06
0.5 M Citric acid	23	79	9.5
0.5 M Glycolic acid	101	380	39

1.5.7 Extraction by Di(2-ethylhexyl)dithiophosphoric Acid

Substitution of two sulfur atoms for oxygen atoms in HDEHP (to produce HDEHSSP) greatly reduced its extractive power and the separation between the lanthanides (Table 1.5.7).

Table 1.5.7. Extraction by Di(2-ethylhexyl)dithiophosphoric Acid

Organic phase: 0.3 M HDEHSSP in DIPB

Concentration of Glycolic Acid in Aqueous Phase (M)	E_a^o		
	Ce	Eu	Am
0.075	1.2	1.3	0.8
0.75	0.023	0.023	0.023

1.6 Extraction of Nitric Acid, Lanthanides, and Transplutonium Elements by Amines

(B. Weaver, F. A. Kappelmann)

1.6.1 Extraction of Nitric Acid from Nitrates

In previous work on extraction by tertiary amine nitrates from concentrated lithium nitrate solutions, it had been observed that distribution coefficients decreased with successive back extractions.[1] This had been attributed to loss of reagent to the aqueous phase. More recent work showed that the decrease in extraction was caused by high extraction of nitric acid from the aqueous solution.

Nearly all the acid in a mixture 6 N in $LiNO_3$ and 0.1 N in HNO_3 was extracted by an equal volume of 0.5 M Alamine 336 nitrate. Back extraction with a similar aqueous solution added more acid to the organic.

The lower acid extraction isotherm in Fig. 1.6.1 was obtained by nine successive contacts of 0.497 M Alamine 336 nitrate plus 10% tridecanol in diisopropylbenzene with equal volumes of a mixture 6 N in $LiNO_3$ and 0.1 N in HNO_3 and a separate series consisting of five contacts with a mixture 6 N in $LiNO_3$ and 0.513 N in HNO_3. In each test, the free nitric acid was determined in both phases. The system was still approaching

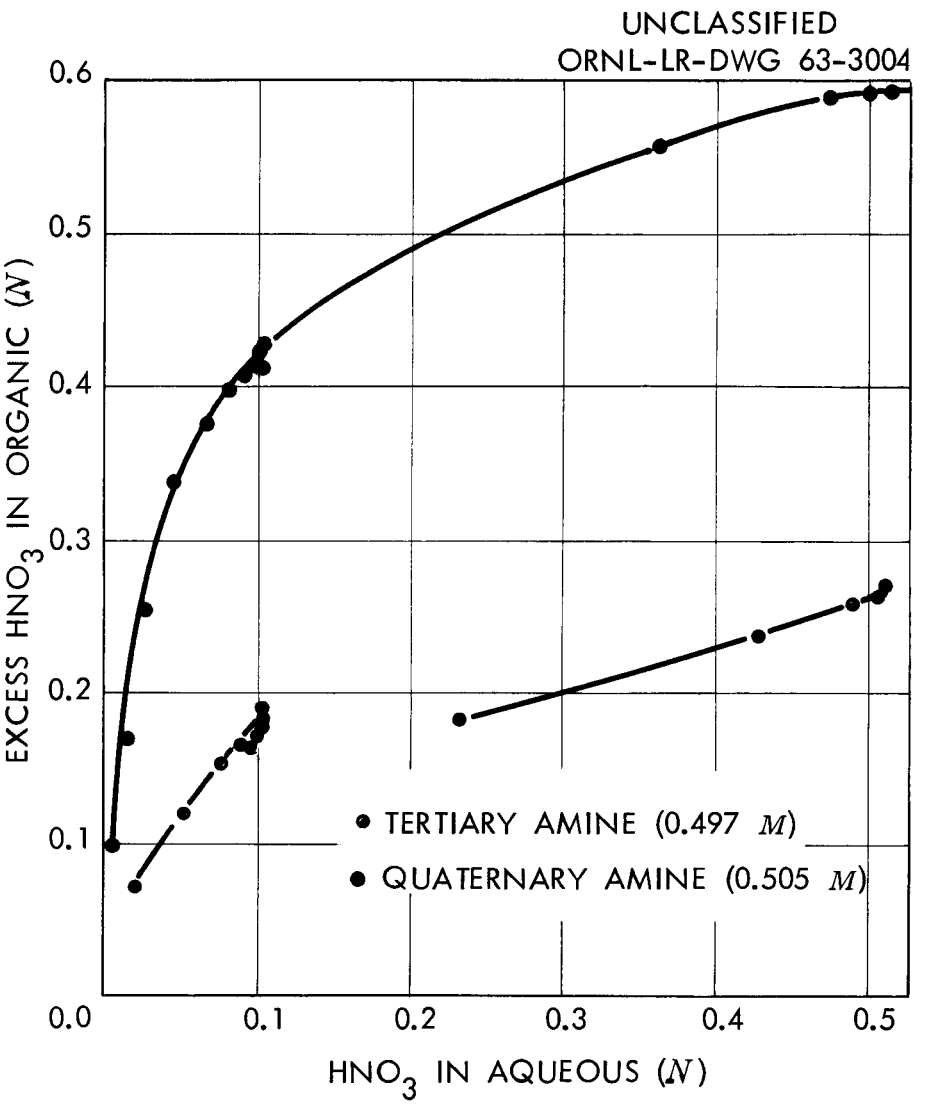


Fig. 1.6.1. Extraction of Nitric Acid from 6 N $LiNO_3$ Solutions by Amines.

equilibrium after the first nine contacts and appeared to be leveling off with the higher acidity at slightly more than 0.5 mole of excess nitric acid per mole of amine.

Similar results were obtained in extraction by a tetraheptylammonium nitrate (THA), except that the final excess-acid level in the organic was slightly more than 1 mole of nitric acid per mole of amine. The upper isotherm in Fig. 1.6.1 was obtained by a series of contacts of 0.505 M Aliquat 336 nitrate plus 5% TDA in DIPB with two nitrate mixtures, one 6 N in $LiNO_3$ and 0.1 N in HNO_3, and the other 6 N in $LiNO_3$ and 0.513 N in HNO_3.

These data show the difficulty of obtaining reproducible data on extraction by amines from solutions containing alkali nitrates and very dilute nitric acid and emphasize the importance of measuring the acidity of the aqueous phase after contact. For the extraction of lanthanides and trivalent actinides by amines, this effect is especially important, since extractability is highly dependent on acidity. Where extractions are made from aluminum nitrate with no excess acid, results are easily reproducible because buffering keeps the effective acidity almost constant.

1.6.2 Extraction of Lanthanides and Transplutonium Elements

The extraction of lanthanides and transplutonium elements by the tertiary amine Alamine 336 in DIPB from tartaric and citric acid was much less efficient than from concentrated solutions of aluminum nitrate (Table 1.6.1). In extractions from carboxylic acids, europium was about 3 times as extractable as cerium in most cases. This order was the reverse of that in extraction from aluminum nitrate solutions. Curium, however, appeared to be a little more extractable than americium in both systems.

Table 1.6.1. Extraction by Tertiary Amine

Organic phase: 0.3 M Alamine 336 in DIPB

Diluent, TDA (%)	Aqueous Phase	Distribution Coefficient, E_a^o			
		Ce	Eu	Am	Cm
	0.1 M Tartaric acid	0.075	0.21	0.19	
	0.25 M Tartaric acid		0.15	0.13	
	0.5 M Tartaric acid	0.027	0.096	0.084	
	0.75 M Tartaric acid		0.072	0.065	
	1.0 M Tartaric acid	0.018	0.057	0.051	
4	1.5 M Tartaric acid		0.036	0.032	
4	2.0 M Tartaric acid	0.0085	0.029	0.026	0.024
10	0.1 M Tartaric acid	0.022	0.12	0.11	0.21
10	0.5 M Tartaric acid	0.014	0.072	0.065	0.106
10	1.0 M Tartaric acid	0.010	0.046	0.038	0.1
10	2.0 M Tartaric acid	0.0069	0.029	0.023	0.062
10	0.1 M Citric acid	0.12	0.40	0.40	
10	0.5 M Citric acid	0.030	0.080	0.083	
10	2.0 M Citric acid	0.006	0.014	0.013	
10	3.4 M Citric acid	0.004	0.0076	0.0082	0.008
	6 N $Al(NO_3)_3$	18	2.9	3.8	8.7

1.7 Extraction of Lanthanides and Transplutonium Elements from Carbonate Solutions

(B. Weaver)

Americium and lanthanides were extracted by a quaternary ammonium carbonate from dilute potassium bicarbonate solutions. Previous work with concentrated carbonate and bicarbonate solutions had given no extraction by quaternaries or other amines.[1] With the low concentrations of potassium bicarbonate, 0.5 M Aliquat 336 carbonate in DIPB gave high distribution coefficients (Table 1.7.1). However, there was little difference between the extractabilities of cerium, europium, and americium. Consequently, although such extractions might be useful for concentrating the elements, they do not suggest useful separation of the actinide and lanthanide groups or separations of elements within the groups.

Table 1.7.1. Extractions of Cerium, Europium, and Americium by a Quaternary Amine from Potassium Bicarbonate Solutions

Organic phase: 0.3 M Aliquat 336 carbonate in DIPB

Concentration of $KHCO_3$ in Aqueous Phase (M)	E_a^o		
	Ce	Eu	Am
0.01			300
0.1	290	450	280
1.0[a]	0.18	0.20	0.13

[a]Solvent contained 2% TDA to prevent emulsions when contacting 1 M $KHCO_3$.

1.8 Summary of Differences Between the Extractabilities of Americium and Cerium and Europium

(B. Weaver)

A summary of results from studies of several of the foregoing extraction systems is presented graphically in Fig. 1.8.1, where the relative extractabilities of cerium and europium are compared with that of americium. It should be emphasized that the rectilinearity assumed between cerium and europium in this figure is not always true. Also,

UNCLASSIFIED
ORNL-LR-DWG 63-3005

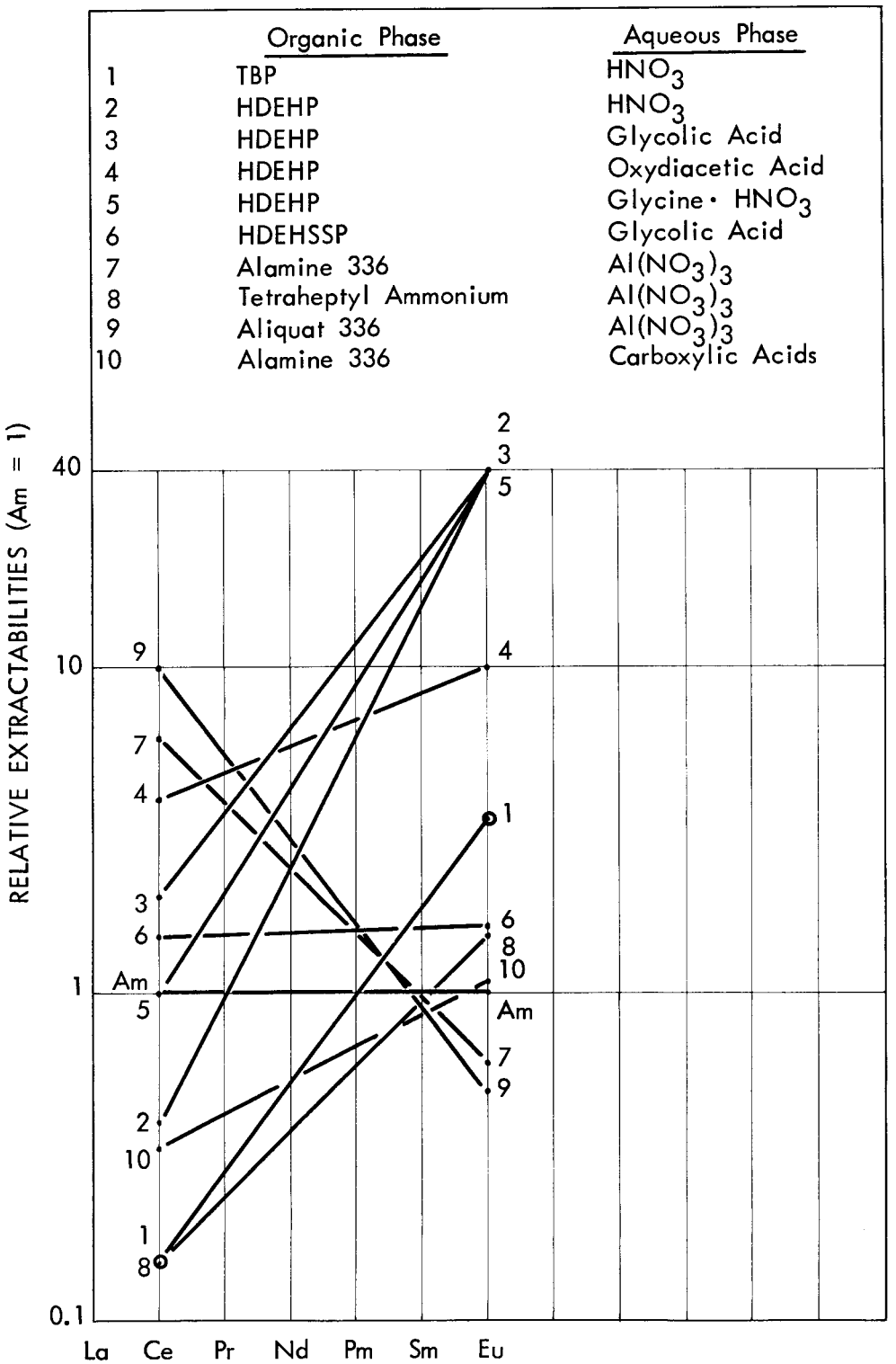


Fig. 1.8.1. Summary of Relative Extractabilities of Americium, Cerium, and Europium.

it should be noted that the absolute values of distribution coefficients and the possible need for their adjustment to obtain suitable extraction factors must also be considered in evaluating the utility of any of the systems as a practicable separation method. The general conclusions are listed below.

1. In the TBP-nitric acid system, americium behaves like promethium and is difficult to separate from either the lighter or heavier lanthanides.
2. The HDEHP-nitric acid system, in which americium is like praseodymium, is even more unfavorable because of the great abundance of fission product elements that "neighbor" praseodymium.
3. Some of the HDEHP-carboxylic acid systems give favorable separations of most heavier lanthanides from americium, and HDEHP extraction from oxydiacetic acid appears to extract all the lanthanides with a considerable preference over americium.
4. Similarity in the extractability of all the lanthanides, with a small separation from americium, is indicated for the HDEHSSP-glycolic acid system.
5. In the amine-aluminum nitrate systems, the behavior of americium is similar to that of samarium, and the order of extractability of the lanthanides is opposite with the two quaternaries tested.
6. In the amine-carboxylic acid systems, the separation of americium from the light lanthanide elements is less than that in the aluminum nitrate system.

According to the above conclusions, it appears that a combination of two multistage cycles consisting of the optimum HDEHP-carboxylic acid system and an amine-aluminum nitrate system or a tributyl phosphate-nitric acid system[8] could give good separation between the lanthanides and americium and probably curium. Separation from the other transplutoniums would depend on their relative extractability in each case. However, still greater differences between the groups than have been observed in the systems described would be desirable.

1.9 Extraction of Californium and Einsteinium*

(B. Weaver, F. A. Kappelmann)

There are thus far no adequate extraction methods for the separation of californium from einsteinium. Four of the extraction systems under study for lanthanide-transplutonium extraction were tested in single experiments with small amounts of these elements. Extraction by HDEHP from glycolic acid and from glycine-nitric acid solution, and by tertiary and quaternary amines from lithium nitrate solutions, showed differences between these elements similar to those expected from any pair of adjacent lanthanides (Table 1.9.1). Comparison with lanthanides and other transplutoniums would be of interest but could not be made directly under the conditions of these tests.

Table 1.9.1. Extraction of Californium and Einsteinium

Type and Concentration of Extractant	Composition of Aqueous Phase	E_a^o Cf	E_a^o Es	Separation Factor, Es/Cf
0.25 M HDEHP	3 M Glycolic acid	1.8	2.8	1.6
0.25 M HDEHP	1 M Glycine, 1 N HNO_3	1.4	2.8	2.0
0.3 M Alamine 336-DIPB	6 N $LiNO_3$, 0.1 N HNO_3	15	19	1.3
0.5 M Aliquat 336-DIPB-5% TDA	6 N $LiNO_3$, 0.1 N HNO_3	29	48	1.7

1.10 Extraction of Americium(VI)

(B. Weaver)

The relatively high extractability of U(VI) and Pu(VI), compared with that for trivalent rare earths in many systems, indicated a possibility of obtaining separations between americium and curium by oxidizing Am(III) to Am(VI) and extracting it from the curium(III). Alpha emission from the decay of Am^{241} is known to cause the autoreduction of Am(VI), at the rate of about 4% per hour. Since alpha emission of curium isotopes

*With R. D. Baybarz, Chemical Development Section A.

is equally effective in reduction, separation by this means can be limited by the rate of alpha emission and the time required for the operation. Moore[9] reported that fluoride ion stabilized Am(VI), but this would be inapplicable to separations by solvent extraction because of the precipitation of curium.

1.10.1 Preparation of Americium(VI)

Solutions of Am(VI) were prepared by the silver-catalyzed persulfate method of Moore.[9] Since it was desired to eliminate insofar as possible any effect that nitrate might have on extended tests, the nitrate content of the solutions was reduced by replacing the 0.1 N concentration of nitric acid with 0.01 N H_2SO_4. Complete avoidance of nitrate would be possible only be substituting another silver salt for the very small amount of silver nitrate used. Silver sulfate is not a suitable substitute because of its low solubility. Very effective oxidation of americium was indicated by the results of the extraction tests. Also, solutions of Am(VI) prepared in strict accordance with Moore's procedure gave almost the same results under identical extraction conditions.

Samples of oxidized solutions were prepared by first mixing the following materials in a total volume of 8 ml: Am^{241} tracer, 0.1 meq H_2SO_4, 0.8 millimole $(NH_4)_2S_2O_8$, and 1 drop of 10% $AgNO_3$. The solution was heated 10 min at 85 to 100°C, and another 0.2 millimole of $(NH_4)_2S_2O_8$ was added, and heating was continued 1 min. The solution was cooled rapidly to room temperature and the volume adjusted to 10 ml. In most extraction experiments 1-ml aliquots of this solution were diluted to 10 ml to give a final solution containing 2×10^{-7} M Am^{241}, 3×10^{-5} N HCl, 1×10^{-3} N H_2SO_4, 3×10^{-5} M $AgNO_3$, plus the decomposition products of 0.01 M $(NH_4)_2S_2O_8$, and the variable added constituents. Solutions of the same composition containing Am(III) could also be prepared since there is no oxidation without heating.

1.10.2 Procedure

Distribution data were obtained by thoroughly contacting prepared solutions in separatory funnels, separating the phases by centrifugation, and measuring the gamma activity of 2-ml samples in a well-type scintillation counter.

With some reagents, the extraction of acid has an important effect on their behavior, and, in these cases, the solvent was usually preconditioned to near equilibrium conditions by contacting at least twice with aqueous solutions of the same composition used in the experiments, except that no americium was present. In other cases where distribution coefficients were sufficiently high, as in several tests with Am(III), the same result was attained by successive scrubs of the solvent with the inactive aqueous solution after the extraction of Am^{241}. The extraction of Am(III) and Am(VI) under similar conditions gave data from which americium-curium separations could be calculated when the relative extractabilities of Am(III) and Cm(III) were known.

The rapid autoreduction of Am(VI) required a minimum lapse of time between the oxidation of the americium and the separation of the phases. Accordingly, with no delays in preparation, it was possible to complete a series of four extractions in about 30 min. It should be assumed that, in most tests, there will be at least 2% Am(III) in the Am(VI). In some tests, such as extraction with HDEHP, there was indication of less reduction owing to stabilization of the Am(VI). It should also be noted that errors in the reported extraction coefficients for Am(VI) may be relatively large for systems when the extractability of Am(III) is high.

1.10.3 Extraction by Tri-n-octylphosphine Oxide

Extractabilities of Am(III) and Am(VI) by a 0.2 M solution of tri-n-octylphosphine oxide (TOPO) were measured from various solutions containing nitric and sulfuric acids and alkali nitrates (Fig. 1.10.1). The most significant observation from these data is that, in most cases, the extraction of Am(III) was greater than that of Am(VI). Under some conditions the separation factor between the two species was greater than 100. Extraction from a mixture 0.1 N in HNO_3 and 2 N in $LiNO_3$ appears particularly favorable for separation, since the extraction of Am(III) was maximum at this concentration of nitrate in this system, whereas the extraction of Am(VI) from lithium nitrate solutions that were 0.1 N in HNO_3 was low and almost independent of the concentration of lithium nitrate. High separations were also obtained from a mixture 0.1 N in H_2SO_4 and 4 N in $NaNO_3$.

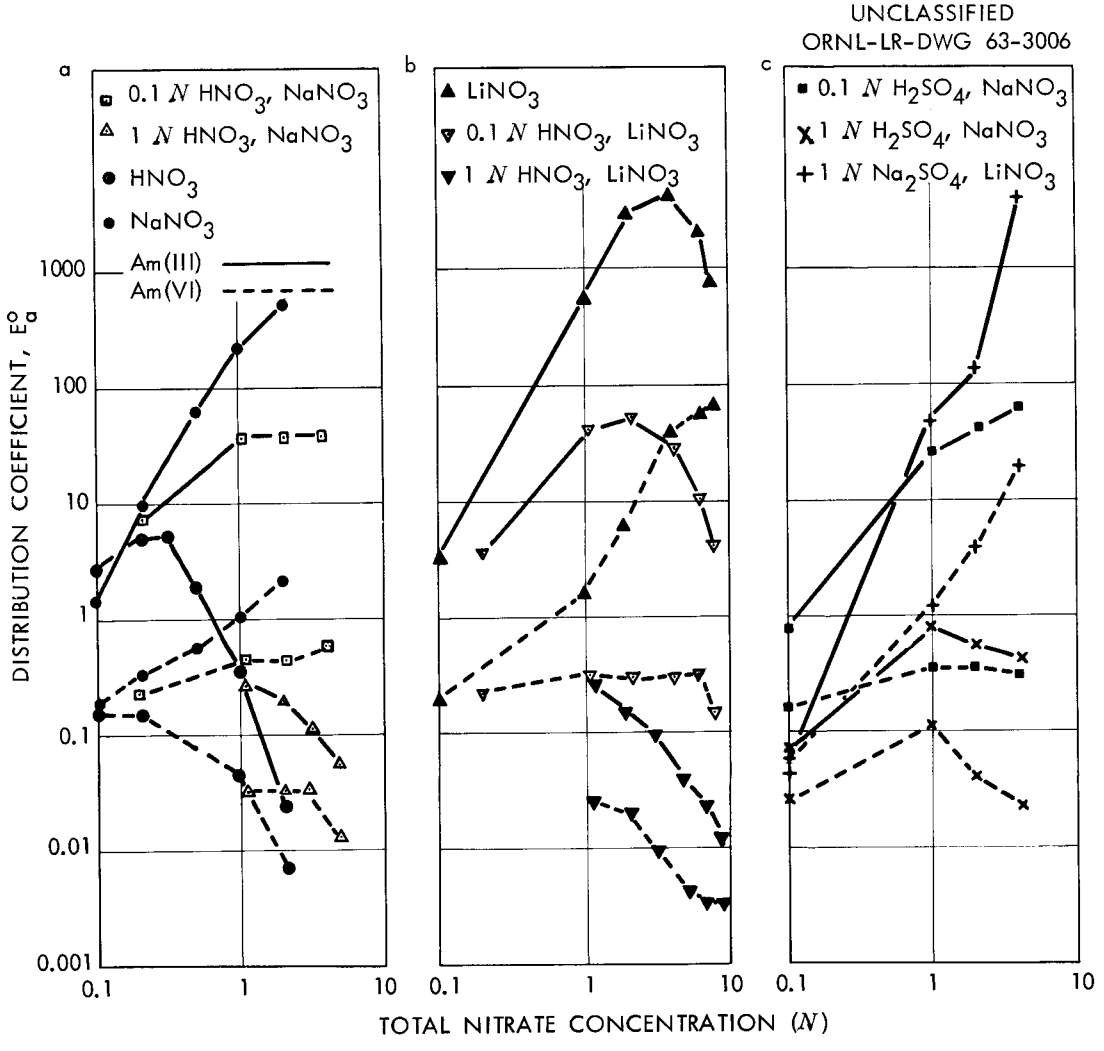


Fig. 1.10.1. Extraction of Americium(III) and Americium(VI) by Tri-n-octylphosphine Oxide. Organic phase: 0.2 M in TOPO in diisopropylbenzene. Aqueous phase: 0.001 N in H_2SO_4 and 0.01 N in $(NH_4)_2S_2O_8$.

If the reagent-concentration dependence for Am(III) extraction is third power, like that of the rare earths, and is less than third power for Am(VI) extraction, as might be expected, still higher separation could be obtained with more concentrated TOPO solutions.

1.10.4 Extraction by Tributyl Phosphate

A comparison was made of the extraction of Am(III) and Am(VI) by TBP from nitric acid and from sodium and lithium nitrate solutions (Fig. 1.10.2). In extractions by pure TBP from nitric acid, Am(III) was more extractable than Am(VI) when the concentration of nitric acid was more than about 2 N. The Am(III)/Am(VI) separation factor was nearly constant at 4 to 5 from 2 N to 10 N HNO_3. The Cm(III)/Am(VI) separation factor should be about twice as high in this system. With 1 M TBP in Amsco 125-82, the extraction coefficients were too low to be of practicable use, and the size and direction of the separation factors varied erratically with acidity.

In extractions with 1 M TBP in Amsco 125-82 from nitrate salt solutions, the sodium nitrate concentration had a much greater effect on the extraction of Am(III) than on the extraction of Am(VI). At 5 N $NaNO_3$, the Am(III) extraction coefficient was about 3, and the separation factor for Am(VI) was about 30. From lithium nitrate solution, the extraction coefficients were greater at high salt concentration, but the separation factor was lower.

1.10.5 Extraction by Di(2-ethylhexyl)phosphoric Acid

Preliminary tests showed that Am(III) is far more extractable than Am(VI) by 0.3 M di(2-ethylhexyl)phosphoric acid (HDEHP) from nitrate solutions (Table 1.10.1). A very high degree of separation between curium and Am(VI) should be obtainable by extracting from acid solutions up to 0.1 N in HNO_3. For example, a single-stage extraction by one volume of 0.3 M HDEHP in DIPB from 20 vols. of 0.01 N HNO_3 should recover more than 99% of the curium and leave more than 99% of the oxidized americium in the aqueous phase. A single-stage extraction should also give high separation from solutions up to 1 N in $LiNO_3$. These data are in disagreement with a previously published suggestion[10] that HDEHP can be used for the preferential extraction of Am(VI) from similar solutions.

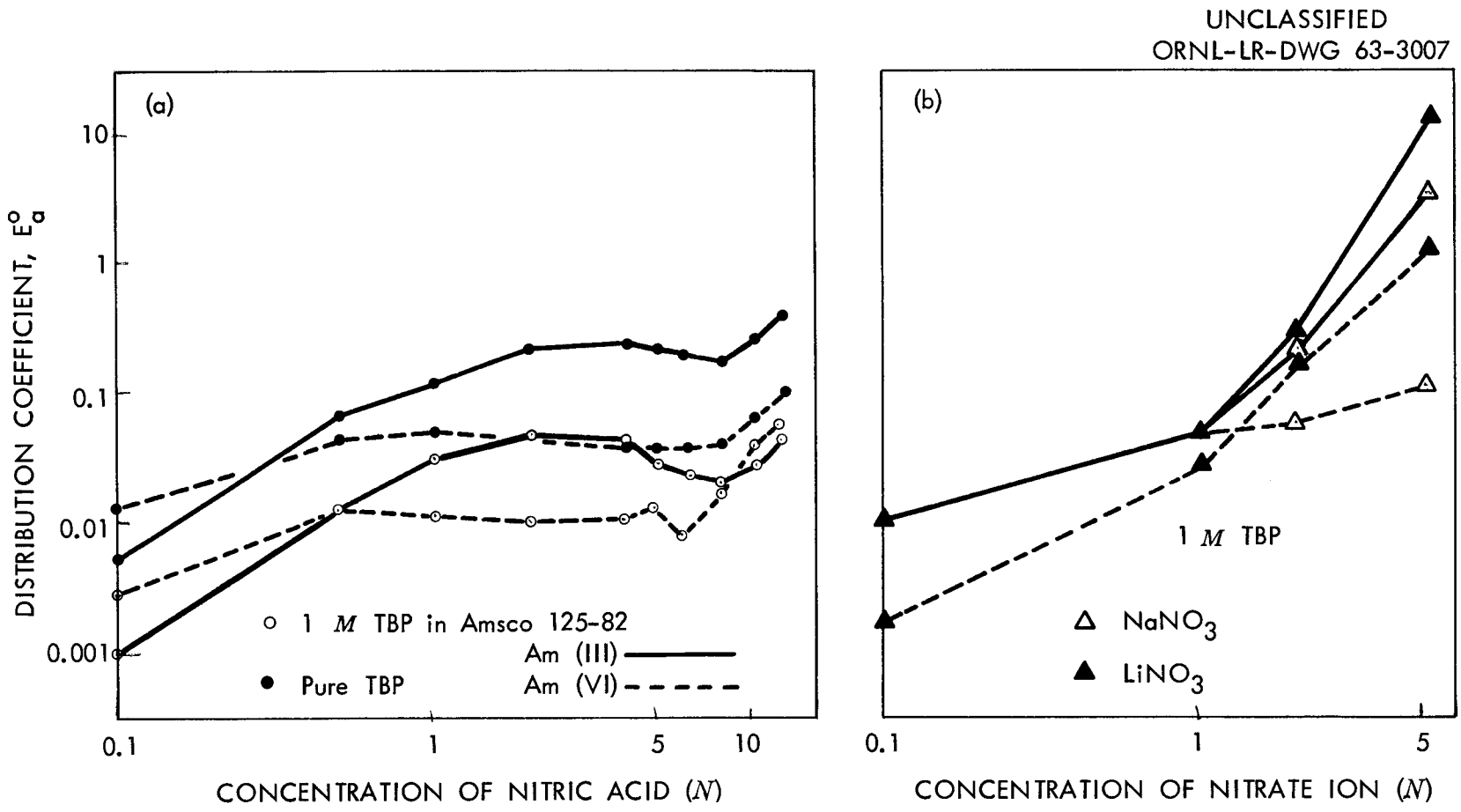


Fig. 1.10.2. Extraction of Americium(III) and Americium(VI) by Tributyl Phosphate. (a) Extraction from nitric acid, (b) extraction from nitrates.

Table 1.10.1. Extraction of Am(III) and Am(VI) by Di(2-ethylhexyl)phosphoric Acid

Organic phase: 0.3 M HDEHP in DIPB

Aqueous Phase	Distribution Coefficient, E_a^o	
	Am(III)	Am(VI)
0.01 N HNO_3	≥5000	0.12
0.05 N HNO_3	12	--
0.1 N HNO_3	1.1	0.019
1.0 N HNO_3	0.0003	≤0.0002
0.1 N $LiNO_3$	≥8000	1.9
1.0 N $LiNO_3$	≥5000	3.3
2.0 N $LiNO_3$	≥1500	2.3
5.0 N $LiNO_3$	80	1.6

It is interesting to note that the extractions from 0.1 N HNO_3 indicate that no more than 4% of the Am(VI) could have been reduced in this test, even if Am(VI) were completely inextractable.

1.10.6 Extraction by a Tertiary Amine

A very brief comparison was made of Am(III) and Am(VI) extractions by Alamine 336 nitrate in DIPB from lithium nitrate solutions. In order to obtain appreciable extraction from dilute nitrate solutions, no acid was added beyond the 0.001 N H_2SO_4 derived from the preparation of Am(VI). The data in Table 1.10.2 show that Am(III) was less extractable than Am(VI) at low nitrate concentrations, but a difference in nitrate-concentration dependency reversed the preference at concentrations above 4 N $LiNO_3$.

The extraction of Am(VI) by 15% Alamine 336 was about half that by 30% from 4 N $LiNO_3$; from 8 N $LiNO_3$ the ratio of coefficients was only one-fourth, indicating a change in the nature of the extractable species. When extractant containing Am(VI) that had been extracted from 4 N, 6 N, or 8 N $LiNO_3$ was allowed to stand overnight and was then contacted with similar aqueous solutions, the extraction coefficients were very

similar to those obtained the previous day. These results indicate stabilization of Am(VI) in the extract.

Table 1.10.2. Extraction of Am(III) and Am(VI) by Tertiary Amine

30% Alamine 336 Nitrate in DIPB
0.001 N H_2SO_4, 0.01 M $(NH_4)_2S_2O_8$

	Distribution Coefficient, E_a^o		
$LiNO_3$ (N)	Am(III)	Am(VI)	Am(VI)-15% Amine
1	0.009	0.082	
2	0.079	0.25	
3	0.36	0.65	
4	1.51	1.66	0.78
5	11	4.7	
6	48	11	4.3
7	93	23	
8	330	81	19
9	860	87	

1.11 Separation of Transplutonium Elements from Iron

(B. Weaver, F. A. Kappelmann, J. R. Collins)

One potential method of producing transplutonium elements consists in subjecting quantities of uranium or plutonium to the extremely high neutron flux of a thermonuclear explosion in a salt dome. According to one preliminary process proposal, thousands of tons of salt would be treated to obtain a few grams of the desired products in millions of gallons of dilute nitric acid. Many different elements would be present in the liquor and, of these, a relatively large quantity of iron would probably constitute the most difficult separation problem. Consequently, various methods are being considered for the removal of the iron and concentration of the product.

1.11.1 Precipitation Methods

Plutonium can probably be scavenged effectively by adding alkali to give a coprecipitate with a small fraction of the iron. However, little, if any, of the transplutonium elements would be precipitated at this low pH. Transplutonium phosphates have low solubilities, but in tests with iron and rare earths the iron was precipitated preferentially. Fluorides are among the most insoluble compounds of the rare earths and the similar transplutoniums. It is unlikely that they can be precipitated from pure solutions of the extremely low concentration expected. However, coprecipitation is likely, and this possibility has been tested.

When potassium fluoride was added to a ferric nitrate solution containing 1 g of iron per liter, the solution became almost colorless at one atom of fluoride per atom of iron. The pH of the solution increased from 2.20 to 2.65. Further addition of fluoride up to 6 atoms per atom of iron gave the first appearance of turbidity. After standing for 1 hr, 92% of the Am^{241} was removed from the solution by centrifugation. In preliminary tests of other solutions containing 0.5 to 1.0 g of iron per liter (traced by Fe^{59}) and (2 to 5) x 10^{-6} g of Am^{241} per liter, more than 90% of the americium was precipitated along with less than 10% of the iron. In one case, the separation was improved further by adding nitric acid to the slurry to redissolve the precipitate and readjusting the pH with potassium hydroxide.

Similar experiments with a liquor containing only 0.1 g of iron per liter did not give a visible precipitate. (The iron content of the liquor that would be obtained in actual process practice is not known accurately at this time.) Pending results from further tests, it is possible that the fluoride coprecipitation method might suffer if the liquor contained too little iron. On the other hand, it is also possible that other metals present in the liquor might cause better recoveries than those obtained with the relatively pure solution described here.

1.11.2 Solvent Extraction

A survey of information available concerning rare-earth extraction and results of some tests on iron extraction indicated the possibility of obtaining high recovery of transplutonium elements in a greatly

reduced volume by extracting with di(2-ethylhexyl)phosphoric acid in diisopropylbenzene from a liquor that has been treated with a carboxylic acid to hinder iron extraction and to prevent its precipitation during pH adjustment to about 4 with sodium hydroxide. Two batch countercurrent extraction experiments were performed with solutions containing 0.1 g of iron per liter and 0.04 M citric acid. Tracer amounts of Fe^{59} were added in both tests and a tracer amount of Am^{241} was added in the second test.

The first test was carried through 31 cycles with three extraction stages, four americium strip stages, and two iron strip stages as shown in Fig. 1.11.1. Solution composition and volume ratios are also shown in Fig. 1.11.1. It should be noted that 4-sec-butyl-2-(α-methylbenzyl)-phenol (BAMBP) was added to the solvent since this or a similar acting additive would be necessary in actual practice to prevent third-phase formation during solvent cleanup by alkaline stripping. It served no useful purpose in this experiment. Phases were contacted 15 min by rotating separatory funnels end-over-end mechanically and were separated with centrifugation. The volume reduction factor of 12.5 was the maximum practicable in this small-scale experiment with feed volumes of only 25 ml.

This experiment was designed only to determine the fate of the iron. Analyses after 30 cycles showed that 90% of the Fe^{59} was leaving the system in the first-stage raffinate, 7.4% was removed from the organic phase by stripping with oxalic acid, and only 0.4% went into the stream that normally would carry the Am^{241} product. Part of the latter could have been removed by including scrub stages in the system. There was no Fe^{59} activity in the organic phase after stripping with oxalic acid. The profile of iron concentration and distribution coefficients in the thirty-first cycle is given in Fig. 1.11.2. It is apparent that the extraction of iron can be limited to a small fraction of that present and that the extracted iron should be effectively separated from americium when the latter is stripped.

The second extraction experiment, which included Am^{241}, was designed to give a larger volume reduction across the system, as shown in Fig. 1.11.3. Solution composition, volume ratios, and other experimental details are also shown in Fig. 1.11.3. Phases were contacted for 20 min in separatory funnels by mechanical end-over-end rotation.

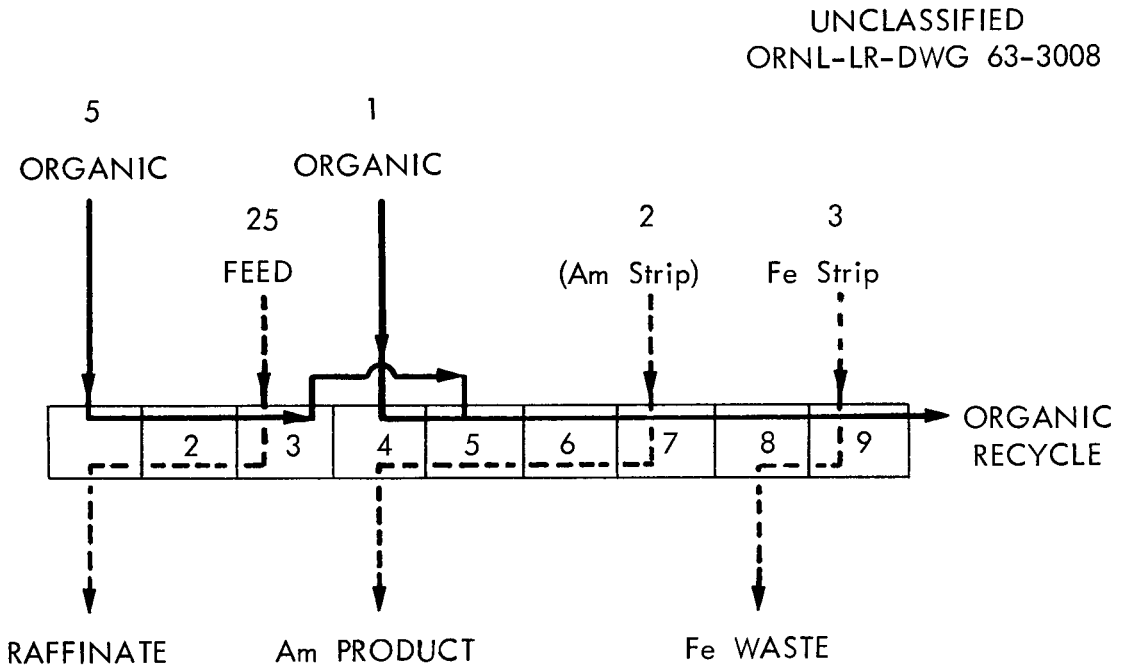


Fig. 1.11.1. Flowsheet for Countercurrent Experiment No. 1.

Solutions:

Organic - (0.3 M di(2-ethylhexyl)phosphoric acid (HDEHP), 0.2 M 4-sec-butyl-2-(α-methylbenzyl)phenol (BAMBP) in diisopropylbenzene (DIPB)

Feed - 1 M HNO_3, 0.04 M citric acid, adjusted to pH 4.15
0.1 g Fe per liter, Fe^{59} (2030 counts sec^{-1} ml^{-1})

Am Strip - 1 M HNO_3, 0.04 M citric acid, adjusted to pH 0.5
(No Am in this experiment)

Fe Strip - 0.5 M oxalic acid
Numbers in circles are batch volumes (ml)

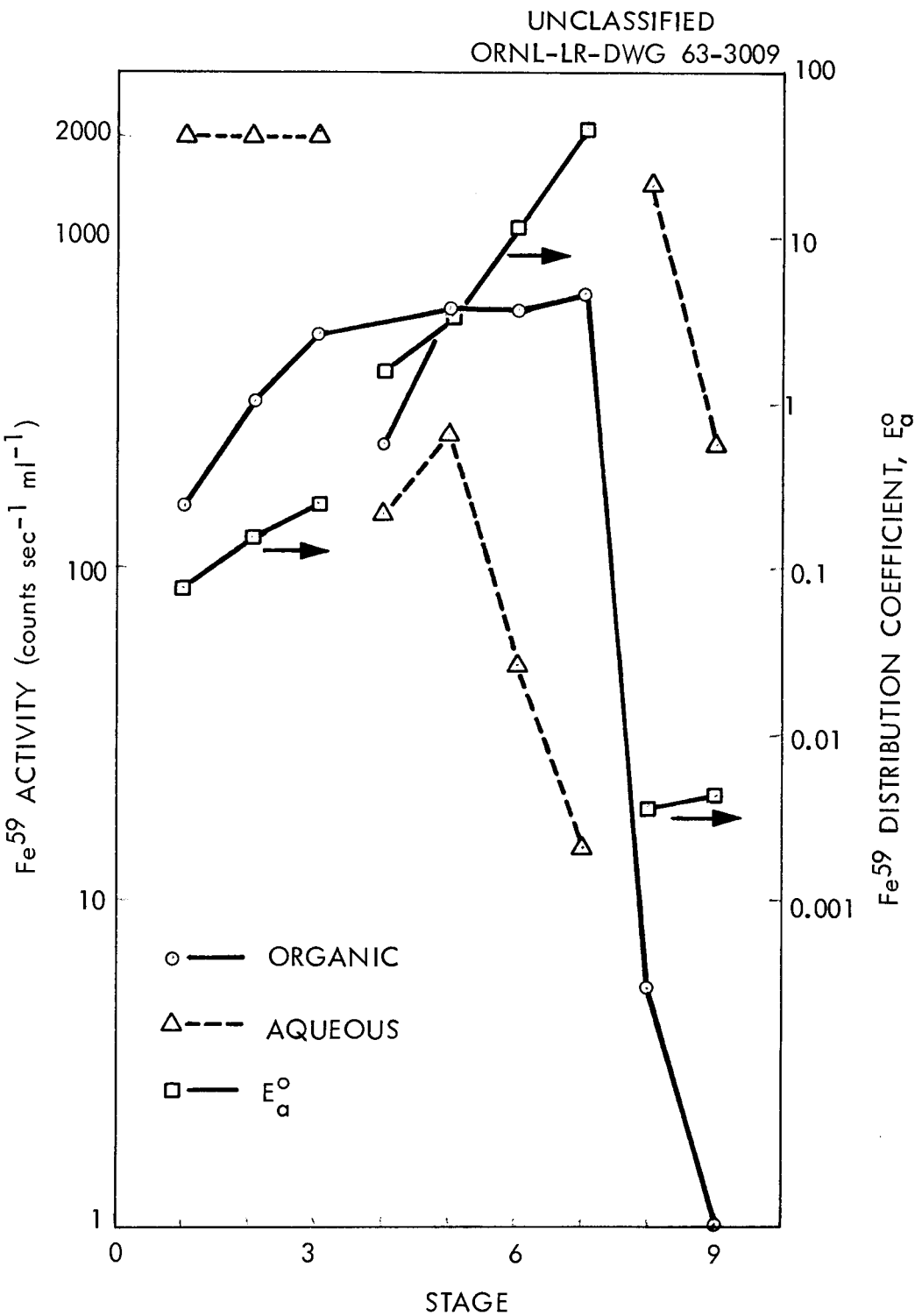


Fig. 1.11.2. Iron Profile for Countercurrent Run No. 1.

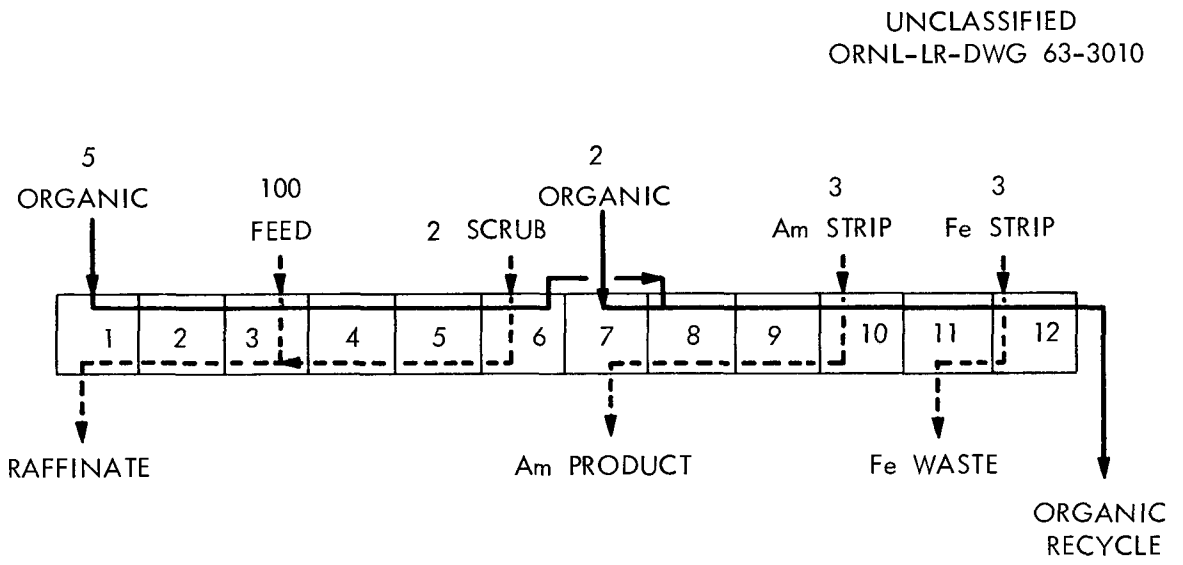


Fig. 1.11.3. Flowsheet for Countercurrent Experiment No. 2.

Solutions:

Organic - 0.3 M di(2-ethylhexyl)phosphoric acid (HDEHP) in diisopropylbenzene (DIPB)

Feed - 1 N HNO_3, 0.04 M citric acid, adjusted to pH 4.18
0.09 g of Fe per liter, Fe^{59} (1030 counts sec^{-1} ml^{-1}), Am^{241} (1065 counts sec^{-1} ml^{-1})

Scrub - 1 N HNO_3, 0.04 M citric acid, adjusted to pH 4.2

Am Strip - 1 N HNO_3, 0.04 M citric acid, adjusted to pH 0.78

Fe Strip - 0.5 M oxalic acid
Numbers in circles are batch volumes (ml)

Analyses after the twenty-seventh cycle showed removal of 94% of the Fe^{59} in the raffinate and 5.6% in the iron-strip stream. Only 0.028% of the Fe^{59} was found in the Am^{241} product. There was no detectable Am^{241} in the raffinate (less than 0.01%) and only 0.006% in the iron-strip stream. A profile of the concentrations of both elements in the twenty-eighth cycle is given in Fig. 1.11.4, and a profile of distribution coefficients is given in Fig. 1.11.5.

A time study was also made of iron and americium extraction from the same feed solution used in the countercurrent experiment. Ten-milliliter volumes of 0.1 M HDEHP in DIPB and the feed solution were contacted for 1 min by vigorous shaking, separated, and sampled. After analysis, the phases were recombined and subjected to several periods of contact by mechanical end-over-end rotation, with intermittent separation and sampling. The total of these contact times was 150 min. The amounts of Fe^{59} and Am^{241} found in the organic phase are plotted against contact time in Fig. 1.11.6, while distribution coefficients and separation factors are plotted in Fig. 1.11.7. It is seen that americium extraction reached a constant level very rapidly, while iron extraction increased gradually over the entire period. Thus, rapid operation would be of considerable importance in application of this system to a separation process.

Further experiments will include studies of the effect of higher iron concentrations, the use of other complexing agents, and the fate of calcium when present in the feed liquor.

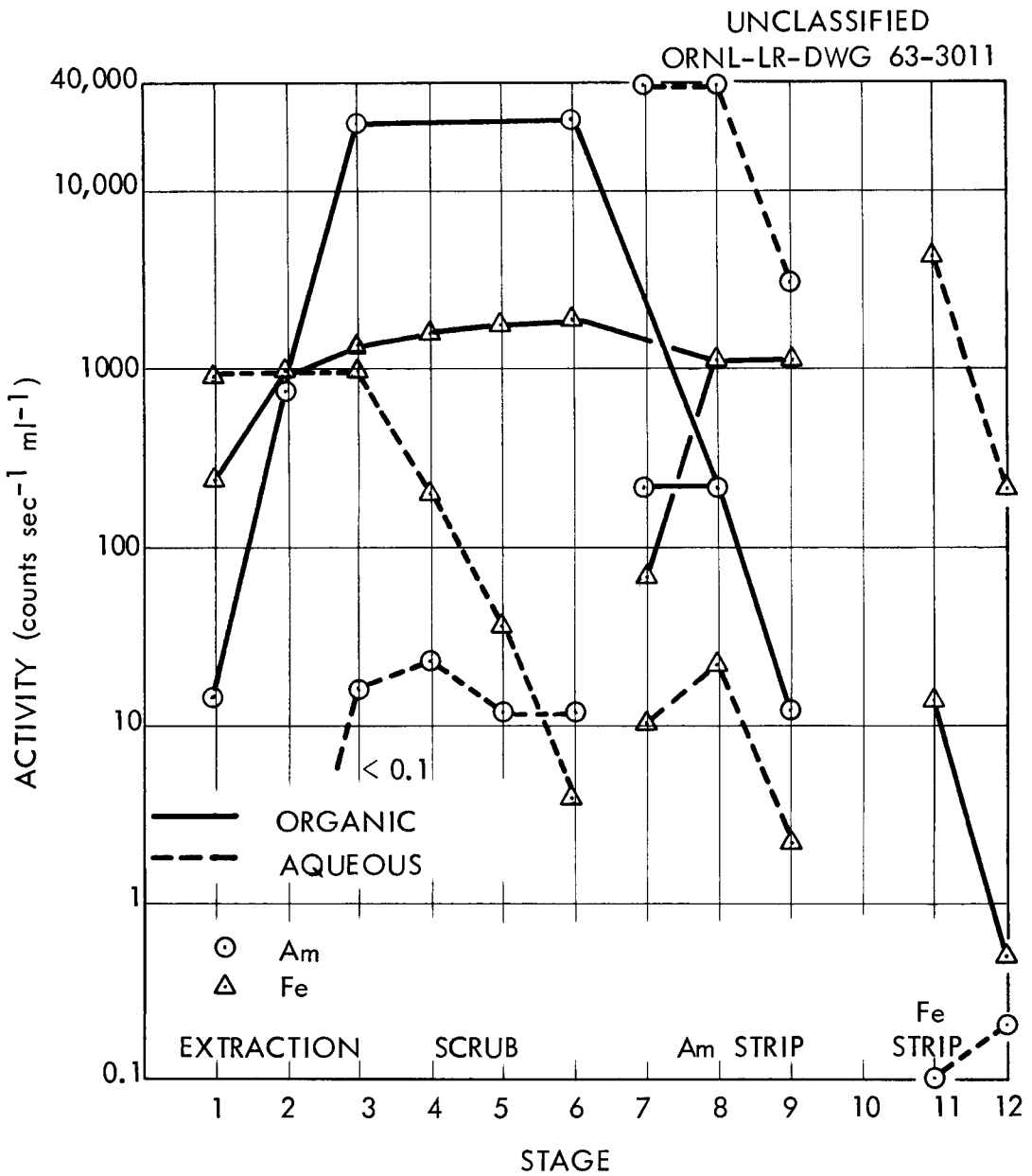


Fig. 1.11.4. Americium-Iron Profile for Countercurrent Run No. 2.

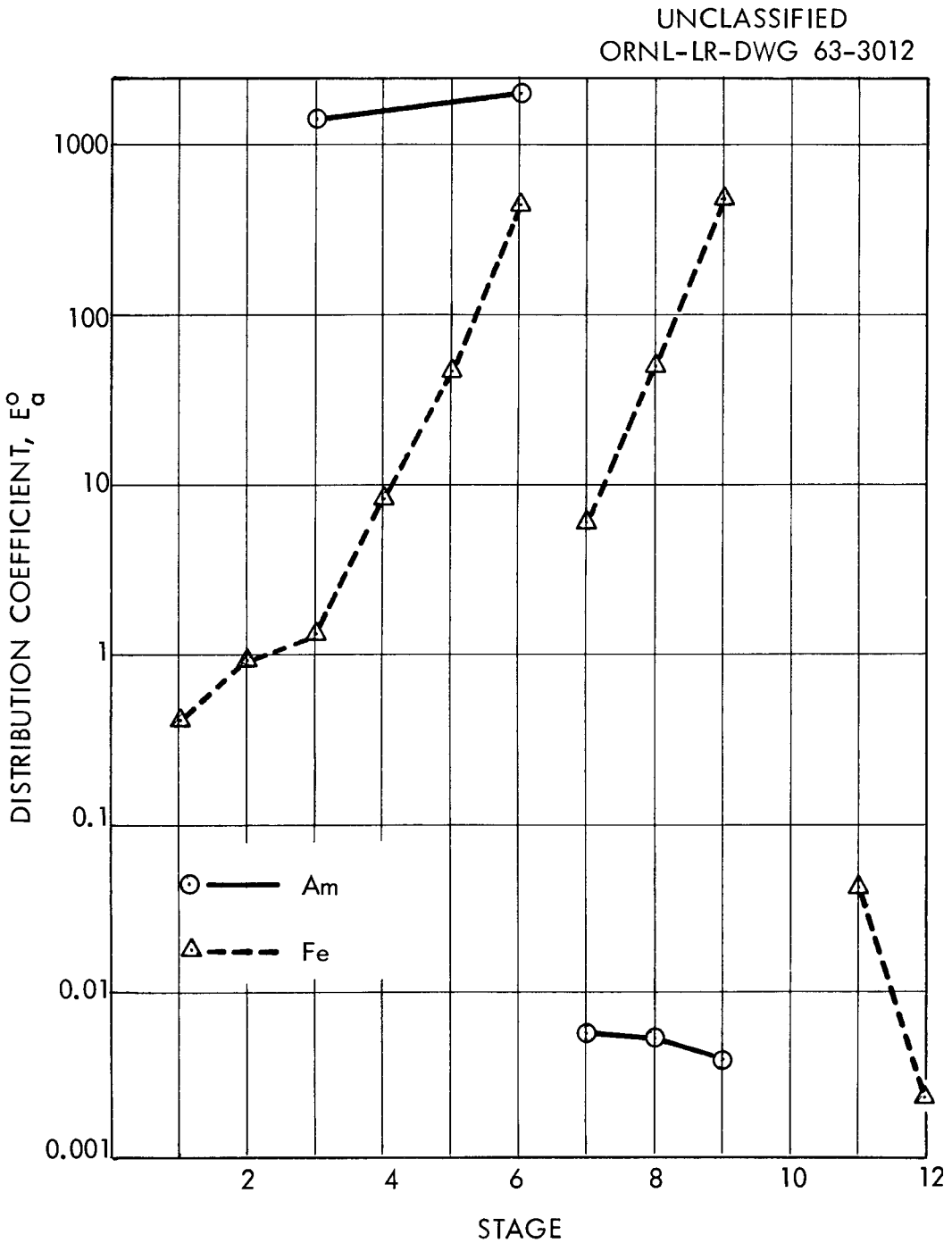


Fig. 1.11.5. Profile of Americium-Iron Distribution, Countercurrent Run No. 2.

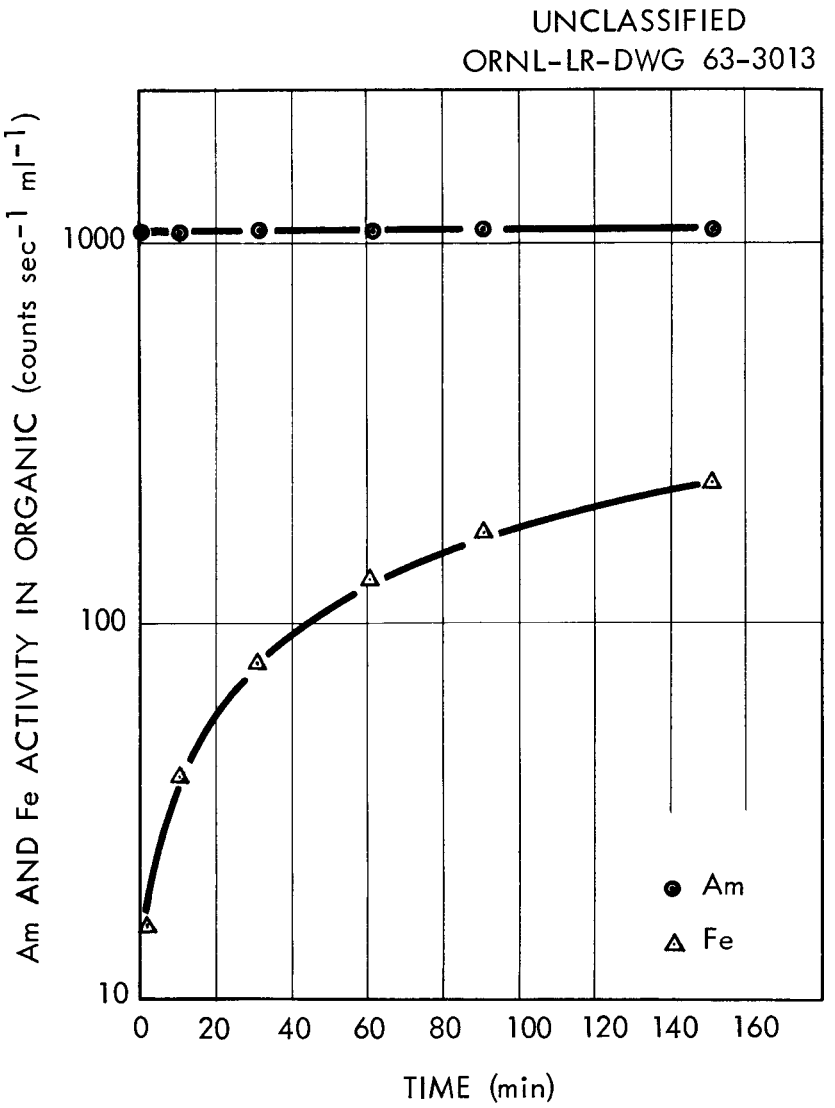


Fig. 1.11.6. Americium-Iron Extraction Rates. Activity in Organic.

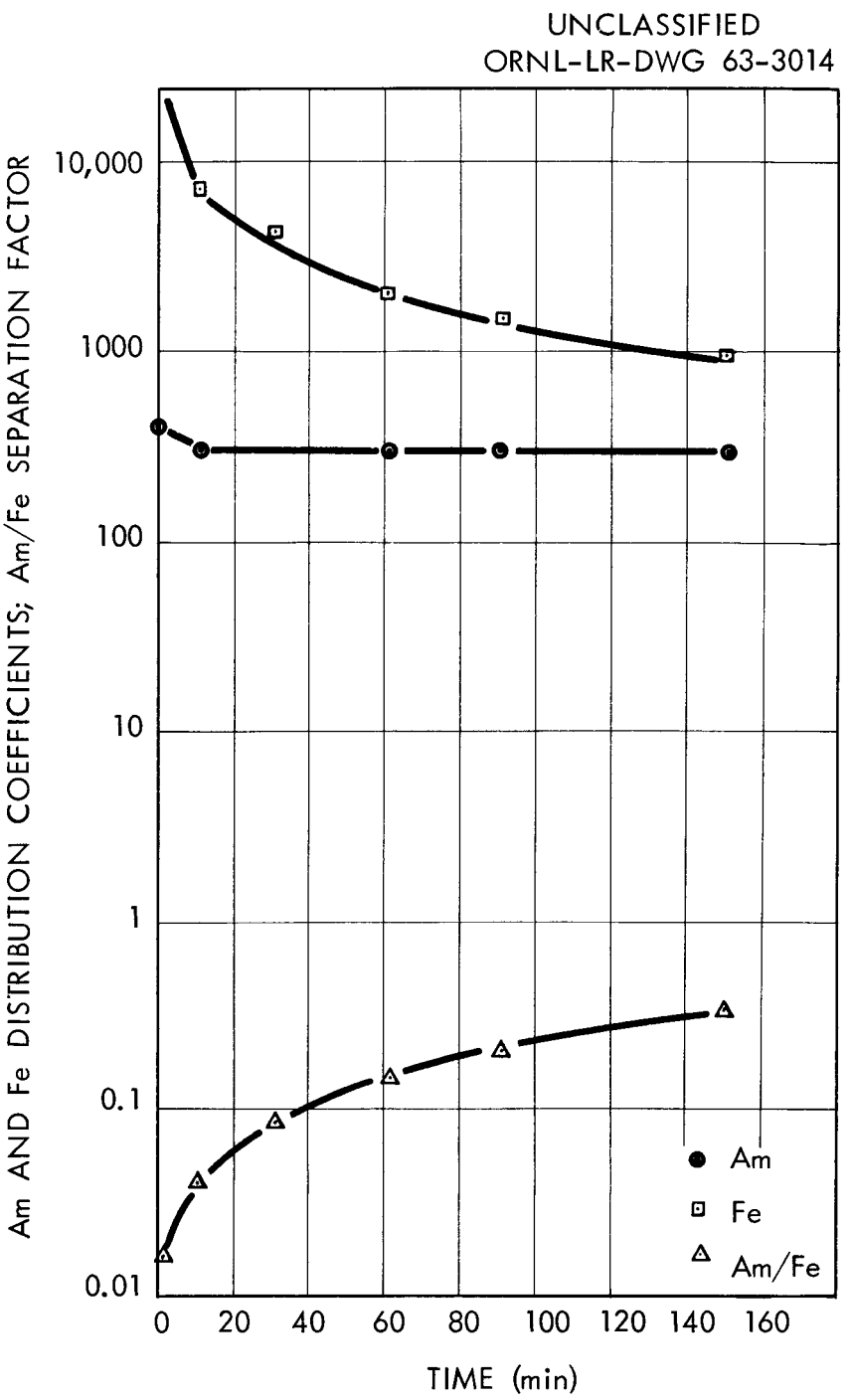


Fig. 1.11.7. Americium-Iron Extraction Rates. Distribution and Separation.

2. FUNDAMENTAL AND DESCRIPTIVE CHEMISTRY OF SOLVENT EXTRACTION SYSTEMS

2.1 Extraction of Metals from Chloride Solutions with Amines (D. J. Crouse, F. G. Seeley)

In a continuation of a program to survey the extraction of many metals from hydrochloric acid and acidified chloride salt solutions with typical primary, secondary, tertiary, and quaternary amines, data were obtained for the extraction of germanium, selenium, rubidium, strontium, yttrium, niobium, and molybdenum. Extraction data for thirteen other metals were reported previously.[1,3,4]

2.1.1 Procedures

The amines chosen to represent the different amine types in standard metal extraction tests were Primene JM (primary amine), Amberlite LA-1 (secondary amine), Alamine 336 (tertiary amine), and Aliquat 336 (quaternary amine). Concentration of the amines was 0.1 M, and the diluent used was diethylbenzene (DEB), except for Aliquat 336, where the addition of 3 vol % tridecanol (TDA) was necessary to prevent third-phase formation at high chloride concentrations. Radiochemical analyses were used to determine the distribution of the metals between the phases except in tests with germanium and rubidium, for which ionic analyses were obtained.

2.1.2 Germanium(IV)

Extraction coefficients from both HCl and LiCl—0.2 M HCl solutions were less than 0.04 (analytical detection limit) for all four amines below aqueous chloride concentrations of 5 M (Fig. 2.1.1). From salt solutions extraction results for all the amines were approximately equivalent. Coefficients increased rapidly with increase in chloride concentration above 5 M, reached a maximum of 50 to 70 at a chloride concentration of about 8 M, and then decreased slightly with further increase in chloride concentration to 10 M. From hydrochloric acid solutions, the extraction order was: Aliquat 336 > Alamine 336 > Amberlite LA-1 > Primene JM.

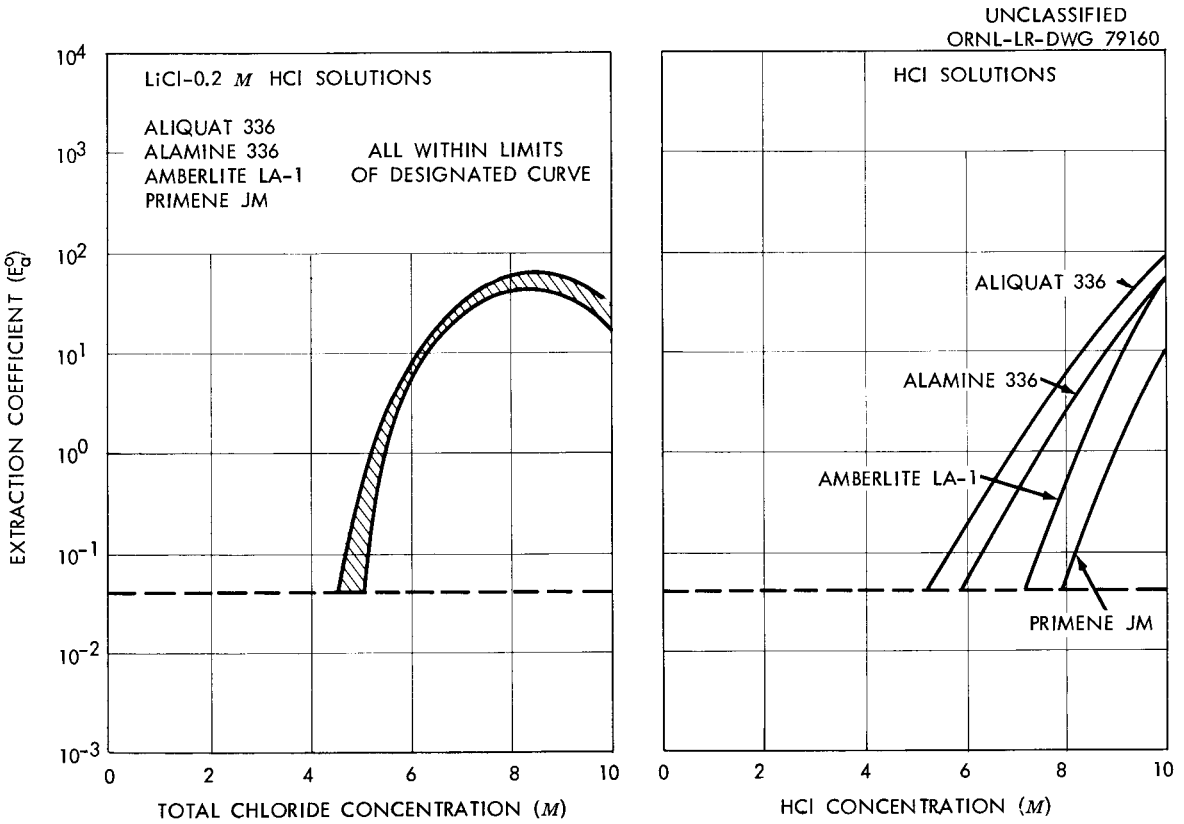


Fig. 2.1.1. Extraction of Germanium(IV) from Chloride Solutions by Amines. Organic phase: 0.1 M amine chloride in DEB (97% DEB—3% TDA for Aliquat 336). Aqueous phase: HCl or LiCl—0.2 M HCl solutions ranging from 0.5 M to 10 M total chloride and containing 0.01 M Ge(IV). Contact: 10 min at 1/1 phase ratio.

Extraction coefficients increased with increase in chloride concentration, reaching a maximum value of about 90 for Aliquat 336 at a chloride concentration of 10 M. Germanium in the organic phase was determined by neutron activation analysis, while conventional ionic techniques were used to determine its concentration in the aqueous phase.

2.1.3 Selenium(IV)

Extractions from both acid and salt solutions increased with increasing chloride concentration from 0.5 to 10 M (Fig. 2.1.2). From salt solutions, extraction coefficients at 10 M chloride were 12 with Aliquat 336, 7 with Alamine 336, 0.6 with Amberlite LA-1, and 0.03 with Primene JM. In extractions from hydrochloric acid, coefficients were slightly higher than from the salt solutions, and the extraction order was different in the 5 to 10 M chloride concentration range. Extraction coefficients at 10 M HCl were about 60 for Alamine 336 and Amberlite LA-1, 22 for Aliquat 336, and 0.7 for Primene JM.

2.1.4 Rubidium

In extractions from both acid and salt solutions, extraction coefficients for all four amines were less than 6×10^{-4} (analytical detection limit) over the chloride concentration range 0.5 to 10 M. The rubidium concentrations were determined by flame photometry.

2.1.5 Strontium

Extraction coefficients for all four amines were less than 0.004 from both acid and salt solutions over the chloride concentration range 0.5 to 10 M.

2.1.6 Yttrium

Extraction coefficients from both acid and salt solutions were quite low, reaching a maximum of only 3×10^{-2} from salt solutions and 8×10^{-3} from acid solutions with Aliquat 336 (Fig. 2.1.3). Extractions were considerably weaker with Alamine 336 and were negligible (E_a^o less than 5×10^{-4}) with Amberlite LA-1 and Primene JM.

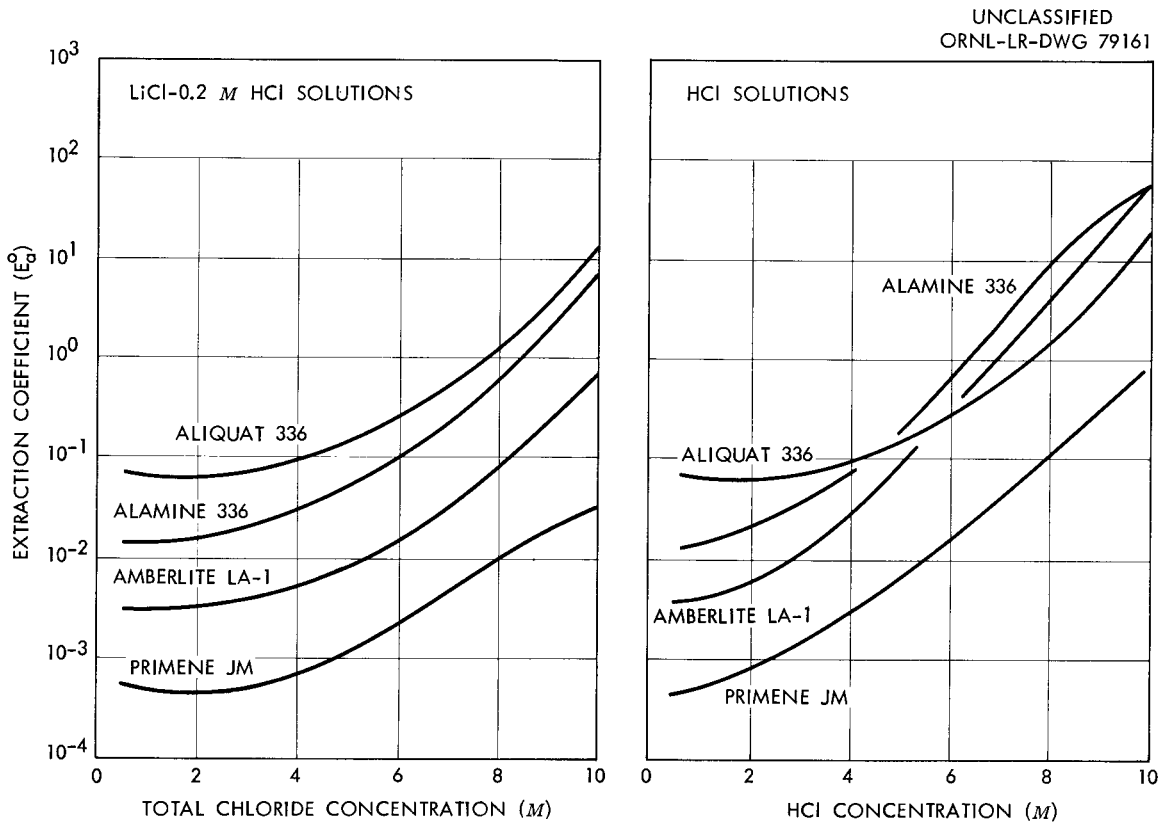


Fig. 2.1.2. Extraction of Selenium(IV) from Chloride Solutions by Amines. Organic phase: 0.1 M amine chloride in DEB (97% DEB—3% TDA for Aliquat 336). Aqueous phase: HCl or LiCl—0.2 M HCl solutions ranging from 0.5 M to 10 M total chloride and containing 0.01 M Se(IV) and Se^{75} tracer. Contact: 10 min at 1/1 phase ratio.

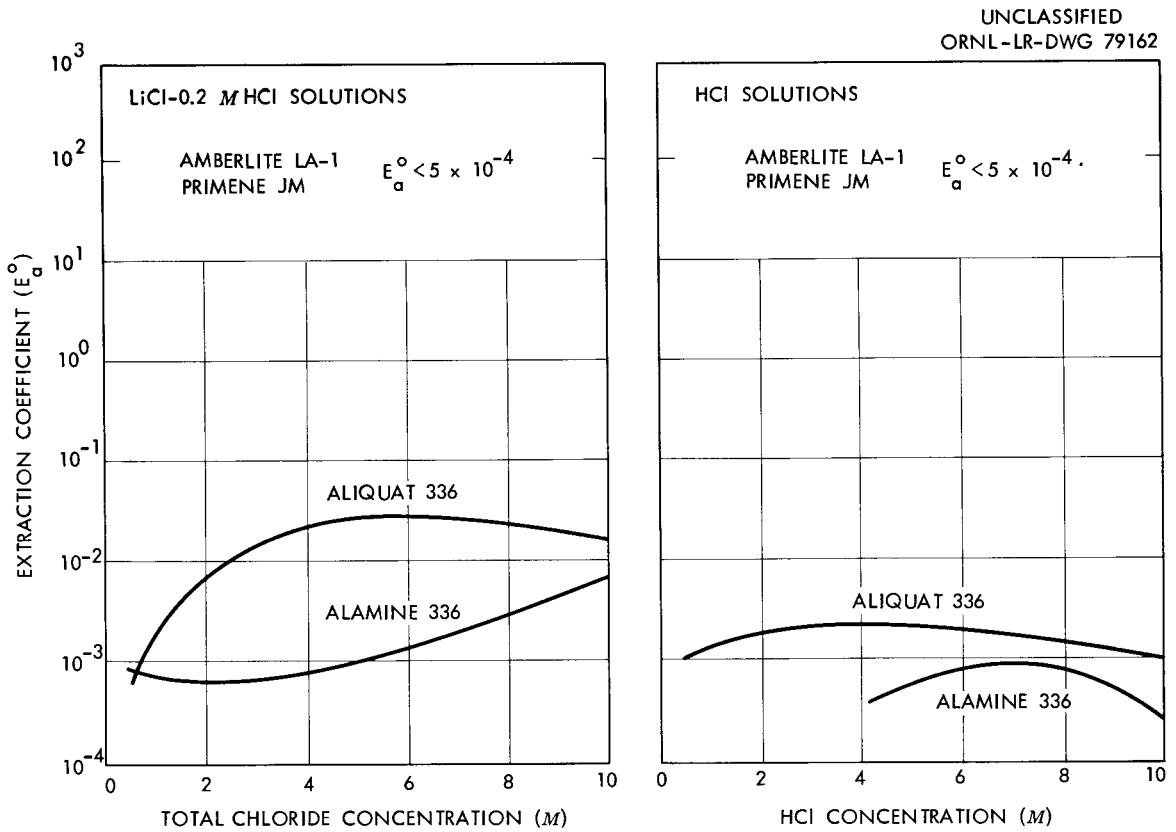


Fig. 2.1.3. Extraction of Yttrium(III) from Chloride Solutions with Amines. Organic phase: 0.1 M amine chloride in DEB (97% DEB—3% TDA for Aliquat 336). Aqueous phase: HCl or LiCl—0.2 M HCl solutions ranging from 0.5 M to 10 M total chloride and containing 0.01 M Y(III) and Y^{91} tracer. Contact: 10 min at 1/1 phase ratio.

2.1.7 Niobium(V)

Coefficients for the extraction of niobium(V) from hydrochloric acid decreased with increase in acid concentration from 0.5 to 4 M and then increased rapidly as the chloride concentration was increased to 10 M (Fig. 2.1.4). The extraction order was: Aliquat 336 > Alamine 336 > Amberlite LA-1 > Primene JM. The maximum coefficients obtained (10 M HCl) were about 110 for Aliquat 336 and about 80 for Alamine 336. Niobium extractions from the salt system were stronger than from the acid system at chloride concentrations below 5 M but were weaker from the salt system at high chloride concentrations, i.e., 8 to 10 M. A maximum coefficient of about 12 was obtained with Aliquat 336 at 10 M chloride.

Because of the low solubility of niobium in acid solutions, only tracer concentrations were used. The tracer solution, as received, contained oxalate, which was destroyed by treatment with $KMnO_4$ (excess $KMnO_4$ then destroyed with $NH_2OH \cdot HCl$) before it was added to the test solutions. In earlier tests in which the oxalate was not destroyed (11 ppm of oxalate in the test solutions) niobium extraction coefficients were only a tenth as high in the chloride concentration range 2 to 6 M, although there was no discernible effect at a chloride concentration of 10 M.

2.1.8 Molybdenum(VI)

The extraction power of the different amines for molybdenum varied widely (Fig. 2.1.5). The extraction order was: Aliquat 336 > Alamine 336 > Amberlite LA-1 > Primene JM, with the first giving extraction coefficients 1000 to 10,000 times higher than the last. In extractions from LiCl—0.2 M HCl with Aliquat 336, the coefficient reached a maximum value of about 2000 in the range 8 to 10 M chloride. Extractions were much weaker from hydrochloric acid; the maximum coefficient obtained with Aliquat 336 was about 40 and occurred at an acid concentration of about 5 M.

It should be noted that extraction coefficients for molybdenum(VI), like those of vanadium(V), are dependent on the molybdenum (or vanadium) concentration in the aqueous phase, with the coefficients at low solvent loadings decreasing with decreasing aqueous molybdenum concentration.

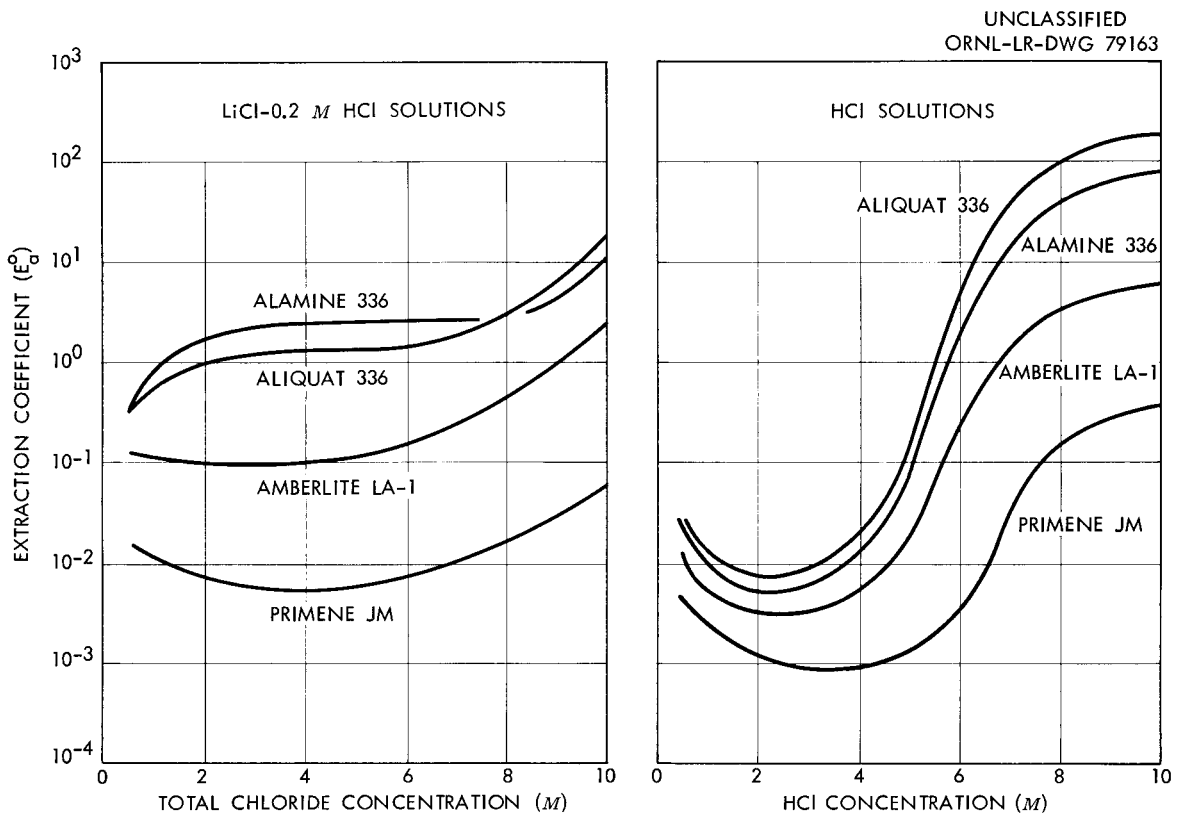


Fig. 2.1.4. Extraction of Niobium(V) from Chloride Solutions with Amines. Organic phase: 0.1 M amine chloride in DEB (97% DEB—3% TDA for Aliquat 336). Aqueous phase: HCl or LiCl—0.2 M HCl solutions ranging from 0.5 M to 10 M total chloride and containing Nb^{95} tracer only (oxalate in tracer destroyed). Contact: 10 min at 1/1 phase ratio.

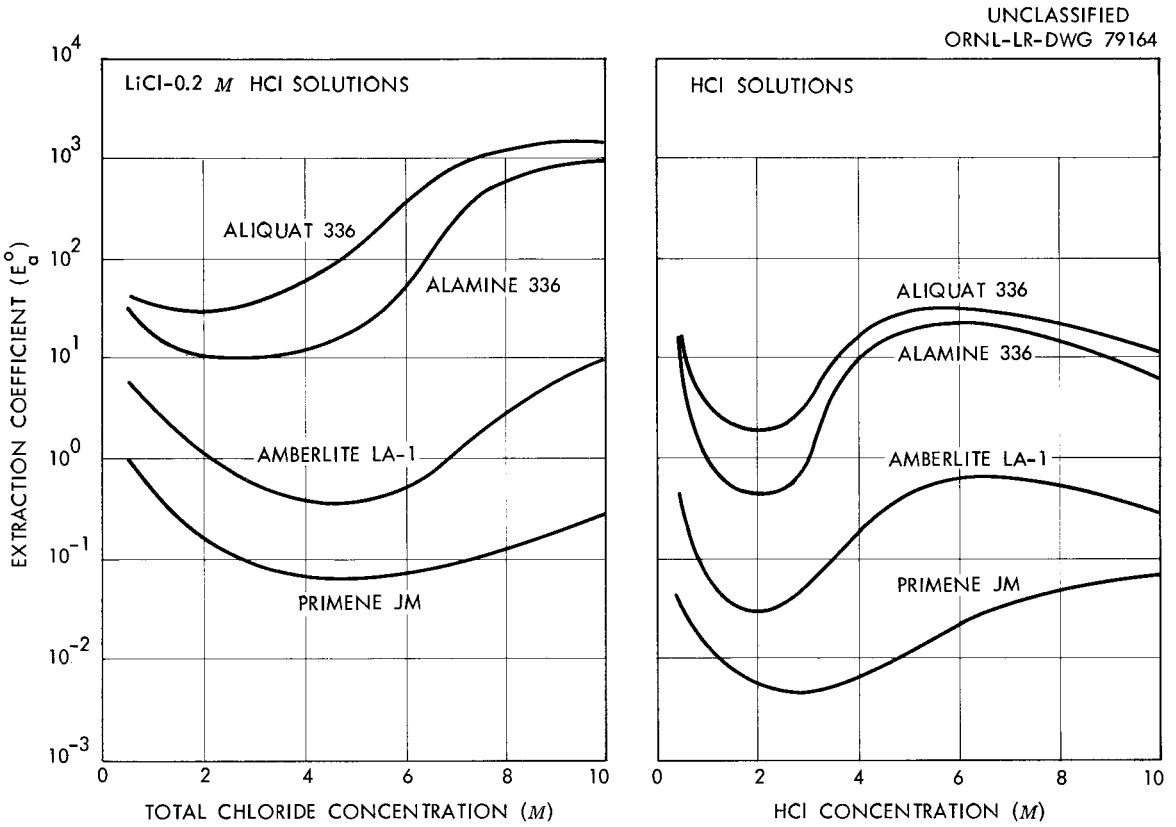


Fig. 2.1.5. Extraction of Molybdenum(VI) from Chloride Solutions with Amines. Organic phase: 0.1 M amine chloride in DEB (97% DEB—3% TDA for Aliquat 336). Aqueous phase: HCl or LiCl—0.2 M HCl solutions ranging from 0.5 to 10 M total chloride and containing 0.01 M Mo(VI) and Mo^{99} tracer. Contact: 10 min at 1/1 phase ratio.

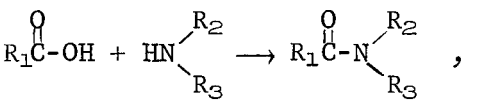
In extractions with Aliquat 336 from LiCl—0.2 M HCl containing 0.03 M molybdenum, coefficients were 2 to 4 times higher than shown in Fig. 2.1.5 for tests in which the initial aqueous molybdenum concentration was 0.01 M. Extractions were also time dependent, coefficients being about 50% higher for 60-min contact times, compared with 10-min contact times.

2.2 N,N-Dialkyl Amides as Extractants

(C. A. Blake, J. M. Schmitt, W. E. Oxendine)

Fourteen amides were tested for their ability to extract uranium and thorium, and several of them to extract zirconium, hafnium, europium, cerium, americium, and nitric acid from various aqueous solutions. In 1952[11] this class of compounds was examined briefly at this laboratory to determine their potential for uranium extraction from ore leach liquors. It was shown that the amides, in particular the phosphoramides, would extract uranium from nitrate systems but were poor extractants from solutions containing other anions, such as phosphate. Subsequently, additional phosphoramides were prepared, and a useful extraction of uranium was achieved from sulfate-nitrate and phosphate-nitrate systems,[12] but the reagents lacked suitable stability against hydrolysis. Since that time, other workers have been interested in the amides as extractants, notably Feder and Ader,[13] who examined the ability of a number of amides to extract uranium from acid and neutral solutions containing nitrate, chloride, sulfate, phosphate, and other anions. Best results were achieved with dialkylacetamides, especially N,N-di-n-butylacetamide, dissolved in kerosene or carbon tetrachloride. The extracted uranium was recovered by scrubbing the organic phase with uranium-complexing alkaline solutions.

It is the purpose of the present investigation to study the extraction properties of amides of different structures and to compare their behavior with that of TBP and of di(sec-butyl)phenylphosphonate (DSBPP).[14] Information available on the purity of the amides is also reported. Several were stated by the respective vendors to contain about 95% amide, and all contained less than 2.6% carboxylic acid. Since the amides are prepared from amines and carboxylic acids (or their derivatives), for example,



it is relatively easy to prepare a variety of compounds by using different combinations of the two components.

As shown by the preliminary results reported below, extractions of uranium and thorium from nitrate solutions varied widely with structure of the amides. Some of them with unbranched alkyl chains had about the same extraction power for thorium and uranium. Branching the alkyl chains usually caused a greater decrease in thorium than in uranium extraction. Thorium extraction was characterized by a strong dependence on the acidity of the aqueous phase. The data suggest that thorium and uranium can be recovered separately or simultaneously by choosing the appropriate amide structure and nitric acid concentration of the aqueous phase. None of the amides gave uranium extraction coefficients as high as those obtained with TBP or DSBPP at the same concentration in the solvent. However, all of the amides tested indicated uranium-thorium separations that were at least as good as that obtained with TBP. Uranium was stripped from the solvent by water or dilute nitric acid (less than 0.1 M). Stripping with sulfuric or hydrochloric acids may also be useful when conditions that avoid emulsions or third-phase formation are chosen. Poor phase separations were also obtained in several extraction tests. The rate of phase separations varied with the amide and was ordinarily more rapid with aromatic rather than aliphatic diluents. The amides gave poor extractions of strontium and cesium from nitrate solutions and poor extractions of uranium and thorium from hydrochloric and sulfuric acid solutions. However, they provided synergistically enhanced extraction with di(2-ethylhexyl)phosphoric acid (HDEHP) and were about as effective as the widely used TBP in synergistic combination with HDEHP for uranium extraction from sulfate solutions.

Extraction tests with zirconium, hafnium, and europium with some branched-chain amides have indicated uranium separations from these metals which are 2 to 10 times higher than those obtained with TBP. Preliminary results also showed a possibility of group separation of the transplutonium and lanthanide elements with diisopropyl propionamide and tetraethyl phthalamide.

The amides extracted nitric acid readily. Organic-phase ratios approaching 2.5 moles HNO_3 per mole of reagent were obtained with the dimethyl amides of long-chain fatty acids. In tests with 1 M amide solutions, the extracted acid caused third-phase formation and, in at least one case, decomposition of the extractant. Cursory tests were made of the stability of two amides against hydrolysis with nitric acid. After the rather severe treatment of boiling with 2 M HNO_3 for 4 hr, the amides were about 20 to 40% hydrolyzed.

2.2.1 Uranium and Thorium Extraction from Nitric Acid

Uranium and thorium were extracted separately from nitric acid (1.7 M at equilibrium) by 1 M solutions of several amides in diethylbenzene (DEB) (Table 2.2.1). With the homologous series of N,N-dimethylamides prepared from n-alkyl (C_8 to C_{16}) carboxylic acids, the thorium coefficients were all alike, at $E_a^o = 0.1$. Except for the $C_{16.9}$ derivative, the uranium extraction coefficients were also nearly alike, at $E_a^o = 5$ to 6. The $C_{17.6}$ derivative (oleic, unsaturated alkyl chain) behaved like the other compounds in the series. The $C_{16.9}$ derivative gave a higher uranium extraction, $E_a^o = 16$, which, pending results from further tests, may be attributable to the presence of an impurity. The branched chain N,N-dimethyl C_{13} amide showed markedly lower extraction of both uranium and thorium: $E_a^o = 0.7$ and less than 0.01, respectively.

While intercomparisons may be affected by appreciable and variable losses of some of the lighter amides to the aqueous phase, not yet measured, the results so far indicate wide variation of uranium and thorium extraction and separability when alkyl groups other than methyl were attached to the nitrogen atom. For example, N,N-dibutyl acetamide showed the highest uranium extraction coefficient ($E_a^o = 21$) and also the highest thorium extraction coefficient ($E_a^o = 0.8$, E_U/E_{Th} about 26) of all the amides tested. In comparison, the n-propyl derivative gave a uranium extraction coefficient of about $E_a^o = 5$, whereas the thorium extraction coefficient was 0.013 (E_U/E_{Th} more than 400). The number of compounds examined is not yet sufficient to predict the structural factors of greatest importance in determining extraction behavior.

Table 2.2.1. Uranium and Thorium Extraction with 1 M Amide-Diethylbenzene Solutions from 1.7 M HNO_3 (Equilibrium Aqueous Concentration)

Amide Constituents			Extraction Coefficient		Computed Separation Factor, U/Th
	Carboxylic Acid				
N-Alkyls	Principal Components	Avg. No. of Carbon Atoms	U	Th	
Dimethyl	Caprylic-capric	8.8	5.0	0.1	50
	Lauric	12	6.6	0.1	66
	Coco acids[a]	12.5	5.6	0.1	56
	Myristic	14	6.1	0.1	61
	Palmitic-stearic	16.9	16	0.1	160
	Tallow acids[b]	17	6.3	0.1	63
	Oleic	17.6	7	0.1	70
	Neo-Tridecanoic[c]	13	0.7	<0.01	>70
Diethyl	Capric	10	2.7	0.05	54
Di-n-propyl	Propionic	3	5.4	0.013	410
Di-iso-propyl	Propionic	3	Ppt	<0.01	
Di-n-butyl	Acetic	2	21	0.8	26
		Diamides			
Tetramethyl	"Dimer acid"[d]	34	14	0.5	28
Tetraethyl	Phthalic	8	0.1	<0.002	
		Organophosphorus Reference Standards			
TBP			27	1.1	25
DSBPP (xylene)			38	0.1	380

[a]Principally lauric and myristic acids.

[b]Principally palmitic and stearic acids.

[c]$C_9H_{19}C(CH_3)_2CON(CH_3)_2$.

[d]Amide groups approximately 16 carbon atoms apart.

The results of tests with two diamides are included in Table 2.2.1. The tetramethyl amide from the branched-chain C_{34} acid showed high uranium and thorium extraction, whereas the tetraethylamide of phthallic acid gave very low extractions of both metals.

For comparison, the results of similar tests with TBP and di-sec-butyl phenylphosphonate (DSBPP) are also shown in Table 2.2.1. The uranium extraction with these reagents was higher than that obtained with any of the amides. However, all the amides gave uranium/thorium separations that were as good as or better than that obtained with TBP. The di-n-propyl derivative and the amide from phthallic acid gave a better uranium/thorium separation than that obtained with DSBPP.

The variation in uranium extractability with aqueous nitric acid concentration was similar for the N,N-dimethyl fatty amides and TBP (Fig. 2.2.1). For example, extraction increased with nitric acid in the range 1.5 to 4 M, attained maximum values in the range 4 to 6 M, and then decreased. Extractions with the 1.0 M amides in diethylbenzene (DEB) were everywhere lower than those obtained with 1.0 M TBP in DEB and 1.0 M DSBPP in xylene. The dimethyl amide made from Neo-Tridecanoic acid had a uranium extraction coefficient at low acid concentration which was about 10 times smaller than the other amides. However, the uranium extraction ability of this compound increased with increased nitric acid more rapidly than did any of the other amides, and the coefficient continued to increase in the range 4 to 7 M HNO_3, although there was indication of some leveling off above 5.5 M. At 7.0 M HNO_3, uranium extraction by this reagent equalled that of the N,N-dimethyl amide of the mixed octanoic and decanoic acids.

Thorium extractions by the amides of the fatty acids were characterized by a very strong dependence on nitric acid concentration (Fig. 2.2.1). At 1.7 M HNO_3, the extraction coefficients were about a tenth of that obtained with TBP and were about equal to that with DSBPP. However, at 3.5 M HNO_3, the amide and TBP extraction coefficients were about equal, and, at 7.0 M HNO_3, the extraction coefficients with the amides were 4 to 5 times larger than that with TBP. Uranium and thorium extraction coefficients for several of the amides were nearly equal at 7.0 M HNO_3. Thorium extraction with DSBPP remained low throughout the acidity range.

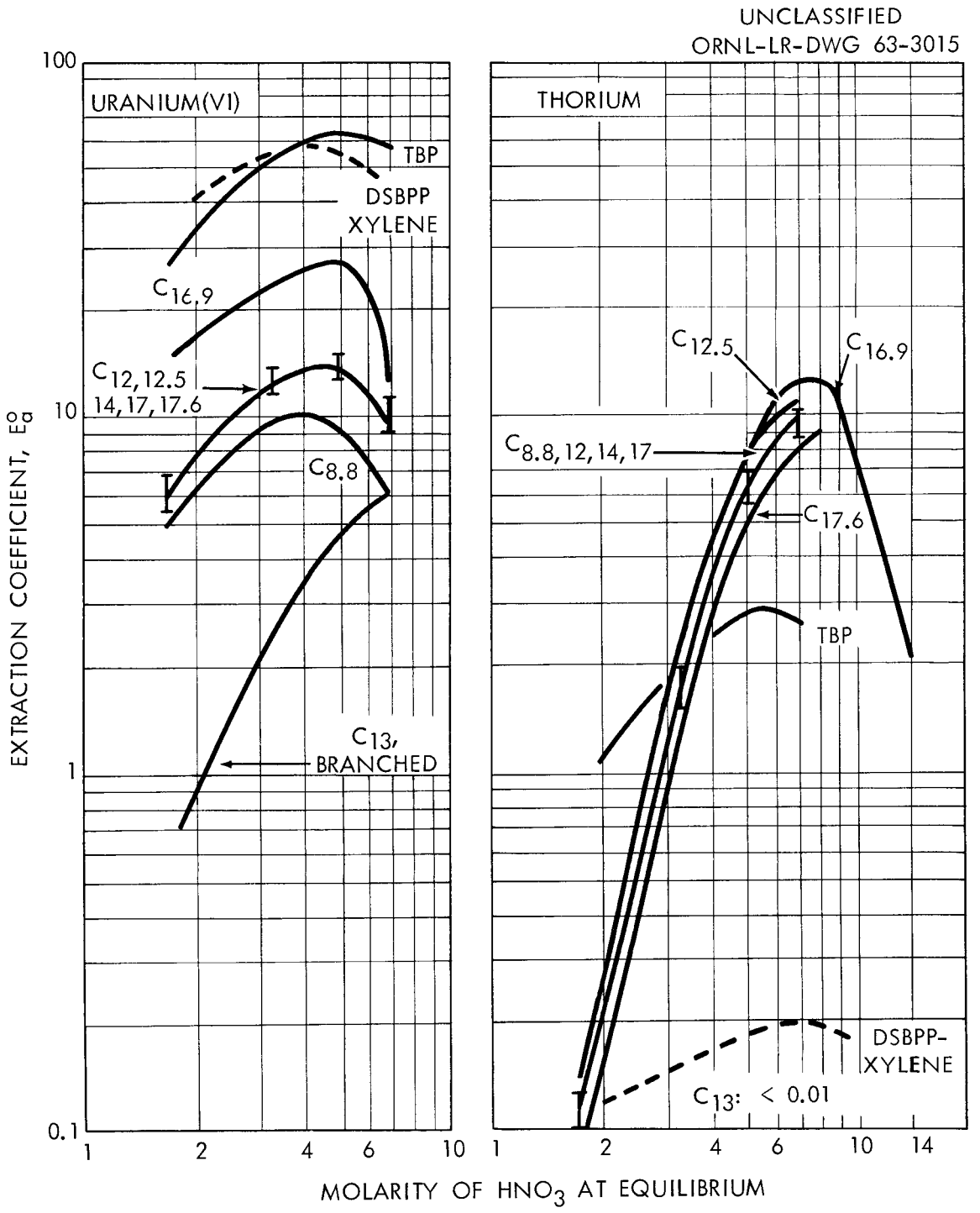


Fig. 2.2.1. Uranium and Thorium Extraction from Nitric Acid by 1 M Solutions of N,N-Dimethyl Amides in Diethylbenzene. Code numbers are the average carbon atom numbers from column 3 of Table 2.2.1. C_{13} is branched, all others straight chain.

The foregoing data suggest that, by appropriate choice of structure of the amide extractant and nitric acid concentration of the aqueous phase, thorium and uranium may be recovered either simultaneously or separately.

Three of the amides at different concentrations in DEB were examined briefly with regard to their extraction from solutions containing uranium at an original concentration of 1 g/liter and nitric acid at an equilibrium concentration of 2 M. Figure 2.2.2 gives log-log plots of the uranium extraction coefficients vs the extractant concentrations. (Since the organic-phase loadings were low, that is, uranium:reagent mole ratios were less than 1:250, the initial reagent concentration was assumed to be equal to the final free-reagent concentration.) The dashed lines of slope 2, drawn arbitrarily through the experimental points, fit the data fairly well. On the basis of these preliminary tests, it is suggested that, at these low uranium loading levels in the amide extractant phase, there is a combination of two reagent molecules with each uranium atom extracted.

An isotherm for the extraction of uranium from 5 M HNO_3 by a 1 M solution of the dimethyl-oleic (C-17.6) amide is shown in Fig. 2.2.3. The data were obtained by mixing the amide and uranium solutions at a series of varying phase ratios. The initial uranium concentration in the 5 M HNO_3 was 122 g of uranium per liter, and the amide solution was equilibrated prior to extraction with a 5 M HNO_3 solution containing no uranium so that the aqueous-phase nitric acid concentration would remain almost constant. Although the equilibrium curve as far as measured lies below the expected asymptotic limit at 1 mole of uranium for each 2 of amide, analysis of its shape suggests that on extension it would reach higher than 1:2 loading. The 1 U:2 amide combining ratio suggested by Fig. 2.2.2 and the uranium extraction coefficient of $E_a^o = 14$ (see Fig. 2.2.1 for the dimethyl-oleic amide, C-17.6, at 5.0 M HNO_3) were used to calculate the equilibrium curve shown as the dashed line on Fig. 2.2.3. This isotherm (which does approach the 1:2 level asymptotically) begins to level off at a much lower loading of uranium than does the experimental curve. These data tentatively suggest that there is more than one complex and that the average complex contains fewer than two amide molecules for each one of uranium at high solvent loadings.

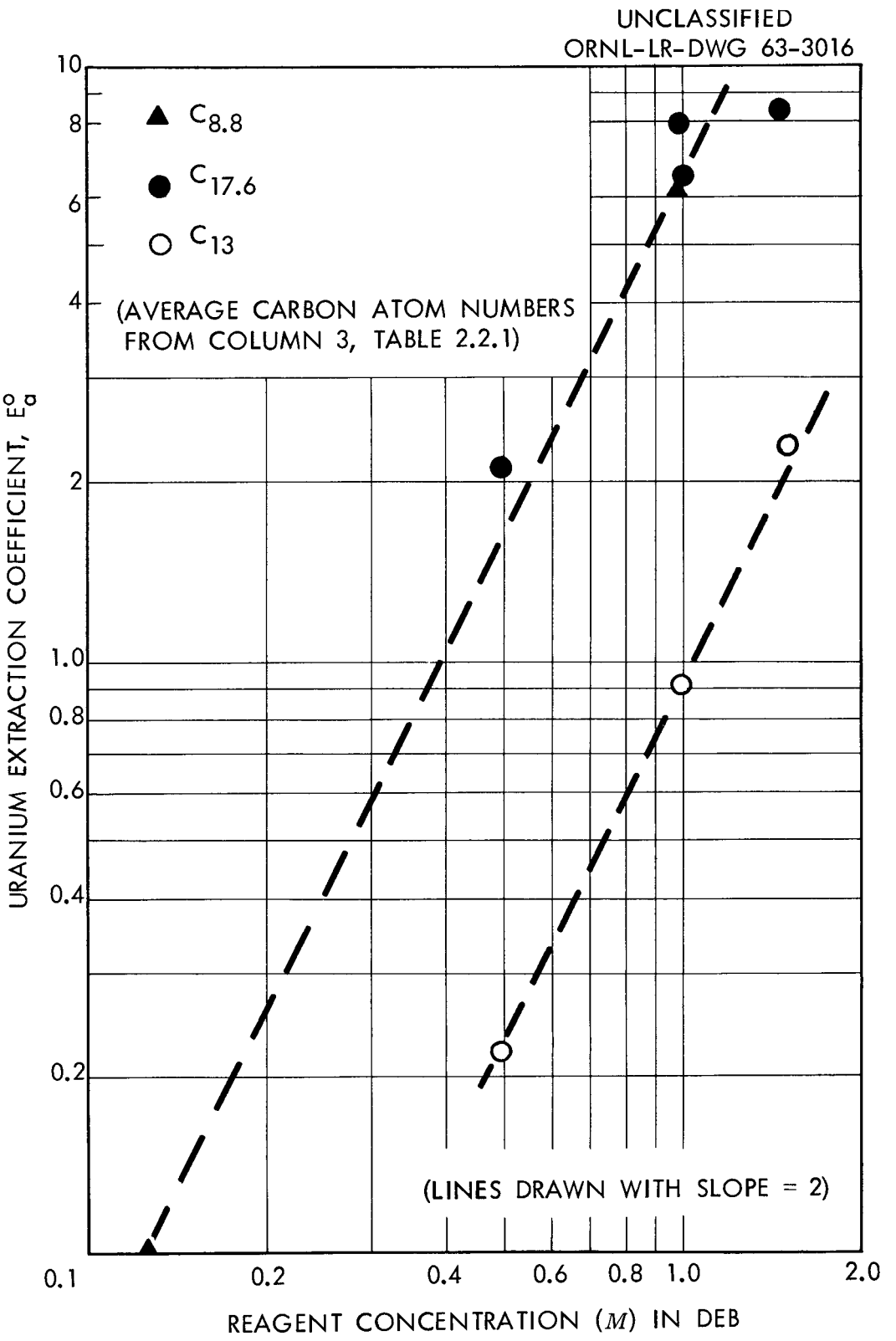


Fig. 2.2.2. Effect of Amide Concentration on Uranium Extraction. Equilibrium concentration of nitric acid in aqueous phase = 2 M.

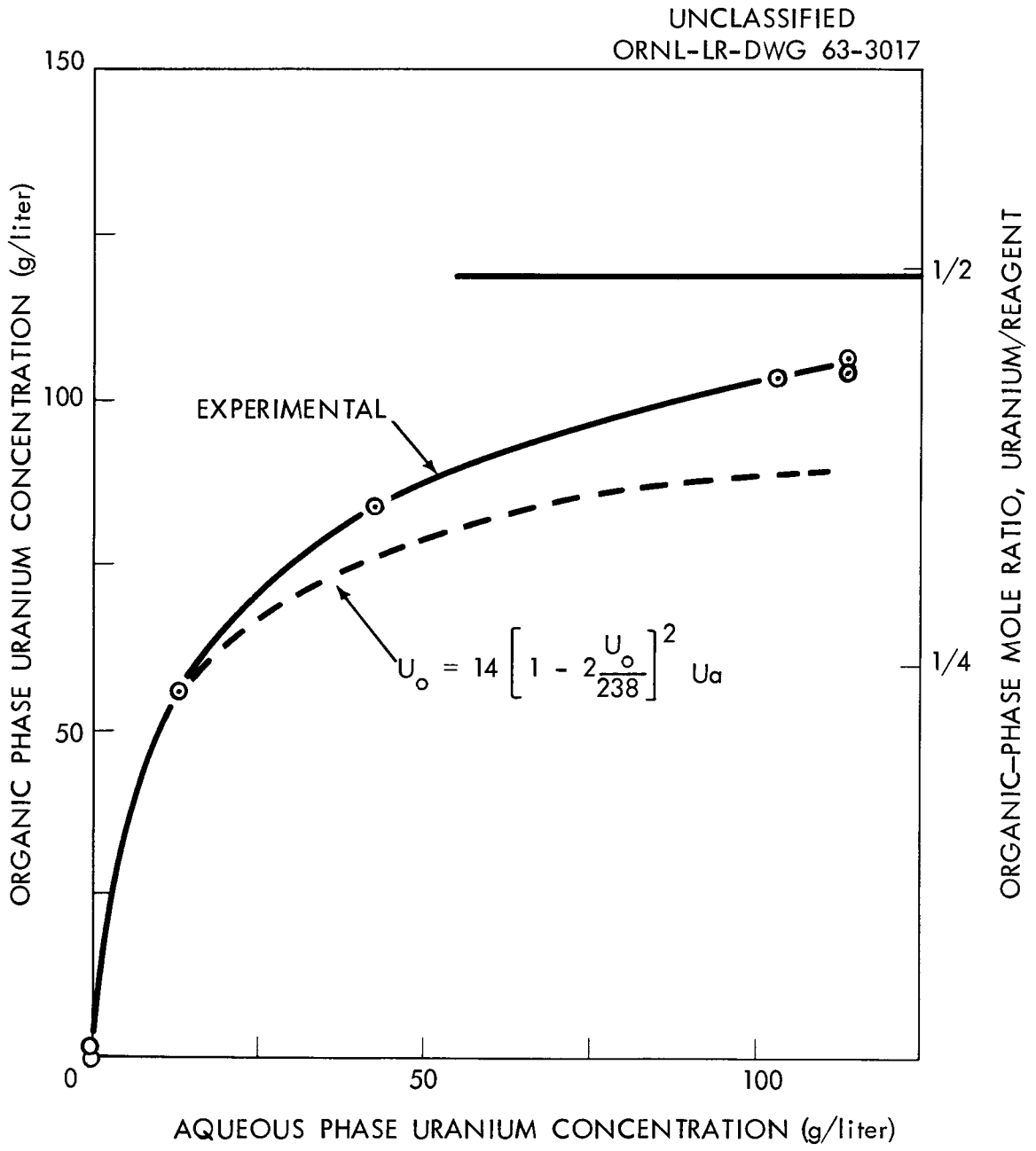


Fig. 2.2.3. Uranium Extraction Isotherm from 5 M HNO_3 with 1.0 M N,N-Dimethyl $C_{17.6}$(oleic) Amide.

2.2.2 Extraction of Nitric Acid

The amides extract nitric acid readily. In tests with 1 M amide solutions in diethylbenzene and with relatively concentrated nitric acid solutions, the extracted acid caused third-phase formation and, in at least one case, decomposition of the extractant. As shown in Table 2.2.2, a nitric acid/amide mole ratio of nearly 2.5 was obtained upon contacting increasingly concentrated acid solutions with dimethyl $C_{12.5}$ and $C_{16.9}$ amides. After reaching this loading a third liquid phase appeared. The lower-molecular-weight dimethyl $C_{8.8}$ amide formed a third phase after reaching a loading of but 1.2 moles of acid per mole of amide. Extractions of acid by these three amides were about equal when contacting solutions of the same nitric acid concentration. Extraction by the dimethyl amide of branched Neo-Tridecanoic acid (C_{13}) was noticeably lower, and, at a loading of about 1.3 moles HNO_3 per mole of amide from 12 to 13 M HNO_3, decomposition of the amide occurred, as evidenced by an exothermic reaction, which produced brown, sweet-smelling fumes.

2.2.3 Zirconium, Hafnium, and Europium Extraction from Nitric Acid

Extractions of tracer Eu^{152}, Zr^{95}, and Hf^{181} from 2 to 8 M HNO_3 solutions with several of the N,N-dimethyl amides and TBP are shown in Fig. 2.2.4. Like TBP, the straight-chain $C_{8.8}$ and $C_{16.9}$ amides showed increased zirconium extraction with increased concentration of nitric acid in the aqueous phase. Their extraction coefficients were 1.5 to 3 times lower than those of TBP, but, in the same acidity range, the uranium extraction coefficients (Fig. 2.2.1) with TBP were 5 to 10 times greater than those of the $C_{8.8}$ amide, and 1.5 to 3 times greater than those of the $C_{16.9}$ amide. Consequently, the uranium-zirconium separations with these compounds were no better than those attainable with TBP. With the branched chain C_{13} amide, however, the zirconium extraction coefficient did not increase so rapidly with increasing aqueous nitric acid concentration. The indicated uranium-zirconium separation was much better than that shown by TBP when extracting from 5 to 7 M HNO_3.

Table 2.2.2. Extraction of Nitric Acid by 1.0 M Dimethyl Amides in Diethylbenzene

Equal volumes aqueous and organic phases
Both phases titrated with aqueous NaOH

Equilibrium Aqueous HNO_3 (M)	Equilibrium Organic-Phase Nitric Acid Concentration (M) a/o Ratio, Moles HNO_3/Moles Amide in Organic Extract			
	Average carbon atom numbers from Column 3, Table 2.2.1			
	$C_{8.8}$ Amide	$C_{12.5}$ Amide	C_{13} Amide	$C_{16.9}$ Amide
1		0.16		0.16
2	0.40	0.40	0.22	0.38
3	0.61	0.64	0.40	0.60
4	0.78	0.82	0.55	0.78
5	0.90	0.97	0.68	0.92
6	1.04	1.09	0.80	1.06
7	1.18	1.24	0.92	1.20
8	3rd phase formed	1.41	1.01	1.38
9		1.62	1.10	1.58
10		1.85	1.18	1.86
11		2.22	1.26	2.17
12		2.46		2.38
13			Decomposed	2.48
14		3rd phase formed		3rd phase formed

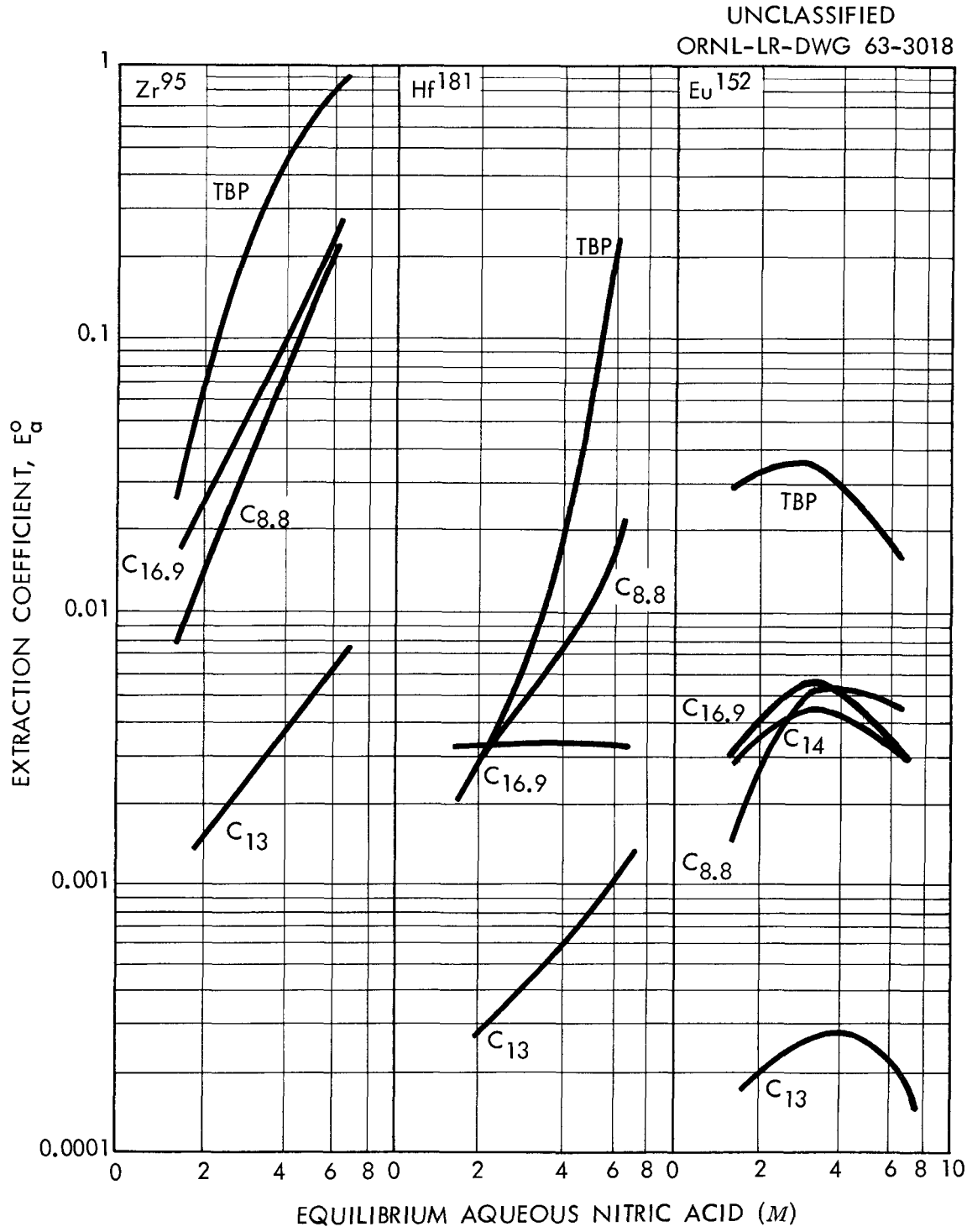


Fig. 2.2.4. Extraction of Zirconium, Hafnium, and Europium from Nitric Acid by 1.0 M Solutions of N,N-Dimethyl Amides in Diethylbenzene. Code numbers are the average carbon atom numbers are the average carbon atom numbers from column 3 of Table 2.2.1. C_{13} is branched, all others are straight chain.

With the $C_{8.8}$ and branched C_{13} amides, the increase in hafnium extraction with increased nitric acid concentration was similar to the behavior with zirconium, but the extractability of hafnium was in all cases lower. With the $C_{16.9}$ amide, the practically constant hafnium extraction coefficient obtained throughout the acidity range studied was unexpected and is unexplained.

Like zirconium and hafnium, europium (chosen to typify rare earth fission products) was extracted by the various reagents in the order TBP > straight-chain amides > C_{13} branched-chain amide. Extraction by each reagent was at a maximum in the acidity range 3 to 5 M HNO_3. The data of Figs. 2.2.1 and 2.2.4 indicate that in comparison with TBP, the separation of uranium from rare earths could be improved by a factor up to 2 with the straight-chain amides and by factors of from 3 to 10 with the branched-chain amide.

Several additional amides are being synthesized, including compounds that contain branching of different types of both the amine and carboxylic acid components. It is hoped that some of the compounds will provide even better separations of uranium from fission product elements.

2.2.4 Extractions from Solutions High in Nitrate and Low in Acidity (Lanthanides, Transplutonium Elements, Cesium, Strontium)

The amides are being examined as a part of a program of systematic evaluation of reagents for the separation of lanthanide and transplutonium elements, and these data will be reported separately. Preliminary results from that investigation show that two amides, diisopropyl propionamide and N,N,N',N'-tetraethyl phthalamide, may give separations of americium (typifying transplutonium elements) from cerium and europium (typifying lanthanide elements). The extractions were from 6 M $LiNO_3$ solutions containing tracer amounts of Am^{241}, Ce^{144}, and Eu^{152}. The branched-chain amides now being synthesized should prove useful in this study also.

The dimethyl $C_{16.9}$ amide gave very low extractions of strontium and cesium from neutral sodium nitrate solutions:

Element (20 ppm in neutral 1.0 M $NaNO_3$)	Extraction Coefficient with 1.0 M $C_{16.9}$ Amide in DEB
Cs	0.0002
Sr	0.002

Equal volumes of the organic and aqueous phases were mixed for 10 min at room temperature.

2.2.5 Uranium and Thorium Extraction from Chloride and Sulfate Solutions

Negligible extraction of uranium and thorium from sulfate or chloride solutions was found with 1.0 M diethylbenzene solutions of dimethyl-C_{14} amide:

Aqueous Phase (1 g U or Th per liter)	Extraction Coefficient, E_a^o	
	U	Th
2 M HCl	0.06	0.002
2 M H_2SO_4	<0.001	<0.001
(2 M HNO_3)	(8)	(0.2)

The 1 M amide solutions in diethylbenzene formed emulsions and/or precipitates when shaken with hydrochloric and sulfuric acids at concentrations greater than 2 M.

A synergistic enhancement of the uranium extraction coefficient from sulfate solutions was obtained with a combination of di(2-ethylhexyl)-phosphoric acid (HDEHP) and dimethyl-C_{12} amide. The combination gave about the same results as did HDEHP with TBP.[15]

Reagent in Amsco 125-82	Uranium Extraction Coefficient, E_a^o	
	from 0.5 M SO_4, pH 1	from 1.5 M H_2SO_4
0.1 M HDEHP	140	4
0.1 M C_{12} Amide	0.001	0.001
0.1 M HDEHP + 0.1 M C_{12} Amide	330	15
0.1 M HDEHP + 0.1 TBP	470	10

In these tests, equal volumes of the organic and aqueous phases were mixed at room temperature. No further tests were made to determine the optimum synergistic combinations or the effect of amides of different structures.

2.2.6 Compatibility of Diluents and Phase Separation

Diethylbenzene (mixture of isomers) was used in most of the extraction tests with amides. This diluent was selected after preliminary evaluations showed that when contacting a wide variety of aqueous systems, it ordinarily gave higher extraction coefficients (Table 2.2.3) and less-frequent emulsion formation or precipitation than did aliphatic diluents such as n-dodecane or Amsco 125-82. Other diluents may perform more satisfactorily, but extensive diluent studies will be delayed until the preferred amide structures have been identified more certainly.

Table 2.2.3. Effect of Diluent on Uranium Extraction

Aqueous phase: 1 g U(VI)/liter
Contact: equal phase ratios; 10-min contact; room temperature

Equilibrium Aqueous HNO_3 (M)	Uranium Extraction Coefficient, E_a^o, with 0.1 M Dimethyl $C_{8.8}$ Amide in:	
	Diethylbenzene	Amsco 125-82
2	0.065	0.008
4	0.20	0.040
6	0.21	0.024
8	0.15	0.004

Some observations on phase separation behavior that were made during the course of the test work are listed below.

1. Nitric acid solutions, low concentrations of metal ions:
   a. The dimethylamides of straight chain carboxylic acids separated into a second liquid phase when dissolved in n-dodecane and contacted with nitric acid at concentrations of 2 M and greater.
   b. Similar results were observed when the same amides were dissolved in Amsco 125-82, except for the $C_{8.8}$ amide, which did not form a third phase until the nitric acid concentration in the aqueous phase reached 6 M.

c. All the amides when dissolved in diethylbenzene performed well at the lower concentrations of nitric acid, but several formed additional liquid phases at higher concentrations, for example, at 10 M HNO_3 with the dimethyl $C_{8.8}$ amide, and at 16 M HNO_3 with the dimethyl $C_{12.5}$ and $C_{17.6}$ (oleic) amides.

2. Nitric acid solutions, high concentrations of metal ions;
   a. The uranium salts of many of the amides had limited solubility in diethylbenzene when the uranium was extracted from 5 M HNO_3. No precipitation resulted, however, with the dimethyl $C_{8.8}$, $C_{17.6}$ (oleic), and C_{13} (branched) amides and dibutyl decanoamide.
   b. The uranium salt of the dimethyl C_{13} (branched) amide formed a third phase in Amsco 125-82 with 5 M HNO_3, but the addition of TBP restored the two-phase system.
3. Hydrochloric and sulfuric acid solutions:
   a. Only dimethyl tetradecanoamide in DEB was tested. Performance was satisfactory with the 2 M acids, but emulsions and precipitates resulted with 4 M and higher acid concentrations.
4. Alkaline solutions:
   a. Dimethyl $C_{17.6}$ (oleic) amide in DEB gave emulsions with 2% NaOH or Na_2CO_3, but the dimethyl C_{13} (branched) amide did not.

2.2.7 Uranium Stripping

Water and dilute nitric acid solutions are useful uranium stripping agents for the 1.0 M amide solutions (Table 2.2.4), and the 1.0 M HNO_3 stripping data for the three amides are consistent with extrapolations of the extraction data of Fig. 2.2.1. The tests were made with equal volumes of organic solvent and aqueous strip solutions. Stripping tests from organic extracts prepared by extraction from uranium solutions containing more than 2 M HNO_3 were not made. Different results would be expected, corresponding to the differences in the quantities of acid extracted.

Stripping with dilute sulfuric or hydrochloric acids may also be useful. Emulsion or third phase formation was encountered when amide solutions were shaken with acids above 4 M, with 0.5 M NaOH, or with 0.2 M Na_2CO_3.

Table 2.2.4. Uranium Stripping

Pregnant organic extract: 1 M amide in DEB; 0.7 g U(VI) per liter; extracted from 2 M HNO_3
Equal volumes, organic and strip phases; 10-min contact; room temperature

	Uranium Stripping Coefficient, S_o^a		
Stripping Agent	$C_{8.8}$ Amide	$C_{12.5}$ (coco) Amide	$C_{17.6}$ (oleic) Amide
Water	3.5	2.6	4.5
0.01 M HNO_3	3.3	2.5	4.2
0.01 M HNO_3	2.3	1.7	2.7
1 M HNO_3	0.35	0.30	0.40

2.2.8 Description of Reagents

An indication of the purity of the amides is given in Table 2.2.5, which also lists the source of the compounds. Many of the commercial reagents contain amides of both higher and lower molecular weight than the principal constituent, and one supplier indicates that this may vary from 5 to 50%. Titration with aqueous sodium hydroxide indicated the presence of free acid, shown in Table 2.2.5 as percent (by weight) of the corresponding carboxylic acid. All these percentages are 2% or lower except for that of the Hallcomid M-18 ($C_{16.9}$), which showed 2.6% acidity.

2.2.9 Reagent Stability

Amides, particularly those of low molecular weight, are subject to hydrolysis in both acid and alkaline media. Two of the amides used in the preceding study ($C_{8.8}$, C_{12}) were each boiled (undiluted) with an equal volume of 2 M HNO_3 under total reflux for 4 hr. The degraded amides were diluted to 1 M (based on composition of the original sample) with DEB. These solutions were scrubbed several times with water and once with 0.2 M Na_2CO_3 to remove nitric acid. The scrubbed solutions were titrated with sodium hydroxide and were used to extract uranium and thorium from 2 M

Table 2.2.5. Description of Reagents

Proprietary Name	Source[a]	Approx. MW	Components: Amine	Components: Acid[b]	Percentage of: Amide[c]	Percentage of: Free Acid[d]
Hallcomid M 8-10	H	171-199	Dimethyl	8.8	95	1.9
Hallcomid M-12	H	227	Dimethyl	12	95	0.6
Hallcomid M-14	H	256	Dimethyl	14	95	1.1
Hallcomid M-18	H	312	Dimethyl	16.9	95	2.6
Hallcomid M-18-OL	H	310	Dimethyl	17.6	95	2.0
Coco	GM	227-256	Dimethyl	12.5		1.4
Tallow	GM	282-312	Dimethyl	17		1.6
EK-4977	EK	171	Dibutyl	2		0.2
EK-5727	EK	227	Diethyl	10		0.4
EK-7528	EK	157	Diisopropyl	3		0.4
EK-7531	EK	157	Di-n-propyl	3		0.1
Neo-tridecanoamide	ORNL[e]	241	Dimethyl	13[f]		2.0
DIMER	GM	550	Bis(dimethyl)	34 (branched)[g]		1.7
EK-6534	EK	276	Bis(diethyl)	8 (phthallic)		0.2

[a]H ≡ C. P. Hall Company of Illinois, Chicago, Illinois.
GM ≡ General Mills, Inc., Minneapolis, Minnesota.
EK ≡ Distillation Products Industries, Rochester, N.Y.
ORNL ≡ Synthesized at Oak Ridge National Laboratory by W. H. Baldwin, ORNL, Chemistry Division.

[b]Straight-chain fatty acid unless otherwise noted. Average number of carbon atoms given as in Table 2.2.1.

[c]Where given by supplier. Signifies total amide present, usually contain amides of molecular weight both higher and lower than nominal.

[d]By titration with aqueous sodium hydroxide. Acid calculated as corresponding carboxylic acid.

[e]Prepared by Dr. Willis H. Baldwin, ORNL, Chrmistry Division.

[f]Neo-Tridecanoic acid, $C_9H_{19}C(CH_2)_2CO_2H$, Enjay Chemical Co., Elizabeth, New Jersey.

[g]34-carbon dicarboxylic acid, amide groups approximately 16 carbon atoms apart.

HNO_3 (Table 2.2.6). The decrease in uranium extraction coefficient, $E_a^o \propto [amide]^2$, indicated a decrease of amide concentrations by 40% and 30%, respectively. The concentrations of carboxylic acid found (about 20% of initial amide) were in fair agreement with this, considering the probable loss of some carboxylic acid to the sodium carbonate scrub.

Table 2.2.6. Degradation of Amides

Uranium and thorium extraction from 2 M HNO_3; equal phase ratio; room temperature; 10-min contact

	Amide			
	$C_{8.8}$		C_{12}	
Analysis	Initial	Degraded[a]	Initial	Degraded[a]
Titration (wt % acid)[b]	2	24	1	20
U extraction coefficient	5.0	1.9	6.6	3.2
Th extraction coefficient	0.10	0.02	0.11	0.04

[a]Undiluted amide boiled 4 hr under reflux with an equal volume of 2 M HNO_3. Degraded amide diluted to 1 M with fresh DEB. 1 M solution scrubbed with water and 0.2 M Na_2CO_3.

[b]Titration was with aqueous sodium hydroxide. Percent acid calculated as weight percent of corresponding carboxylic acid.

2.3 Distribution Coefficients and Separation Factors as Functions of Diluent Type: Tributyl Phosphate Diluted by Aromatics vs Tributyl Phosphate Diluted by Aliphatics

(C. A. Blake, J. M. Schmitt)

It has been reported that uranium extraction coefficients and separation factors from thorium and fission products were higher when the aromatic diluents Solvesso 100 and xylene were used, rather than the aliphatic diluents Amsco 125-82 and n-dodecane, with TBP and other neutral organophosphorus reagents.[14,16,17] The following data show that the behavior of some simple alkylbenzenes is similar to that of the other aromatic diluents tested previously. In the present tests, hafnium, as

Hf^{181} tracer, was used as a stand-in for fission product zirconium-niobium. Extractions were from separate 2 M HNO_3 solutions, and the separation factors were calculated as the ratio of the separate extraction coefficients.

As shown in Table 2.3.1, solutions of TBP in diethylbenzene, n-butylbenzene, and 1,2,3-trimethylbenzene extracted uranium with greater coefficients than did the TBP-aliphatic combinations by factors of 1.6, 1.6, and 1.4, respectively. The hafnium extraction coefficients were lower by factors of about 1.5, and the indicated separation of uranium from hafnium was better by factors of 2.4, 1.8 and 1.8, respectively. Each of the three simple alkylbenzene-TBP solutions extracted uranium better than did the Solvesso-TBP. These and other alkylbenzenes are being studied with regard to their reactivity with nitric acid.[14,18,19]

Table 2.3.1. Uranium and Hafnium Extraction by 1 M TBP in Aromatic or Aliphatic Diluents

Aqueous phases: 2 M HNO_3 initially, with 0.8 g U(VI)/liter or 10^4 γ counts sec^{-1} ml^{-1} Hf^{181}
Organic phases: 1 M TBP in indicated diluent
Test conditions: equal volumes aqueous and organic phases; 10-min contact at room temperature

Diluent	Source[a]	Extraction Coefficients, E_a^o		Computed Separation Factor $SF = E_U/E_{Hf}$
		Uranium	Hafnium	
Diethylbenzene	D	65	0.07	950
1,2,3-Trimethylbenzene	E	65	0.09	700
n-Butylbenzene	EK	60	0.09	650
Solvesso 100	H	55	0.08	700
Amsco 125-82	A	50	0.12	400
n-Dodecane	EK	40	0.12	350

[a]Sources: D = Dow Chemical Co.
E = Enjay Chemical Co.
EK = Distillation Products Industries
H = Humble Oil and Refining Co.
A = American Mineral Spirits Co.

2.4 Improved Stability of Amsco 125-82

(C. A. Blake, Stephen Rosenblum)

Although Amsco 125-82, a specially prepared aviation naphtha, is considered to be one of the most stable of the commercial aliphatic hydrocarbons, it can be degraded severely by heating or irradiating in the presence of nitric acid.[2] This is attributed to the fact that Amsco 125-82 is composed of 17 or more compounds in the C_{12}-C_{14} range,[20] many of which are highly branched and are reactive toward nitric acid. For improved performance in radiochemical processing, the stability can be improved by destroying most of the reactive sites. Experimentally this has been done by (1) treating with concentrated sulfuric acid, and by (2) preliminary degradation in nitric acid followed by scrubbing with sulfuric acid. The sulfuric acid treatment is most effective at increased temperature or when very concentrated acid is used (obtained by addition of oleum).

In Fig. 2.4.1, results are shown for tests in which untreated Amsco and Amsco treated with sulfuric acid were made 1 M in fresh TBP and then degraded by boiling with 2 M nitric acid for periods up to 24 hr. The extent of degradation was monitored by the usual tests,[18] which involved measurements of Hf^{181} extractability[21] after converting the nitroparaffin in the solvent to the enol (most reactive) form by treating with sodium carbonate and calcium hydroxide. Whereas the solution in untreated Amsco, after 8 hr of degradation by nitric acid, showed a hafnium extraction coefficient of 16, those in Amsco pretreated with 96%, 98%, or 100% sulfuric acid showed coefficients of 0.3, 0.15, and 0.03, respectively. Solutions in Amsco pretreated with 100% and 105% H_2SO_4 at room temperature and with 95.6% acid at 50°C for 30 min all had extraction coefficients of only about 0.15 even after a 24-hr degradation. Apparently, the sulfuric acid destroys the reactive sites by sulfonation to sulfuric-acid soluble byproducts or rearranges the molecule to a more stable configuration.[22] No sulfur has been detected in the diluent after treatment.

Amsco degraded with nitric acid, scrubbed with concentrated sulfuric acid at room temperature, made 1 M in TBP and then boiled for 24 hr with 2 M HNO_3 was as stable as Amsco pretreated with 100% and 105% sulfuric acid at room temperature or with 95.6% acid at elevated temperatures.

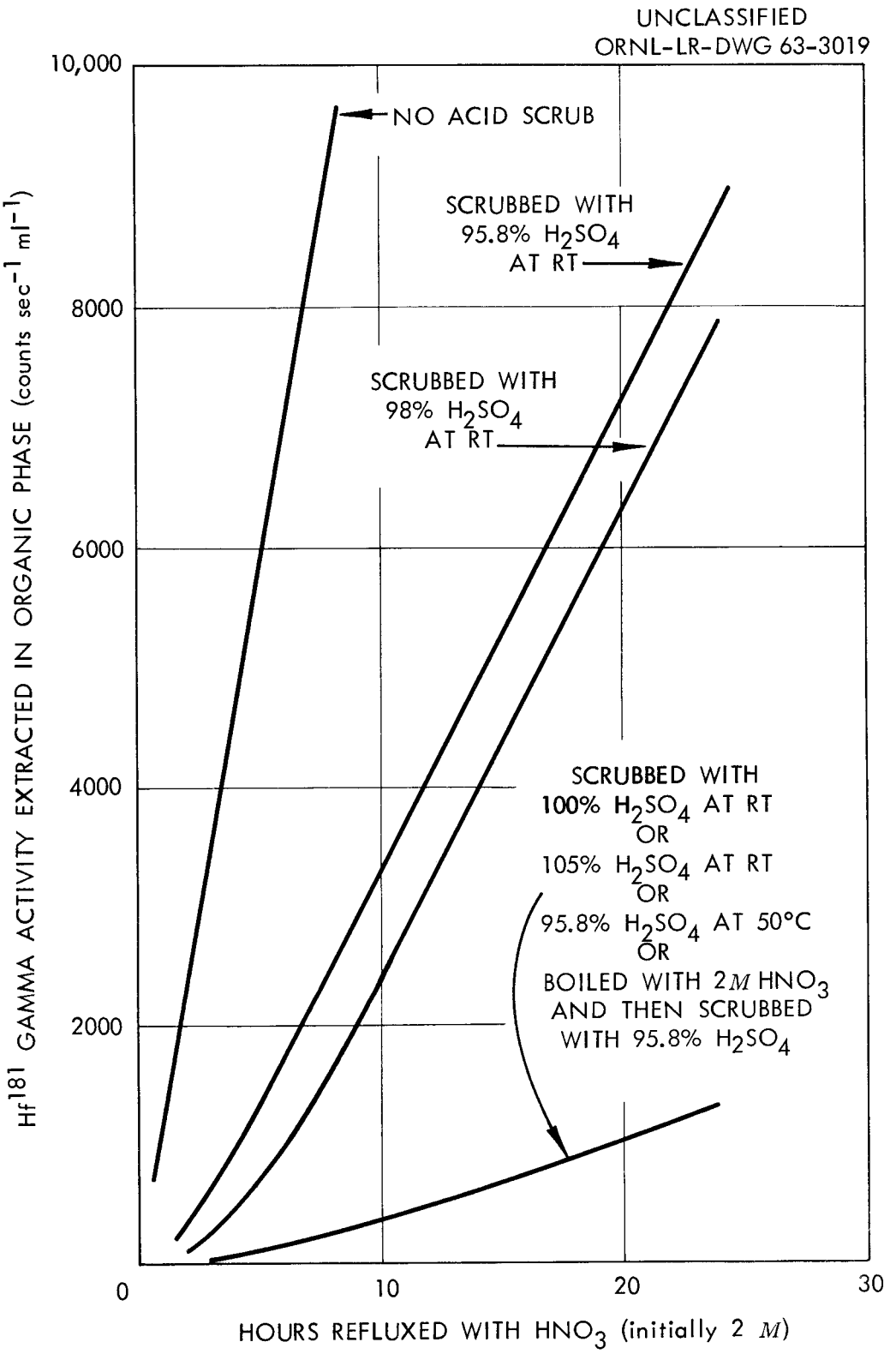


Fig. 2.4.1. Hafnium Extraction by 1 M TBP Solutions in Acid-Treated Amsco 125-82.

In this treatment, the sulfuric acid scrubs the nitroparaffins from the unreacted Amsco. Such scrubbing is not practical on degraded solvents containing TBP since the TBP also distributes to the sulfuric acid.

Other tests were made to determine whether additional treatment would further improve the Amsco. For example, some was recovered from the 24-hr degraded 1 M TBP solutions by extracting the TBP and nitroparaffins with concentrated sulfuric acid. The recovered Amsco was again made 1 M in fresh TBP and subjected to an additional 24-hr degradation with 2 M HNO_3. After this treatment, the hafnium extraction coefficient was still about 0.15. Repetition of the cycle four additional times produced the same results. Apparently, after the initial treatments to remove or deactivate the sites susceptible to easy nitration, the remaining Amsco degrades at a consistently low rate, and its behavior becomes very similar to that of the relatively stable n-dodecane.

2.5 Diluent Effect on Strontium Extraction by Di(2-ethylhexyl)phosphoric Acid

(C. F. Coleman, W. J. McDowell, G. N. Case)

As reported previously,[2] the logarithmic plot of the strontium extraction coefficient vs pH, for extraction from 4 M $NaNO_3$ solution by a benzene solution of di(2-ethylhexyl)phosphoric acid (HDEHP or HA), rises with increasing pH to a maximum near pH 5 then drops slightly and levels off to a constant value above pH 7. In the course of these studies, other tests (not previously reported) were made with additives in the benzene and with some other diluents. The principal purpose was to predict the nature of possible effects of organic contaminants that might be encountered. It was found that the log-E_{Sr}-vs-pH curve was sometimes shifted to lower or higher pH but with little change in the maximum value of E_{Sr}.*

*E_{Sr} values were nearly constant at constant values of the $NaA/\Sigma A$ mole ratio, while the pH of the aqueous phase required to reach a given value of $NaA/\Sigma A$ changed with different diluents. The glass-electrode pH is proportional to -log $[H^+]$ over the range of interest in these 4 M nitrate solutions.

Recently these tests have been reviewed and extended to a wider variety of diluents and additives, because synergistic strontium extraction has been reported on addition of tributyl phosphate (TBP) to kerosene solutions of HDEHP.[23] The result of this work has been to confirm both the synergism with TBP (and also antagonism with dodecyl alcohol) in an aliphatic hydrocarbon as diluent, and the almost complete lack of synergism (and antagonism) in benzene.

In the following discussion, first the pH shifts of $NaA/\Sigma A$ and E_{Sr} are considered, and then the synergism and antagonism.

2.5.1 pH Shift

Figure 2.5.1 shows log $E_{Sr} = \left\{\frac{[Sr]org}{[Sr]aq}\right\}$ vs pH for 0.10 M di(2-ethylhexyl)phosphate (DEHP) in benzene and in nonane as well as in each diluent + 0.05 M TBP and + 0.05 M dodecyl alcohol. The basic (electron donor) additive, TBP, shifts the extraction curve to lower pH values in each diluent, while the acidic (proton donor) additive, dodecyl alcohol, shifts it to higher pH values. Similar effects on strontium extraction were observed in using intrinsically acidic or basic diluents for DEHP. In Fig. 2.5.2 the extractions of strontium by 0.125 M DEHP in n-butyl ether, benzene, and chloroform are compared. Here again the presence of the acidic (electron acceptor) solvent, chloroform, shifts the extraction curve to a higher pH, while the basic (electron donor) solvent, n-butyl ether, produces the opposite effect.

A possible explanation of these shifts may be found in the data illustrated in Fig. 2.5.3. Here the pH of the aqueous phase (4 M $NaNO_3$) is plotted as a function of the fraction of DEHP in the sodium form, $NaA/\Sigma A$. It is apparent that at a given organic-phase mole ratio $NaA/\Sigma A$ the pH is lowest when the diluent is nonane or n-butyl ether, intermediate when the diluent is benzene, and highest when it is chloroform. It is well known that basic solvents enhance and that acidic solvents depress the acidic properties of an acid dissolved in them. This appears to be the effect being observed here. Thus, it is reasonable that the shift in the strontium extraction curve along the pH scale is primarily due to changes in the apparent acidity of HDEHP, that is, to shifts in the sodium form-hydrogen form ratio of the reagent in the organic phase.

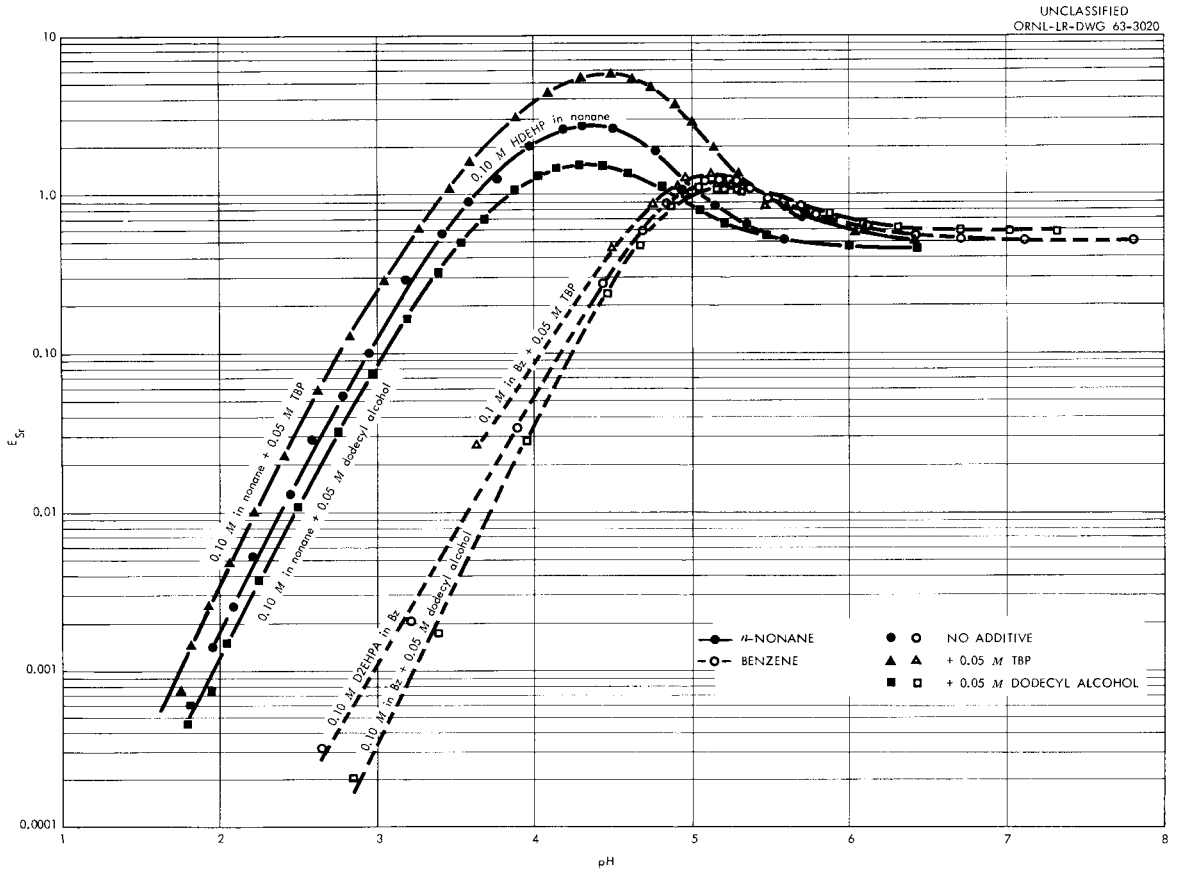


Fig. 2.5.1. Extraction of Tracer Strontium by 0.10 M Di(2-ethylhexyl)phosphate Solutions. Aqueous phase: 4 M $NaNO_3$, 10^{-3} M Sr initially.

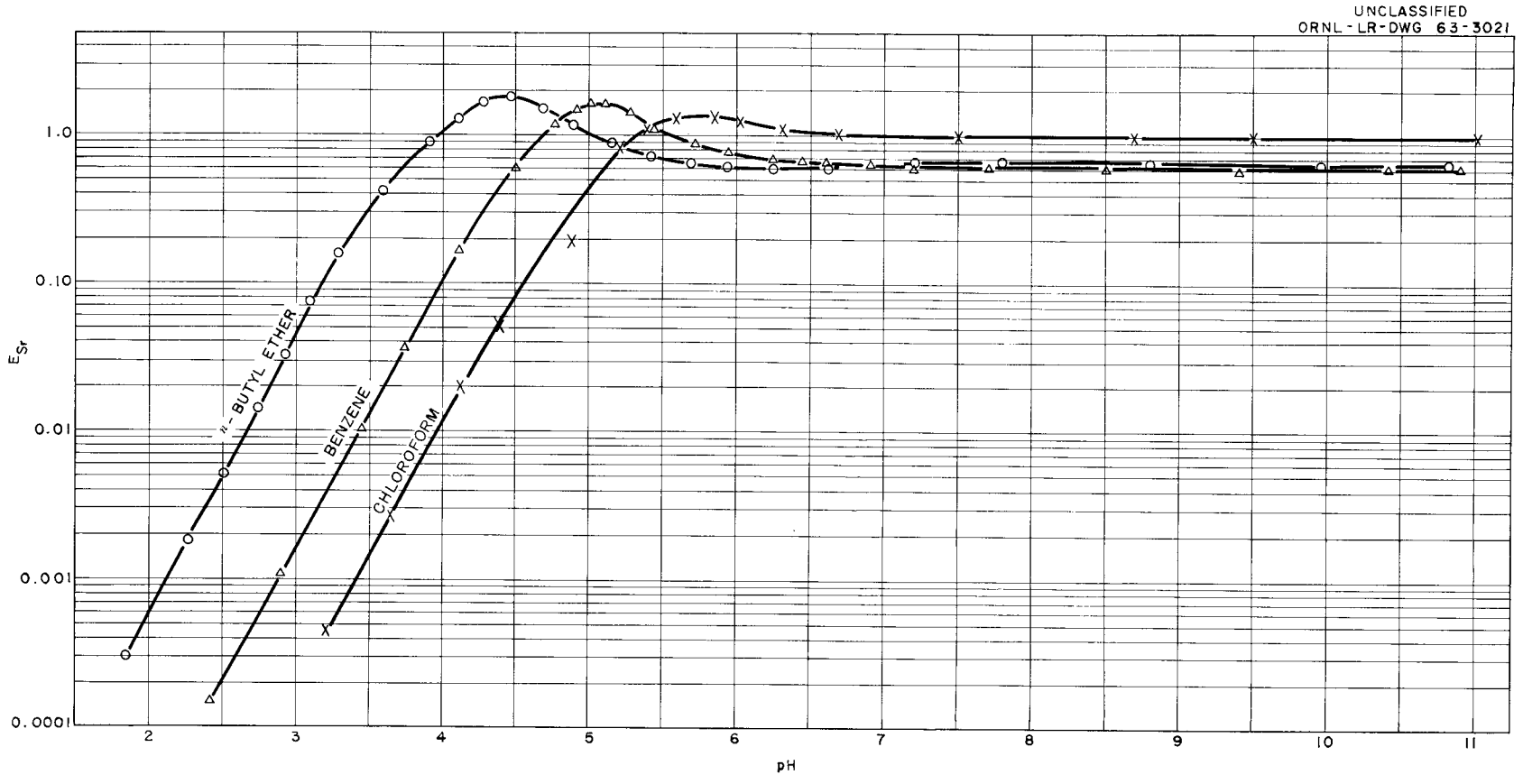


Fig. 2.5.2. Extraction of Tracer Strontium by 0.125 M DEHP in Several Solvents. Aqueous phase: 4 M $NaNO_3$, 10^{-3} M Sr initially.

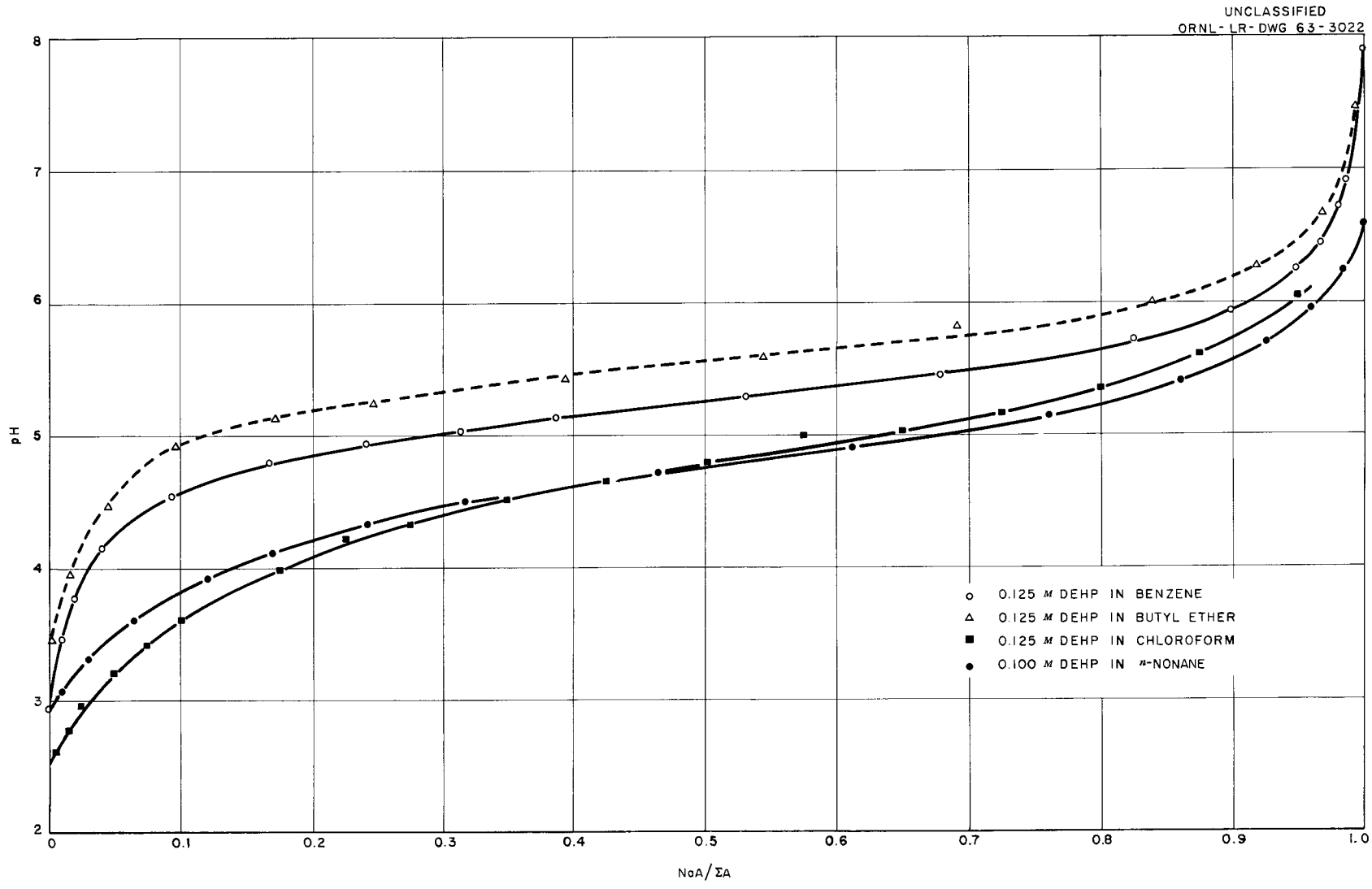


Fig. 2.5.3. The pH of 4 M $NaNO_3$ Solutions in Equilibrium with Di(2-ethylhexyl)phosphate Solutions.

The large shift to lower pH when nonane is used as the organic diluent is somewhat surprising. Saturated hydrocarbons are not usually thought of as basic solvents, nor is benzene thought of as an acidic solvent. However, the apparent acidity observed (Fig. 2.5.3, pH vs NaA/ΣA) for HDEHP in nonane is higher than in benzene or even in n-butyl ether,* thus in agreement with the observed E_{Sr} vs pH shift. Since 99 mole % pure nonane was used, the presence of impurities (such as electron-rich unsaturated compounds) in large enough concentrations to cause such effects is not likely.

Among the possible causes for such large shifts in apparent acidity are actual difference in proton-sharing ability of benzene and nonane (or to be more general, in the average electron-donating ability of all the diluents tested), the differences in dielectric properties of the diluents and possible differences in polymerization of HDEHP and NaDEHP in the several diluents. This latter effect would, of course, be intimately connected with reagent-diluent intermolecular bonding, dielectric properties of the diluent, etc.

If E_{Sr} is indeed dependent primarily on the ratio Na/ΣA, then plots of E_{Sr} vs NaA/ΣA for the four diluents should be identical. In Fig. 2.5.4 we have such a comparison. Here the strontium extraction coefficients in benzene and n-butyl ether are almost identical, but large differences appear in the system where chloroform or nonane is the diluent. It must be concluded then that in addition to changing the apparent acidity of the HDEHP these diluents probably have more specific interaction with or effects on the extractant which modifies its extraction of strontium in other ways. When plotted in the same way, extraction coefficients where benzene or modified benzene is the diluent (Fig. 2.5.5) are in general quite close together at identical NaA/ΣA values for the three systems. An exception again appears to occur with the portion of the curve for the acidic additive (dodecyl alcohol) beyond NaA/ΣA = 0.5.

---

*Note that the differences would have been still greater if the 0.1 M DEHP in nonane had been increased to 0.125 M as in the other diluents provided that the aqueous pH—ΣDEHP relationship is the same here as when benzene is the diluent, that is, lower when ΣDEHP is higher at a given NaA/ΣA ratio.[2]

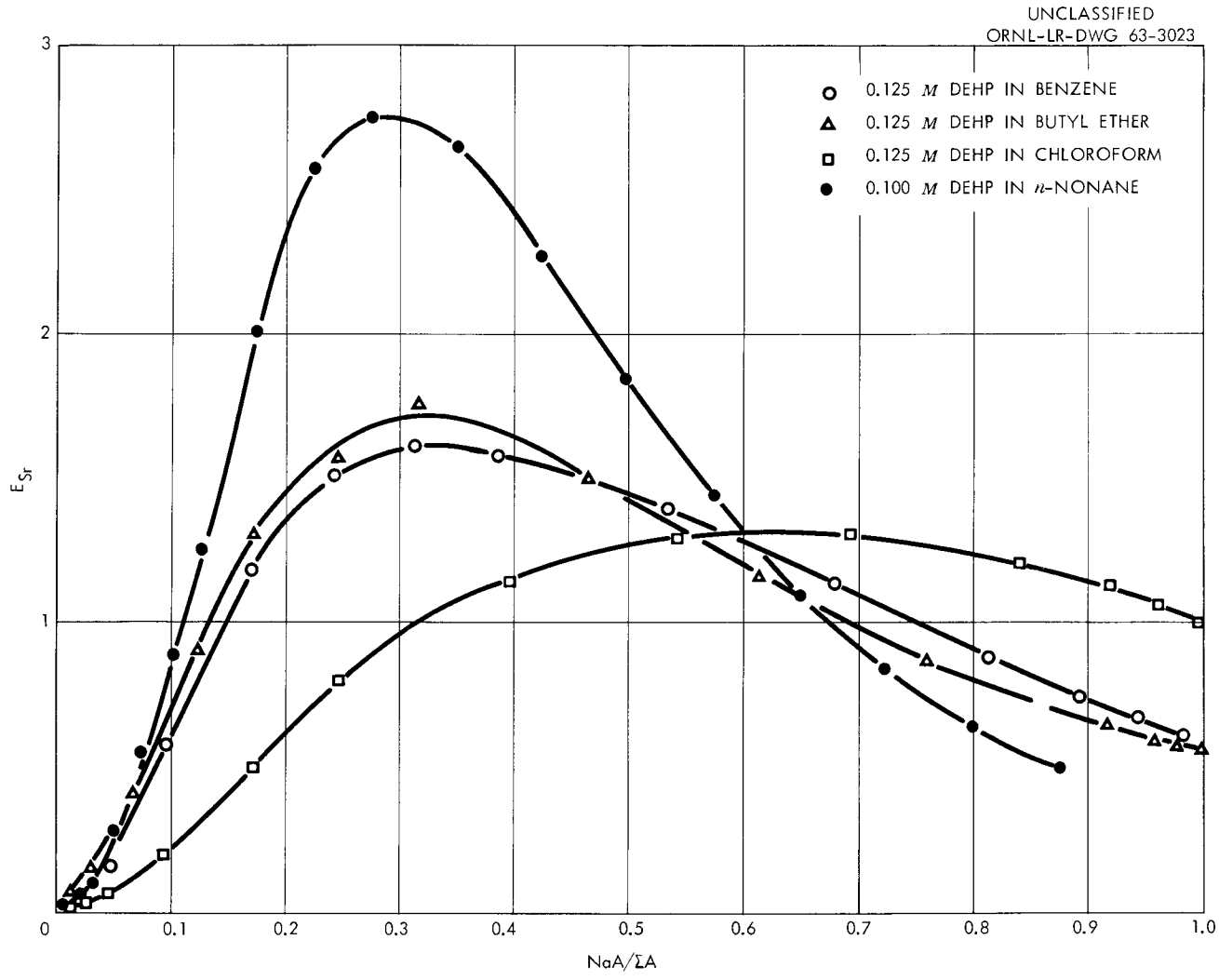


Fig. 2.5.4. Strontium Extraction by Di(2-ethylhexyl)phosphate as a Function of the Mole Ratio NaA/ΣA. Aqueous phase: 4 M $NaNO_3$, 10^{-3} M Sr initially. Note that the difference of the n-nonane curve from the others would have been still greater if its DEHP concentration had also been 0.125 M.

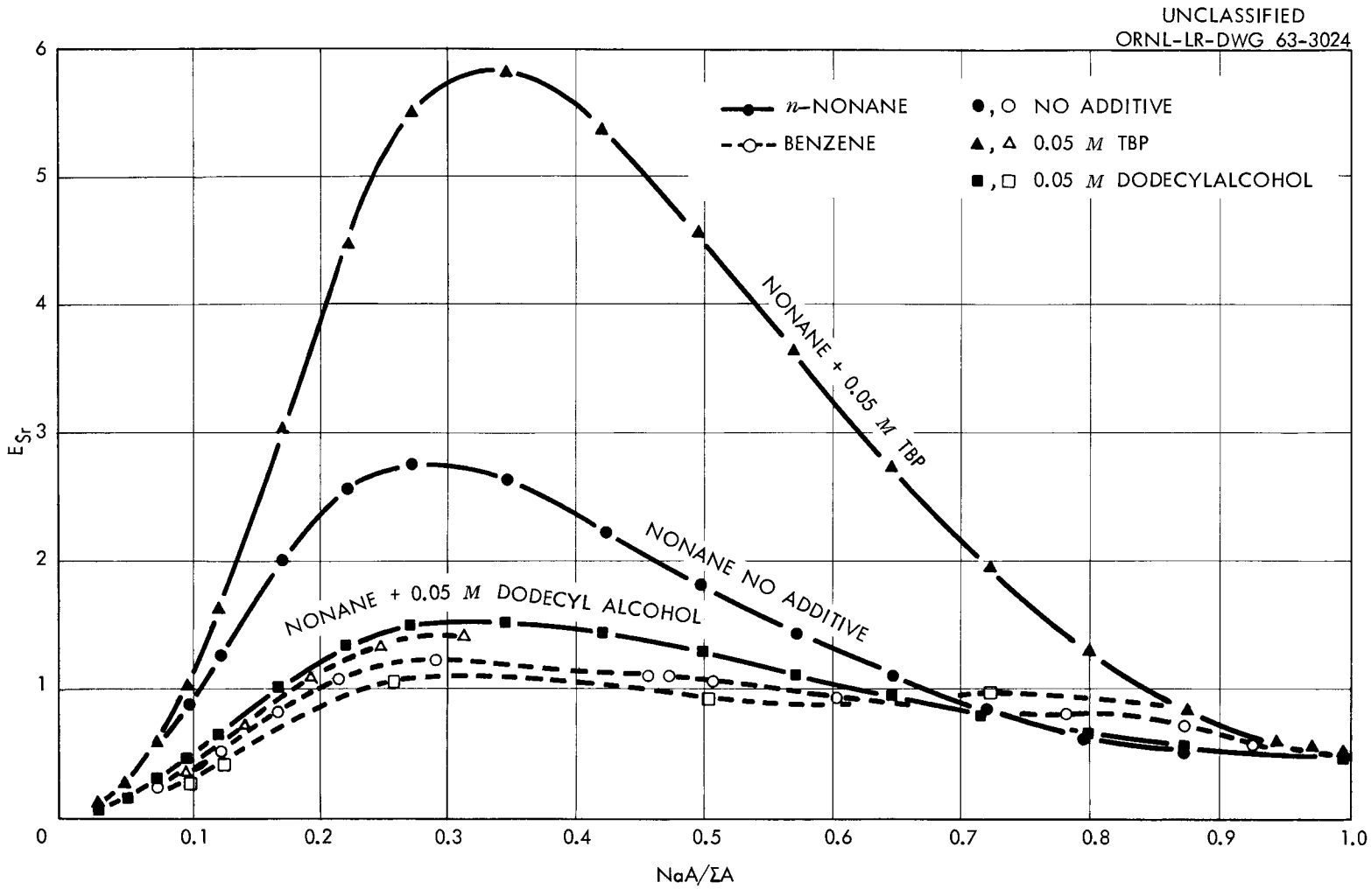


Fig. 2.5.5. Strontium Extraction by 0.10 M Di(2-ethylhexyl)phosphate Solutions as a Function of the Mole Ratio NaA/ΣA. Aqueous phase: 4 M $NaNO_3$, 10^{-3} Sr initially.

2.5.2 Synergism and Antagonism

In Fig. 2.5.5, E_{Sr} vs NaA/ΣA curves for nonane and modified-nonane diluents are also compared. Here, a rather dramatic difference in E_{Sr} appears with the addition of dodecyl alcohol or TBP. This difference seems to be primarily associated with the extraction peak or maximum, a feature of alkaline earth extraction by DEHP which has been viewed with interest for some time. This maximum always occurs somewhere near the NaA/ΣA value of 0.3 (Fig. 2.5.5), with extrapolations of the linear regions intersecting close to NaA/ΣA = 0.25.[2] This suggests that the maximum is due to some particular composition of the organic reagent, possibly involving the ratio 3HDEHP·1NaDEHP. If this is the case, it is reasonable to speculate that nonane, being a more inert diluent, allows the formation of these structures favorable to strontium extraction to a greater extent. Another possibility is that an organic phase strontium species which may be near this composition (probably $SrA_2/\Sigma A = 0.33$) is more easily formed for the same reason. In either case, this lack of solvating ability of nonane should allow the addition of TBP or dodecyl alcohol to have a more profound effect than in diluents which themselves have considerable solvating or intermolecular bonding ability.

Some preliminary investigations as to the effect of various concentrations of TBP on strontium extraction by 0.10 M DEHP in nonane may be seen in Fig. 2.5.6. The curves are of the general shape expected from two competing effects, in this case one enhancing and one competing with strontium extraction. Of the four NaA/ΣA values examined, three showed a maximum at a TBP/ΣA ratio of 2. Since other data[24] indicate an important organic-phase strontium species to be $Sr(DEHP)_2 \cdot 4HDEHP$, one possible explanation for the maximum enhancement of strontium extraction by TBP at TBP/ΣA = 2 is to assume that TBP can substitute for HDEHP in the above compound. The information in Fig. 2.5.6 is however also consistent with an explanation involving the addition of TBP molecules to the extracted complex. To differentiate between these two possibilities will require measurement of the HDEHP reagent dependence of strontium extraction in the presence of various amounts of TBP. Such work is now in progress.

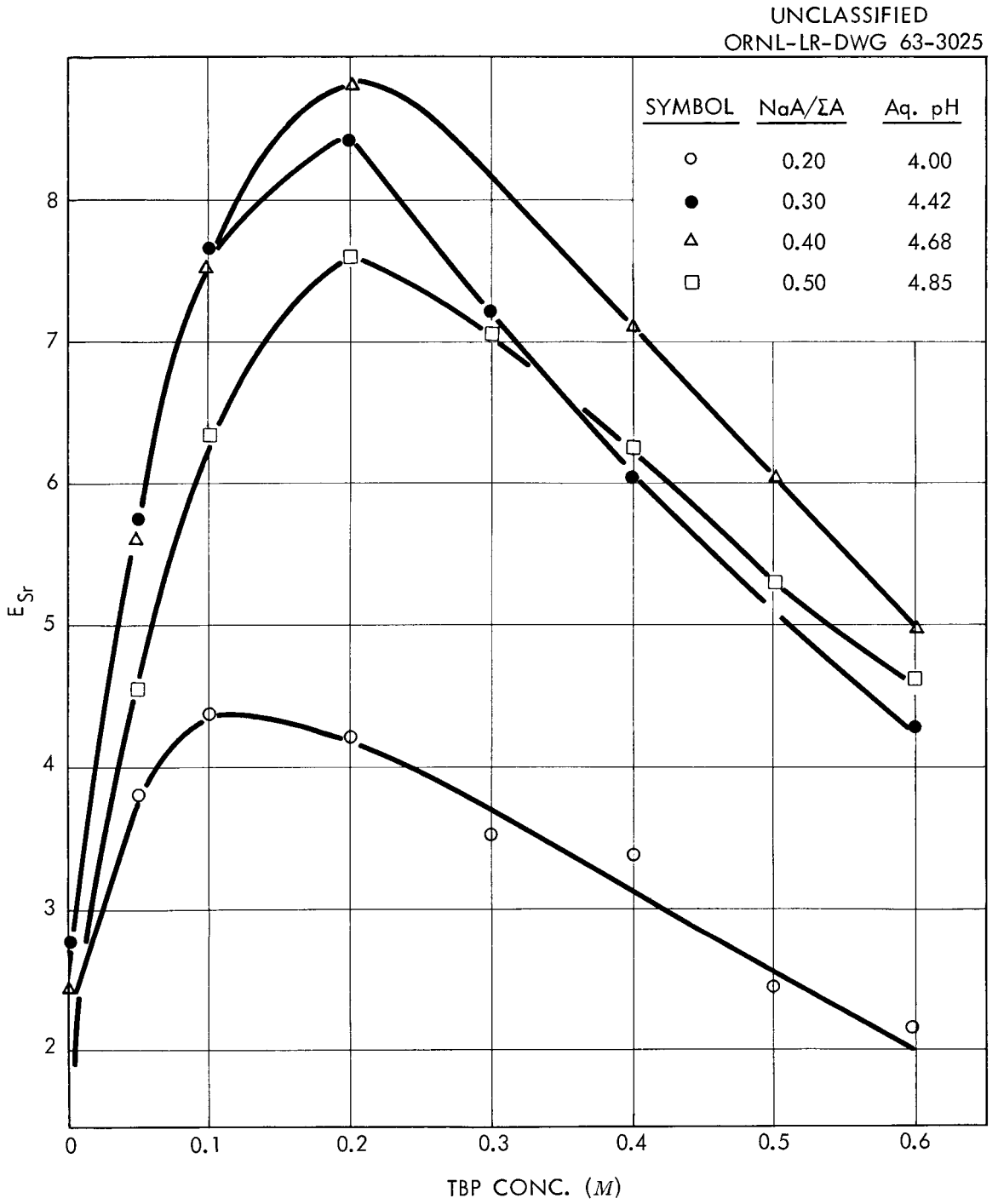


Fig. 2.5.6. Strontium Extraction by 0.10 M DEHP in n-Nonane as a Function of Added Tri-n-butyl Phosphate Molarity.

2.6 The Equilibrium Between Tri-n-octylamine and Sulfuric Acid in Various Diluents of Low Volatility

(C. F. Coleman, J. W. Roddy)

In the physico-chemical study of the amine extraction process, information is needed concerning the activity of various species in the organic phase, including the activity of water. Consequently, a program has been started to obtain at least a relative measure of the water activity in some of the amine systems. Initial experiments, which will be reported in later reports, have indicated that the method of isopiestic osmotic balancing may be used to measure the water activity in the presence of almost nonvolatile diluent and amine. The diluent should possess several properties, including low vapor pressure, low viscosity, and good miscibility with the amine and its sulfate. In addition, the extraction properties of an amine in the new diluent should be similar if not identical to those obtained in the usual diluents, especially benzene, since much of the theoretical work on the amine system has been performed in benzene.

In the present investigation, the relative solubility of tri-n-octylamine (TOA) and its normal sulfate (TOAS) were determined in several diluents. Sulfuric acid-TOA equilibrium data then obtained with the more promising of these indicated that at least two, n-hexadecane and phenylcyclohexane, should be suitable for the projected isopiestic measurements.

The TOA used in this work had a neutralization equivalent of 360 ± 1 (theoretical, 353.8), and its tertiary amine content was 98 ± 1%. Standard solutions (0.1 M in amine) were made on a weight basis, diluted to volume with the appropriate diluent, and stored at 25°C. The equilibrations were done in 60-ml separatory funnels. A run usually consisted of equilibrating 10 ml of the amine solution with about 20 ml of a sulfuric acid solution of the desired concentration. The solutions were shaken for an hour or more by a tumbling motion, the phases were allowed to separate, and both phases were analyzed for acid content. The acid in the aqueous phase was determined potentiometrically with standard sodium hydroxide. The acid in the organic phase was determined by dissolving an aliquot in an alcohol-benzene mixture and titrating with sodium ethoxide to the bromthymol blue end point.

2.6.1 Screening Tests

In Table 2.6.1 are listed the diluents investigated, their nominal vapor pressures and viscosities when available, their purity, and the relative solubility of TOA and its sulfate. Some solids were included in the first testing, envisioned to be used in the form of thin films in case no suitable liquids were found, but they were not examined further after some of the liquids gave promising results. At the same time, the liquids with vapor pressure greater than 100μ, and also the Nujol (because of excessive viscosity) and the alkyl bromide (because of possible specific interaction), were dropped from active consideration. The relative solubility of TOA and TOAS is shown as the solubility or insolubility at a concentration of 0.1 M or 0.1 m. All the diluents dissolved TOA, but several failed to dissolve TOAS. The sulfate was soluble in technical grade n-hexadecane, but purification of the diluent by distillation rendered it only sparingly soluble. However, the addition of 5 vol % dodecyl alcohol (vapor pressure about 25μ, estimated to be less than 2μ at 5%) again permitted its solution. This was also observed in the case of the Welch pump oil, where solutility of the amine sulfate was obtained by addition of the same alcohol.

2.6.2 Sulfuric Acid Distribution

Four of the liquids chosen as described above were used as diluents in the extraction of sulfuric acid by 0.1 M TOA (Table 2.6.2). Plots of $\log a^{1/3}_{H_2SO_4}$ vs the quantity $[H_2SO_4]_{org}/[\Sigma TOA]$ yield the "titration" curves given in Fig. 2.6.1. The sulfuric acid activity $a_{H_2SO_4}$ was calculated for each aqueous solution, but concentrations were used in the organic phase, which is equivalent to assuming the species there to be monomeric and with unit activity coefficients. Included in the figure is the curve obtained by Allen,[25] using benzene as the diluent. The curves show TOA exhibiting the most basic character in the ester, dibutylphthalate, and the least basic in phenylcyclohexane.

In Fig. 2.6.2 the values of $[(TOAH)_2SO_4]/[TOA]^2$ vs $a_{H_2SO_4}$ are plotted on a logarithmic scale for each of the diluents. All the curves deviate markedly from the unit slope to be expected under the foregoing assumption for the reaction:

Table 2.6.1. Various Properties of Diluents Investigated

Diluent	Relative Solubility[a] of TOA	TOAS	Nominal Vapor Pressure[e] (microns)	Nominal Viscosity[f,g] (cp)	Purity
n-Decylbromide	Soluble	Soluble	<10	--	Technical
Diisopropylbenzene	Soluble	Soluble	~500	1.6	Technical
sec-Amylbenzene	Soluble	Soluble	~800	1.5	Technical
1,3,5-Triethylbenzene	Soluble	Soluble	~300	1.2	White Label
Dibutylphthalate	Soluble	Soluble	<0.1	11	White Label
Phenylcyclohexane	Soluble	Soluble	~60	0.8	White Label
Apiezon M[c]	Soluble	Soluble	<0.1	Semisolid	--
n-Hexadecane	Soluble	Insoluble[b]	~5	3.6	Technical
Nujol	Soluble	Insoluble	--	--	--
Welch pump oil	Soluble	Insoluble[b]	<0.01	--	--
Phenanthrene[d]	Soluble	Insoluble	~1	Solid	White Label
Diphenylketone[d]	Soluble	Insoluble	~1	Solid	White Label

[a]Solubility or insolubility at 0.1 M (or 0.1 m[c,d]).

[b]Becomes soluble on addition of 5 vol % dodecanol.

[c]Semisolid.

[d]Crystalline.

[e]From various literature sources.

[f]International Critical Table 7, 1930.

[g]Physical Properties of Chemical Compounds 1, 1955.

Table 2.6.2. Sulfuric Acid—Tri-n-octylamine Equilibria in Various Diluents

0.100 M Tri-n-octylamine

Analytical Sulfuric Acid Concentrations (M)							
Dibutylphthalate		Welch Pump Oil[a]		n-Hexadecane[a]		Phenylcyclohexane	
$[H_2SO_4]_{aq}$	$[H_2SO_4]_{org}$	$[H_2SO_4]_{aq}$	$[H_2SO_4]_{org}$	$[H_2SO_4]_{aq}$	$[H_2SO_4]_{org}$	$[H_2SO_4]_{aq}$	$[H_2SO_4]_{org}$
0.00018	0.00497	0.0007	0.0121	0.00082	0.0099	0.00255	0.00078
0.00047	0.00978	0.0017	0.0190	0.00206	0.0186	0.00484	0.00354
0.00056	0.0147	0.00312	0.0256	0.00331	0.0240	0.00651	0.00846
0.00080	0.0244	0.00431	0.0295	0.00662	0.0319	0.00944	0.0199
0.0013	0.0354	0.00618	0.0349	0.00820	0.0346	0.00975	0.0214
0.0020	0.0451	0.0075	0.0366	0.0111	0.0385	0.0131	0.0300
0.0069	0.0512	0.0113	0.0419	0.0113	0.0386	0.0185	0.0400
0.01129	0.0547	0.0164	0.0441	0.0148	0.0415	0.0224	0.0457
0.0217	0.0594	0.0282	0.0493	0.0208	0.0451	0.0328	0.0520
0.0351	0.0626	0.0287	0.0559	0.0311	0.0492	0.0444	0.0586
0.0582	0.0639	0.0362	0.0494	0.0566	0.0542		
0.0832	0.0667	0.0454	0.0588	0.0831	0.0574		
0.1042	0.0682	0.0621	0.0628	0.1109	0.0599		
0.1741	0.0751	0.1040	0.0645	0.1694	0.0636		
0.2314	0.0775	0.1413	0.0666	0.2296	0.0662		

[a]Contains 5 vol % dodecyl alcohol.

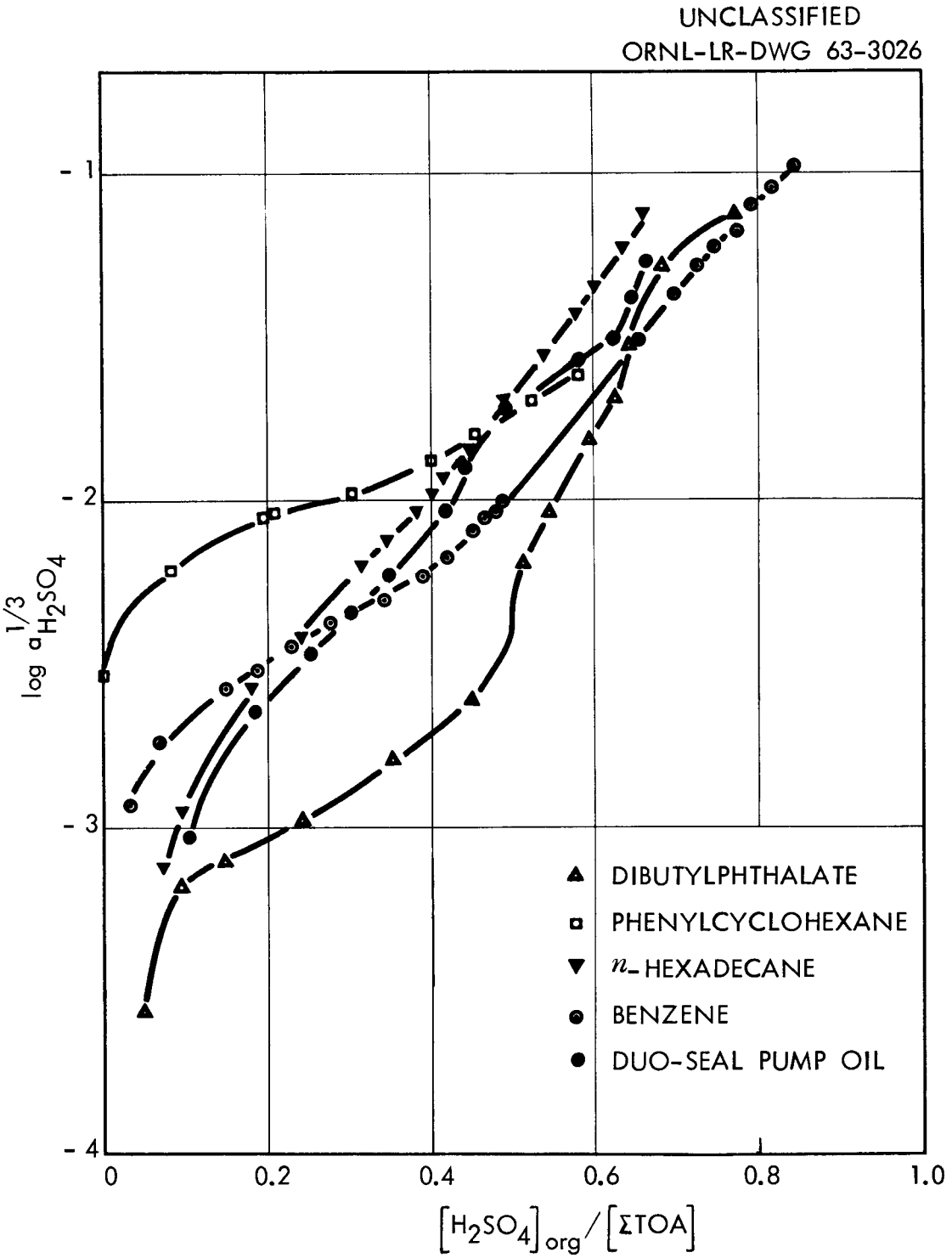


Fig. 2.6.1. Two-Phase "Titration" Curves for Tri-n-octylamine in Various Diluents. Points represent separate batch equilibrations. 0.1 M in tri-n-octylamine.

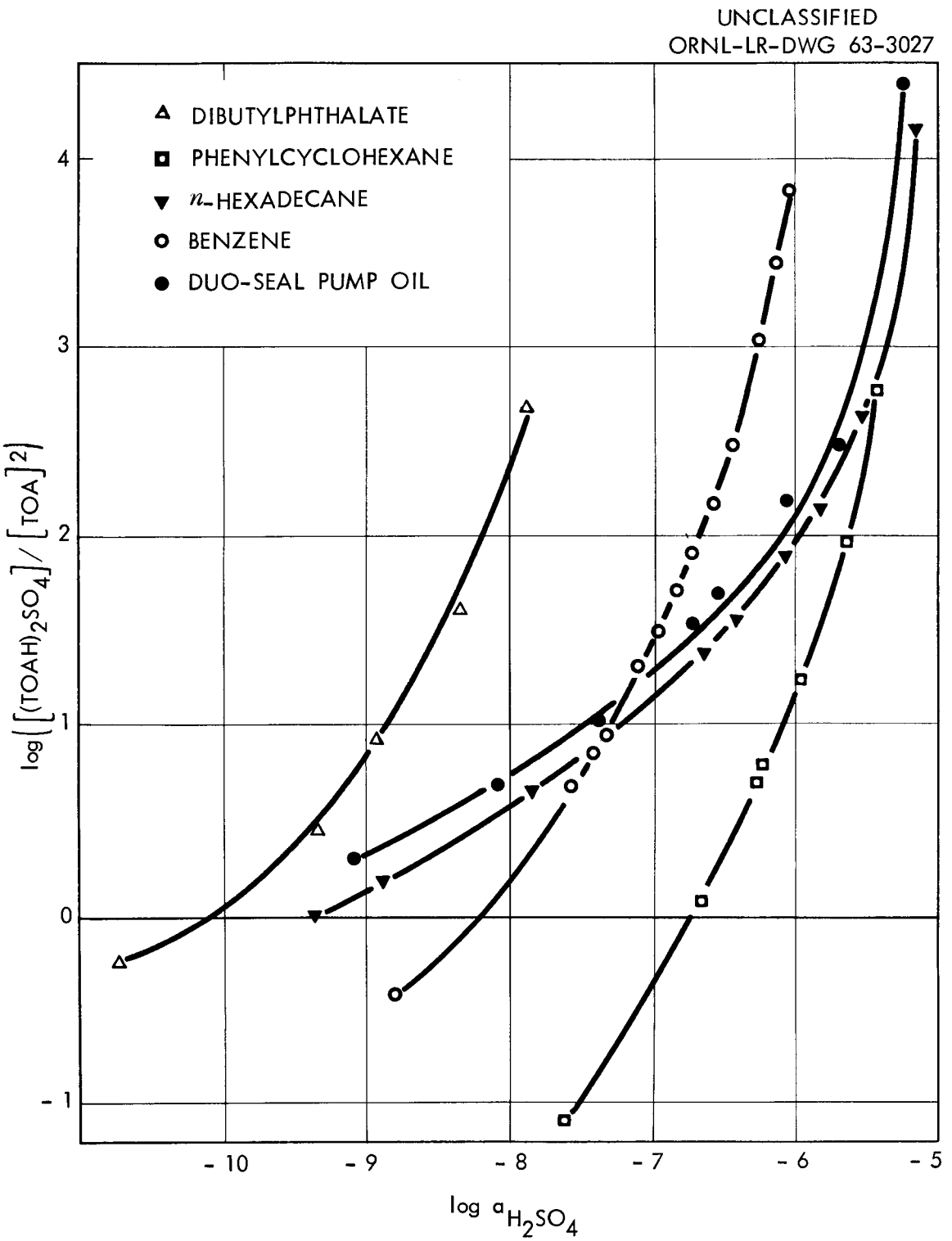


Fig. 2.6.2. Equilibria for the Two-Phase Reaction H_2SO_4 + 2TOA = $(TOAH)_2SO_4$ in Various Diluents. 0.1 M tri-n-octylamine (TOA).

$$H_2SO_4 + 2TOA_{org} \rightleftharpoons (TOAH)_2SO_{4_{org}} \quad , \tag{1}$$

$$K'a_{H_2SO_4} = [(TOAH)_2SO_4]/[TOA]^2 \quad .$$

Since this deviation was already known in the case of benzene,[25] it was at least not surprising for the other diluents. Qualitative intercomparisons of the curves in both figures, together with the acid activities at the half-neutralization* and neutralization points (Table 2.6.3), show considerable differences among these diluents, and yet enough resemblance to benzene for each to be considered usable in the projected isopiestic tests.

Of these four, the phthalate has the disadvantage of potential interaction occurring with the ester functional groups, and the pump oil is excessively viscous. Hence, the other two, n-hexadecane and phenylcyclohexane, are being tried in the isopiestic tests.

Table 2.6.3. Comparison of Corresponding Points from Acid Extraction Equilibrium Curves

0.1 M Tri-n-octylamine; Fig. 2.6.1

Diluent	Acidity, $a^{1/3}_{H_2SO_4}$ Half Neutralization	Neutralization
Dibutylphthalate	0.0011	0.0065
n-Hexadecane[a]	0.0040	0.021
Welch Pump Oil[a]	0.0033	0.015
Phenylcyclohexane	0.0093	0.019
Benzene (ref 25)	0.0036	0.011

[a]Modified with 5 vol % dodecanol.

*If the equilibria had conformed to reaction (1), each half-neutralization acidity would have provided an evaluation of the reaction constant, according to:

$$K' = (0.025)/(0.05)^2 \, a_{H_2SO_4} = 10/a_{H_2SO_4} \quad .$$

REFERENCES

1. K. B. Brown, Chem. Tech. Div. Chem. Dev. Sec. C Progress Report for July-December, 1962, ORNL-TM-449.

2. Ibid., for August-September, 1961, ORNL-TM-27.

3. Ibid., for January-March, 1962, ORNL-TM-181.

4. Ibid., for April-June, 1962, ORNL-TM-265.

5. Personal communication, L. A. Bray and G. L. Richardson, Hanford, Washington, Feb. 1, 1963.

6. D. W. Agers, et al., "The Purification of Inorganic Acids by the Amine Liquid Ion Exchange Process," paper presented at AIME Meeting, Dallas, Texas, February, 1963.

7. K. B. Brown, Chem. Tech. Div. Chem. Dev. Sec. C Progress Report for October-December, 1961, ORNL-TM-107.

8. B. Weaver and F. A. Kappelmann, Purification of Promethium by Liquid-Liquid Extraction, ORNL-2863 (Jan. 29, 1960).

9. F. L. Moore, Analytical Chemistry 35, 715-9 (May, 1963).

10. R. A. Penneman and T. K. Keenan, The Radiochemistry of Americium and Curium, NAS-NS-3006 (Jan., 1960).

11. K. B. Brown, Progress Report: Uranium Chemistry of Raw Materials Section, ORNL-1308 (May 23, 1952).

12. Ibid., ORNL-2366 (Sept. 4, 1957).

13. Harold M. Feder and Milton Ader, Solvent Extraction of Uranium Values, USP-2,872,285 (patent applied for Sept. 6, 1956).

14. C. A. Blake, Jr., A. T. Gresky, J. M. Schmitt, and R. G. Mansfield, Comparison of Dialkyl Phenylphosphonates with TBP in Nitrate Systems, ORNL-3374 (Jan. 8, 1963).

15. C. A. Blake, Jr., C. A. Baes, Jr., and K. B. Brown, Ind. Eng. Chem. 50, 1763-7 (1958).

16. K. B. Brown, et al., Chem. Tech. Div. Chem. Dev. Sec. C Progress Report for July, 1959, ORNL-CF-59-7-68.

17. Ibid., for October-November, 1960, ORNL-CF-60-11-126.

18. Chemical Technology Division Annual Progress Report for Period Ending May, 1961, ORNL-3153, pp 109-11.

19. Ibid., for Period Ending June, 1962, ORNL-3314, pp 106-8.

20. J. A. Knight, Final Report, Radiation Chemistry of Organic Substances, Subcontract between Engineering Experiment Station, Georgia Institute of Technology, Atlanta, and Oak Ridge National Laboratory, Oak Ridge, Tennessee (Jan. 31, 1959).

21. E. S. Lane, Degraded TBP-Kerosene Cleanup Using Alkanolamines and Related Compounds, AERE-M-809 (Jan., 1961).

22. W. H. Baldwin, The Reaction Between Sulfuric Acid and Aliphatic Hydrocarbons, ORNL-CF-60-6-48 (June 8, 1960).

23. Private communication, W. D. Schultz, Hanford, Wash., Sept., 1961.

24. W. J. McDowell and C. F. Coleman, J. Inorg. Nucl. Chem. 25, 234-5 (1963).

25. K. A. Allen, J. Phys. Chem. 60, 239 (1956).

ORNL-3496
UC-10 — Chemical Separations Processes
for Plutonium and Uranium
TID-4500 (22nd ed.)

INTERNAL DISTRIBUTION

1. Biology Library
2-4. Central Research Library
5. Reactor Division Library
6-7. ORNL — Y-12 Technical Library
Document Reference Section
8-27. Laboratory Records Department
28. Laboratory Records, ORNL R.C.
29. W. D. Arnold
30. P. S. Baker
31. R. D. Baybarz
32. C. A. Blake
33-37. K. B. Brown
38. T. A. Butler
39. C. F. Coleman
40. D. J. Crouse
41. F. L. Culler
42. W. Davis, Jr.
43. J. S. Drury
44. J. S. Eldridge
45. B. Z. Egan
46. D. E. Ferguson
47. H. R. Gwinn
48. Paul Haas
49. H. L. Holsopple
50. D. E. Horner
51. F. J. Hurst
52. F. A. Kappelmann
53. C. E. Lamb
54. C. E. Larson
55. R. E. Leuze
56. J. T. Long
57. W. J. McDowell
58. J. R. McWherter
59. F. L. Moore
60. J. G. Moore
61. W. R. Musick
62. F. L. Peishel
63. J. W. Roddy
64. A. D. Ryon
65. J. M. Schmitt
66. F. G. Seeley
67-68. E. M. Shank
69. M. J. Skinner
70. J. A. Swartout
71. V. C. A. Vaughen
72. Boyd Weaver
73. A. M. Weinberg
74. M. E. Whatley
75. J. J. Katz (consultant)
76. T. H. Pigford (consultant)
77. P. H. Emmett (consultant)
78. C. E. Winters (consultant)
79. H. L. Hazen (consultant)
80. A. H. Ross (consultant)
81. M. E. Wadsworth (consultant)

EXTERNAL DISTRIBUTION

82. E. L. Anderson, U.S. Atomic Energy Commission, Washington 25, D.C.
83. F. P. Baranowski, U.S. Atomic Energy Commission, Washington 25, D.C.
84. W. K. Eister, U.S. Atomic Energy Commission, Washington 25, D.C.
85. W. L. Lennemann, U.S. Atomic Energy Commission, Washington 25, D.C.
86. J. A. Lieberman, U.S. Atomic Energy Commission, Washington 25, D.C.
87-88. E. C. Van Blarcom, U.S. Atomic Energy Commission, Washington 25, D.C.
89. T. R. Workinger, U.S. Atomic Energy Commission, Washington 25, D.C.
90. L. P. Bupp, General Electric Company, Hanford Atomic Products Laboratories, Richland, Washington
91. Raymond E. Burns, General Electric Company, Hanford Atomic Products Laboratories, Richland, Washington
92. V. R. Cooper, General Electric Company, Hanford Atomic Products Laboratories, Richland, Washington

93. R. L. Moore, General Electric Company, Hanford Atomic Products Laboratories, Richland, Washington
94. G. L. Richardson, General Electric Company, Hanford Atomic Products Laboratories, Richland, Washington
95. W. H. Swift, General Electric Company, Hanford Atomic Products Laboratories, Richland, Washington
96. James A. Buckham, Idaho Chemical Processing Plant, Idaho Falls, Idaho
97. J. A. McBride, Idaho Chemical Processing Plant, Idaho Falls, Idaho
98. R. A. McGuire, Idaho Chemical Processing Plant, Idaho Falls, Idaho
99. Kenneth Rohde, Idaho Chemical Processing Plant, Idaho Falls, Idaho
100. J. I. Stevens, Idaho Chemical Processing Plant, Idaho Falls, Idaho
101. C. M. Slansky, Idaho Chemical Processing Plant, Idaho Falls, Idaho
102. J. W. Morris, E. I. du Pont de Nemours Company, Savannah River Laboratory, Aiken, South Carolina
103. T. H. Siddall, E. I. du Pont de Nemours Company, Savannah River Laboratory, Aiken, South Carolina
104. John W. Irvine, Massachusetts Institute of Technology, Cambridge 39, Massachusetts
105. E. A. Mason, Massachusetts Institute of Technology, Cambridge 39, Massachusetts
106. S. Bernstein, Union Carbide Nuclear Corporation, Paducah, Kentucky
107. J. T. Christy, Atomic Energy Commission, Hanford, Washington
108. B. H. Clemmons, Bureau of Mines, Salt Lake City, Utah
109. R. A. Ewing, Battelle Memorial Institute, Columbus, Ohio
110-121. W. S. Hutchinson, Grand Junction Operations Office, Grand Junction, Colorado
122. E. M. Kinderman, Stanford Research Institute, Menlo Park, California
123. S. Lawroski, Argonne National Laboratory, Argonne, Illinois
124. B. Manowitz, Brookhaven National Laboratory, Upton, Long Island, New York
125. F. W. Melvanin, Eldorado Mining and Refining Company, Limited Ottawa, Canada
126. F. De Laage De Meux, Ambassade de France, 1346 Connecticut Avenue, Washington 6, D.C.
127. J. T. Roberts, International Atomic Energy Agency, Vienna, Austria
128. R. Simard, Canadian Department of Mines and Technical Surveys, Ottawa, Canada
129. C. E. Stevenson, Argonne National Laboratory, Idaho Falls, Idaho
130. R. A. Wells, National Chemical Laboratory, Teddington, Middlesex, England
131. Research and Development Division, AEC, ORO
132-637. Given distribution as shown in TID-4500 (22nd ed.) under Chemical Separations Processes for Plutonium and Uranium category (75 copies — OTS)