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ORNL-2443
Technology-Raw Materials

PROGRESS REPORT ON RAW MATERIALS

FOR SEPTEMBER, 1957

K. B. Brown
C. F. Coleman
D. J. Crouse
A. D. Ryon

OAK RIDGE NATIONAL LABORATORY
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CHEMICAL TECHNOLOGY DIVISION

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FOR SEPTEMBER, 1957

Chemical Development Section C
K. B. Brown, Section Chief

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All studies reported here are preliminary and conclusions are subject to change. The information is published as a formal report only to permit ready dissemination of data to interested persons.

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Preliminary,	ORNL-2268 (20¢)	May,	ORNL-2366 (25¢)
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April,	ORNL-2346 (25¢)	August,	ORNL-2399 ($1.00)

ABSTRACT

Systematic Studies. In di(2-ethylhexyl)phosphoric acid extractions of several metal ions in the presence of radiotracer-labeled inorganic phosphate, the phosphate accompanied extracted Fe(III) and Al, but not V(IV) or Mo(VI) in amounts that could cause significant contamination of a vanadium product.

In the extraction of thorium from sulfate solution with di(2-ethylhexyl)phosphoric acid, extraction coefficients were lowered but still usable in the presence of enough decanol to prevent third-phase formation in alkaline stripping. Tri-n-octylphosphine oxide in kerosene extracted thorium effectively from 1 and 4 M HNO_3 and from 4 but not 1 M HCl. The coefficients increased rapidly with increasing phosphine oxide concentration.

In measurement of acid extraction by amine diluent combinations, the aqueous pH at which enough acid was extracted to neutralize half the amine varied with amine class, primary > secondary > tertiary; with branching, straight chain > branched chain; with diluent, chloroform > benzene > kerosene; and with anion, $HClO_4$ > H_2SO_4.

Melting points, apparent molecular weights, and assay test results are reported for tri-n-octylphosphine oxide batches from several different sources.

Process Development Studies. In continued studies of the Amex vanadium process, the effects of several extraction variables were examined and the vanadium extraction abilities of three different amines were compared. Rate tests showed rapid extraction of most of the vanadium although the final approach to equilibrium was quite slow. Vanadium coefficients, which were low at pH 1.4, increased rapidly with increasing pH particularly in the region of pH 2. The coefficients also increased as the sulfate concentration

decreased. Isotherms for extraction of vanadium with 0.1 M solutions of S-24, 9D-178, and tri-iso-octylamines were of unconventional shape, showing (at least over a portion of the curves) an increase rather than a decrease in vanadium extraction efficiency with increase in vanadium loadings. Maximum vanadium loadings (0.1 M amine) were in the range 11.5-13 g/liter.

Thorium was efficiently recovered from Amex carbonate strip solutions by adjusting the pH to pH > 13 with caustic or to 5-6 with sulfuric acid. Precipitates from the sulfuric acid method filtered much more readily than those produced with caustic. Under certain precipitation conditions thorium was effectively separated from the small amount of uranium in the strip solution.

In the Dapex system, contact of air with the mixed organic and aqueous phases results in some oxidation of iron(II). The amount of iron oxidized, although relatively small, is of sufficient magnitude to suggest that, for best results in a vanadium recovery process, the extraction mixers should be designed to minimize contact with air.

Engineering Studies. The kinetics of vanadium(IV) and iron(III) extraction by Dapex in batch mixer tests were well represented by first-order rate constants similar to those previously reported for uranium extraction. The rate of extraction for each metal increased with approximately the cube root of power input to the mixer. The relative rates of extraction, expressed as rate constants, were 1.62 for uranium, 0.95 for vanadium, and 0.11 for iron at a power input of 30 hp per 1000 gal of mixer volume.

Fundamental Studies. Comparison of the infrared spectra of n-octane solutions of di(2-ethylhexyl)phosphoric acid (D2EHPA), tributylphosphate (TBP), and tri-n-octylphosphine oxide (TOPO) showed some D2EHPA-TBP association, and considerable D2EHPA-TOPO association. Measurements of the latter by the method of continuous variations indicated the formation of an association product at a mole ratio of 1/1.

Molecular weight determinations by light scattering indicated that in benzene solution tri-n-octylamine bisulfate is dimerized, while 1-(3-ethylpentyl)-4-ethyloctylamine and N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine form aggregates averaging ~11 and 15-20 sulfate units, respectively.

Rare-Earth Separations. Distribution of rare earths between their saturated aqueous nitrate solutions and tributylphosphate gives separation factors which increase with acidity up to 16 M HNO_3. Maximum factors between adjoining elements exceed 1.5 in the lighter half of the lanthanide series but decrease to about 1.2 at the end of the series. Operation of multistage separators has produced individual rare earths and confirmed and extended single-stage data.

1.0 SYSTEMATIC STUDIES

In addition to the studies described below, systematic studies during the month included (1) preliminary study of the applicability of amine and organophosphorus extractants to separations in fuel reprocessing and waste disposal, (2) testing of new organonitrogen compounds as uranium extractants, and (3) tracer phosphorus determination of organophosphorus extractant losses.

1.1 Extraction of Inorganic Phosphate with Di(2-ethylhexyl)phosphoric Acid (J. M. Schmitt, W. T. Rainey)

The specifications for vanadium products require very low phosphorus content (ORNL-2399, sect. 2.2), so that the possible extraction of inorganic phosphate is a significant consideration in the Dapex process for vanadium recovery. In batch shake-out extraction tests with radiotracer-labeled inorganic phosphate in the presence of each of several common metal ions, essentially no phosphate was extracted with vanadium(IV) or molybdenum(VI), but significant amounts of phosphate accompanied extracted iron(III) and especially aluminum (Table 1.1). Preliminary tests using macro analyses (ORNL-2399, p. 14) had suggested phosphate accompanying aluminum but not iron(III).

At a specification of $\leq$ 0.05% phosphorus based on contained V_2O_5 (0.27% PO_4 based on V), organic extracts containing 2, 4, or 6 g V/liter would reach the tolerance limit at 5.4, 10.8, or 16.2 mg PO_4/liter, respectively. (This, of course, is on the assumption of no subsequent separation and no other source of phosphorus contamination.) The data of Table 1.1 show that extraction of phosphate in association with aluminum and iron could produce phosphate concentrations of this magnitude in the organic phase.

1.2 Extraction of Thorium with Di(2-ethylhexyl)phosphoric Acid (C. A. Blake, J. M. Schmitt)

Thorium extractions from aqueous liquors with kerosene solutions of di(2-ethylhexyl)phosphoric acid (D2EHPA), alone and in combination with tributylphosphate (TBP), were described previously (ORNL-2346). Extraction was effective either way, but the coefficients were significantly lower when TBP was used, instead of being enhanced as in the extraction of uranium. Thus, the only function of TBP in the extractant would be to permit alkaline stripping without third-phase formation, which could also be accomplished with a lower-cost alcohol. In continued extraction tests, the addition of decanol also decreased the thorium extraction:

	Thorium Extraction Coefficient (o/a)			
Aqueous Solution Extracted	No Decanol	20 g/liter Decanol	50 g/liter Decanol	100 g/liter Decanol
0.5 M SO_4, pH 1.2	45	8.5	2.5	1.1
0.3 M H_2SO_4, pH 0.5	6.4	1.4	0.5	0.17
0.5 M H_2SO_4	1.6	0.3	0.11	0.02

Table 1.1. Extraction of Labeled Inorganic Phosphate* by D2EHPA

Aqueous phase: 0.5 M $SO_4^=$; pH, $PO_4^=$, metal ion as indicated

Organic phase: 0.3 M D2EHPA in kerosene

Contact: end-over-end tumbling at room temperature, aqueous/organic = 1/1

Aqueous Phase				PO_4 Extracted, mg/liter	
Metal Ion	g/liter	PO_4, g/liter	pH	10 min	16 hr
Fe(III)	1.0	1.1	1.6	1.2	0.3
Fe(III)	1.0	4.3	1.6	1.9	1.2
Al	10.4	1.1	1.6	1.3	9.5
Al	10.4	4.3	1.6	11	37
V(IV)	3.2	1.2	1.8	0.03	0.04
V(IV)	3.2	4.6	1.8	0.1	0.1
Mo(VI)	1.0	1	1.5	0.03	0.03
Mo(VI)	1.0	4	1.5	0.1	0.1
Blank-1	-	1	1.6	0.03	0.03
Blank-2	-	4	1.6	0.1	0.1

*$H_3P^{32}O_4$ prepared with the assistance of W. H. Baldwin, ORNL Chemistry Division.

The D2EHPA concentration was 0.1 M in kerosene. The initial thorium concentration in the aqueous solutions was 2 g/liter, aqueous/organic ratio = 1/1.

The concentration of decanol required with 0.1 M D2EHPA to prevent third-phase formation was about 0.1 M, or 16 g/liter. The effect on the extraction coefficient at this level was about the same as that at the corresponding TBP concentration; hence, the alcohol would be preferred for process use because of its lower cost.

Thorium Stripping. Thorium was stripped completely from decanol-modified D2EHPA with alkaline solutions. It reported in solution to 10% Na_2CO_3 at aqueous/organic phase ratio = 1/1 (final thorium aqueous concentration ~2 g/liter), and it was precipitated from the sodium carbonate solution by 10% NaOH solution. In preliminary stripping tests thorium was readily and completely precipitated from unmodified D2EHPA in kerosene with 6 M HF and with 10% oxalic acid.

1.3 Extraction of Thorium with Tri(n-octyl)phosphine Oxide (C. A. Blake, J. M. Schmitt)

Thorium was effectively extracted by tri-n-octylphosphine oxide (TOPO) from both 1 and 4 M HNO_3. Extraction was considerably stronger at the lower nitric acid concentration, and increased rapidly with increasing reagent concentration.

Thorium extraction was much lower from 4 M HCl acid than from 4 M HNO_3, and, in contrast to the nitric acid system, thorium was not extracted from 1 M HCl:

Phosphine Oxide in Kerosene, M	Thorium Extraction Coefficient (o/a)			
	1 M HNO_3	4 M HNO_3	1 M HCl	4 M HCl
0.05	65	5	< 0.1	1.6
0.1	550	60	< 0.1	10
0.2	-	700	< 0.1	40

In both sets of tests, the initial thorium concentration in the aqueous solutions was 2 g/liter, and the aqueous/organic ratio was 1/1. The relative rather than the absolute values of these extraction coefficients should be considered, since the amounts of thorium extracted at $E_a^o \geq 5$ were sufficient to lower the apparent E_a^o values to some extent by loading effects.

An extraction isotherm from 4 M HCl solution containing 1.8 g Th/liter with 0.1 M trioctylphosphine oxide in kerosene showed the thorium loading leveling off at about 3.5 g/liter:

Phase Ratio (a/o)	Final Th (g/liter)	
	Aq	Org
0.2	0.02	0.37
0.5	0.06	0.86
1	0.16	1.6
2	0.53	2.6
5	1.2	3.3
10	1.5	3.4

A few extractions of thorium from sulfate solutions were reported previously (ORNL-1964, p. 49). Those extractions were low, the coefficients being < 1 from 0.02 M $Th(NO_3)_4$ in 0.1 M H_2SO_4 and < 0.1 from a monazite sand leach liquor containing 0.1 M excess H_2SO_4, even with nitric acid added up to 1.5 M.

Uranium(VI) is extracted by phosphine oxides much more readily from these solutions than is thorium. The separately measured extractions indicated separation factors of several powers of 10 from hydrochloric acid and sulfuric acid--nitric acid solutions, and somewhat lower from nitric acid solutions, i.e., about 20 from 1.5 M HNO_3 and 30 from 4 M HNO_3.

1.4 Relative Base Strengths of Amine-Diluent Combinations (J. G. Moore)

The two-phase titration curves obtained in comparing sulfuric acid extractions (ORNL-2399, Fig. 4.3) showed differences in pH at half neutralization of the amines which were considerably larger than the published differences in pK of lower molecular weight amines, and which suggested correlation with alkyl branching and with diluent as well as with amine class. This comparison has been extended to a larger number of amine-diluent combinations by measurement of the aqueous sulfuric acid activity and pH in extractions near the half-neutralization point. The results (Table 1.2) supported the previous suggestions, and showed an even wider range of effective basicity. It varied with amine class---primary > secondary > tertiary---and within each class it decreased with increasing alkyl branching. It may be noted that the difference from highest to lowest secondary amine was considerably greater than some of the differences between classes, suggesting that with still more severely branched compounds the classes might overlap. Where diluents other than benzene were tested, $CHCl_3$ > benzene > kerosene. Modification of the kerosene with an alcohol made it more like benzene in this respect (as also in respect to solvent power for various amine salts), kerosene with 5 vol % tridecanol giving values slightly higher than did benzene.

The trend in extraction power for sulfuric acid by these amines in each diluent resembles the trend in extraction power for several tri- and tetravalent metal ions (ORNL-1754, p. 32). However, the trend with change of diluent is opposite in at least some instances, e.g., the sulfuric acid acid extraction by di(tridecyl)amine was increased by addition of tridecanol to the kerosene diluent, whereas ferric sulfate extraction (ORNL-2306, p. 12) was markedly decreased.

Extraction of other Acids. Nitric acid and perchloric acids are extracted more strongly than sulfuric acid by amines, as well as by anion exchange resins. In extraction of perchloric acid by 0.1 M tri-n-octylamine in benzene, the amine was half neutralized when the aqueous perchloric acid concentration was 2.4×10^{-4} M (pH ~3.5, in contrast to ~2.3 with sulfuric acid.) About 99% of the amine was neutralized when the aqueous acid concentration reached 10^{-3} M. There was no indication of more acid in the organic phase than that equivalent to the amine up to the highest acid concentration tested, 0.03 M.

Essentially no nitric acid was extracted by 0.1 M tribenzylamine in benzene from aqueous solutions at ~0.1 N HNO_3 or less. Some acid was extracted from solutions above ~0.1 N HNO_3, but with precipitation of the amine salt. At 0.2 N HNO_3 about 80% of the amine was precipitated together with equivalent nitrate. Less than 10% of the remaining 0.02 M amine in the benzene solution was neutralized to form the nitrate salt.

Table 1.2 Relative Base Strengths of Amine Diluent Combinations in Extraction of Sulfuric Acid

		Aq. pH at Half Neutralization of Amine			
Amine, 0.1 M	Batch No.	Kerosene	Ker.+ 5 vol % Tridecanol	Benzene	$CHCl_3$
Primary:					
1-(3-ethylpentyl)-4-ethyloctyl	120C			5.17	
Primene JM-R	6C			5.03	
Secondary:					
Di-n-decyl	47G			4.28	4.89
Di(tridecyl)[a]	227A	3.67	4.14	4.00	
N-Benzyl-1-(3-ethylpentyl)-4-ethyloctyl	228B			2.53	2.74
Amine S-24	30D	2.04	2.58	2.44	2.90
Amine 9D-178	193H			2.40	
Tertiary:					
Tri-n-octyl	125H	(1.42)[b]	(1.64)[c]	2.26	3.40
Tri-iso-octyl	239B			2.08	
Tris(tridecyl)[a]	310A	1.08			
Tris(tridecyl B)	163A			1.88	
Tribenzyl	61A			<0[d]	

[a] Mixed branched tridecyl alkyls derived from tetrapropylene, previously designated "tridecyl P."

[b] In n-nonane; some of the amine sulfate precipitated.

[c] In n-nonane + 2% tridecanol.

[d] About 30% of the tribenzyl amine was neutralized on contact with 1 M H_2SO_4. The amine sulfate formed precipitates from the benzene solution.

1.5 Comparison of Tri-n-octylphosphine Oxide Batches (C. A. Blake, D. E. Horner, C. F. Baes, Jr.)

The starting of physicochemical studies in extraction systems involving phosphine oxides (section 4.1), as well as the growing interest in the use of phosphine oxides as extraction agents, has increased the importance of determining reagent purity and identifying characteristic impurities. Some test methods previously developed

Table 1.3 Comparison of Tri-n-octylphosphine Oxide Batches

Batch[a] No.	Melt. Pt., °C	Free Acidity,[b] %	Combined Acidity[b] %	Karl Fischer Titer, eq/mole	Apparent Mol.Wt.[c]	U Extraction Coef.[d] (o/a)
OP-289	48-50	0.03	0.3			110
-403	52.5-53	0.4	0.2			93
-391	53-53.5	1.1	1.1	0.3	410(I)	73
-392	46-48	6.6	5.9			140
-400	51.5-52	<0.5	<0.1	0.3	422(FP) 454(I)	76
-401	51.5-52	<0.2	<0.05	0.04	422(FP) 411(I)	70
-402	52-52.5	<0.05	<0.15			70
-404	51.5-52				422(FP)	100
-405	52.0	0.18	0.14			105

[a] Sources and descriptions given in Table 1.4.

[b] Free acidity determined by titration with aqueous NaOH; combined acidity (material oxidizable and/or hydrolyzable to free acid) determined iodometrically (ORNL-1964, p. 106); both reported as wt % dioctylphosphinic acid, $(C_8H_{17})_2PO_2H$.

[c] Molecule weight determined by (FP) freezing point lowering of benzene or (I) isopiestic measurements in n-octane. Theoretical mol. wt., 387.

[d] Uranium extraction by 0.1 M phosphine oxide in kerosene from 0.004 M U(VI), 0.5 M $SO_4^=$, 0.3 M NO_3^- solution at pH 1, aqueous/organic = 1/1, room temperature. Cf. extractions from other solutions, Table 1.5.

Table 1.4 Preparation of Batches

OP-289: Prepared as described in ORNL-1964; distillation cuts of narrow range from Grignard product, further purified by extended treatment at steam temperature with moist air followed by washing with sodium carbonate solution and aqueous alcohol

OP-403: By W. J. Ross of ORNL Analytical Chemistry Division, following the procedure for OP-289

OP-391: By Westvaco Chemical Corp. (Presumably following the procedure for OP-289, which was submitted to Westvaco)

OP-392: By R. E. Feathers of ORNL Analytical Chemistry Division, following the procedure for OP-289

OP-400: Prepared by a modification of the procedure for OP-289, which included the use of a large excess of Grignard reagent, removal of acid components by passing the product over alumina subsequent to treatment with moist air, and fractional crystallization in place of distillation

OP-401: Prepared as described in ORNL-2399; same as OP-400 except that oxidative treatment with potassium permanganate was substituted for the moist air treatment

OP-402: Prepared from second crop of crystals from batches OP-400 and OP-401

OP-404: By Distillation Products, Inc.

OP-405: By ORNL Analytical Chemistry Division, prepared as described in ORNL-2399

were described in ORNL-1964, and some further tests are now being examined. For convenience in continued study of this problem, the test results from several batches of tri-n-octylphosphine oxide are compiled in Table 1.3 (sources listed in Table 1.4).

Melting Point. The results suggest that the true melting point may be near 53°C; however, the melting point does not so far promise to be very useful as a sensitive criterion of purity.

Free and Combined Acidity. The free (directly titratable) acid is presumed to be mainly if not entirely the corresponding dioctylphosphinic acid. The "combined acidity" is material detectable by an iodometric method (ORNL-1964, p. 106) and is thought to be a dialkylphosphinous acid or dialkylphosphine oxide, R_2HPO (ORNL-1964, p. 4).

Karl Fischer Titer. The considerable reaction with Karl Fischer reagent shown by batches OP-391 and -400 appears to involve an unidentified impurity rather than water, since the titer was neither decreased by desiccation nor increased by exposure to water-saturated air, and was much lower in batch OP-401. This suggests that the Karl Fischer titration may be a sensitive test for an impurity not detected by other tests, and it will be examined further.

Apparent Molecular Weight. The higher-than-theoretical molecular weights (~10% high in benzene solution, ~5-15% high in octane solution) could result either from the presence of impurities, or from intramolecular association between phosphine oxide molecules. Determinations so far completed of the concentration dependence of the apparent molecular weight indicate that intramolecular association does occur.

Uranium Extraction. As described previously (ORNL-1964), the contaminant called "combined acidity" (or at least some component of this) extracts uranium from dilute acidic solutions much more strongly than does the phosphine oxide, so that its presence is reflected by anomolously high extraction coefficients as long as the uranium concentration is quite low. The low-level uranium extractions by these phosphine oxide batches from several types of solution show a general parallel between "combined acidity" and extraction coefficient (Tables 1.3 and 1.5), but the correlation is not exact and suggests that further complexities are involved.

Table 1.5 Comparison of Uranium Extraction at Low Uranium Concentration by Different Batches of Tri-n-octylphosphine Oxide

0.004 M U, 0.1 M phosphine oxide, aqueous/organic = 1/1, room temperature

		Uranium Extraction Coefficients (o/a)					
Aqueous Phase	Diluent	OP-289	OP-391	OP-392	OP-400	OP-401	OP-402
0.1 M NO_3, pH 1	CCl_4	310	326	3000	200	180	200
0.5 M SO_4, 0.3 M NO_3, pH 1	CCl_4	20	31	330	18	15	17
	kerosene	110	73	140	76	70	70
1.4 M PO_4, 0.3 M NO_3, pH 1	CCl_4		0.2	0.7	0.1	0.1	

2.0 PROCESS DEVELOPMENT

In addition to the studies described below, process development projects during the month included (1) evaluation in continuous equipment of the nitrate method for stripping uranium from amines, (2) dissolution of uranium from ores by a sodium carbonate pugging treatment, (3) use of an activated zirconium oxide bed to remove phosphate from Dapex vanadium strip solutions, (4) recovery of molybdenum from Amex nitrate strip solutions by adsorption on activated carbon, and (5) radioactive phosphate tracer studies for determining the distribution of di(2-ethylhexyl)phosphoric acid to acid liquors and carbonate strip solutions.

2.1 Extraction of Vanadium with Amines (F. J. Hurst)

Studies of the Amex process for recovery of vanadium have been described briefly* in previous reports (ORNL-1734, -1959, -1970 (Del.), -2002, and -2268. It was shown that vanadium(V), but not vanadium(IV), is extracted effectively with primary, secondary, and tertiary amines from sulfate solutions of low acidity, i.e. pH 1.7 - 2.5. The vanadium is stripped readily from the solvent by contact with alkaline solutions from which it is easily recovered by conventional precipitation methods.

More recent studies have been concerned with the rate of vanadium extraction and a more extensive examination than previously of the effect of pH and sulfate concentration on the extraction process. In addition, several commercially available amines have been compared as vanadium extractants.

Rate of Extraction. Although most of the vanadium was extracted very rapidly, extended contact times were required for complete equilibrium to be reached. In tests with tri-n-octylamine in 97% kerosene--3% tridecanol diluent, covering a wide range of vanadium loadings, equilibrium was apparently not reached even after 10-20 min vigorous mixing of the phases (Table 2.1). In each case, however, the amount of vanadium extracted after only 30 sec contact was 85-95% of that transferred in 10-20 min.

Effect of pH. The strong increase in vanadium extraction efficiency with increase in pH is illustrated in a series of vanadium(V) extraction isotherms for 0.1 M solutions of 9D-178 and S-24 amines in kerosene (Fig. 2.1). Each isotherm was determined by contacting the amine solution** with a pervanadyl sulfate-sodium sulfate solution (0.5 M SO_4) of the desired pH at various phase ratios.

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* The bulk of information accumulated has not yet been reported in detail. A topical report is being prepared.

** In all the tests subsequently described, the amine, prior to extraction, was converted to the salt form by contact with dilute sulfuric acid. This would probably not be a necessary step in process operation but was done only for convenience in experimental testing to minimize pH changes.

Table 2.1 Rate of Vanadium Extraction by Tri-n-octylamine

Organic: 0.10 M tri-n-octylamine in 97% kerosene--3% tridecanol (pretreated with H_2SO_4 at equilibrium pH 1.8)

Aqueous: 0.28, 1.43, or 3.54 g V(V)/liter, 0.5 M SO_4, pH 1.8

Temperature: 26°C

Final pH: 1.8-1.9

Phase Ratio (a/o)	Contact Time, min	V, g/liter			Vanadium Extraction Coefficient, E_a^o
		Head Aqueous	Aqueous	Organic	
3/1	0.5	0.28	0.20	0.26	1.3
	1		0.20	0.25	1.3
	2		0.21	0.24	1.1
	5		0.20	0.25	1.3
	10		0.19	0.30	1.6
3/1	0.5	1.4	0.38	3.1	8.2
	1		0.36	3.2	8.9
	2		0.34	3.3	9.7
	5		0.30	3.4	11
	10		0.29	3.5	12
1/1	0.5	3.5	0.28	3.0	11
	1		0.25	3.0	12
	2		0.24	3.0	12
	4		0.22	3.1	14
	10		0.20	3.1	15
	20		0.19	3.1	16
	60		0.19	3.2	17
4/1	0.5	3.5	0.82	10.5	13
	1		0.78	10.7	14
	2		0.72	10.8	15
	4		0.69	10.9	16
	10		0.60	11.4	19
	20		0.57	11.6	20
	60		0.53	11.7	22

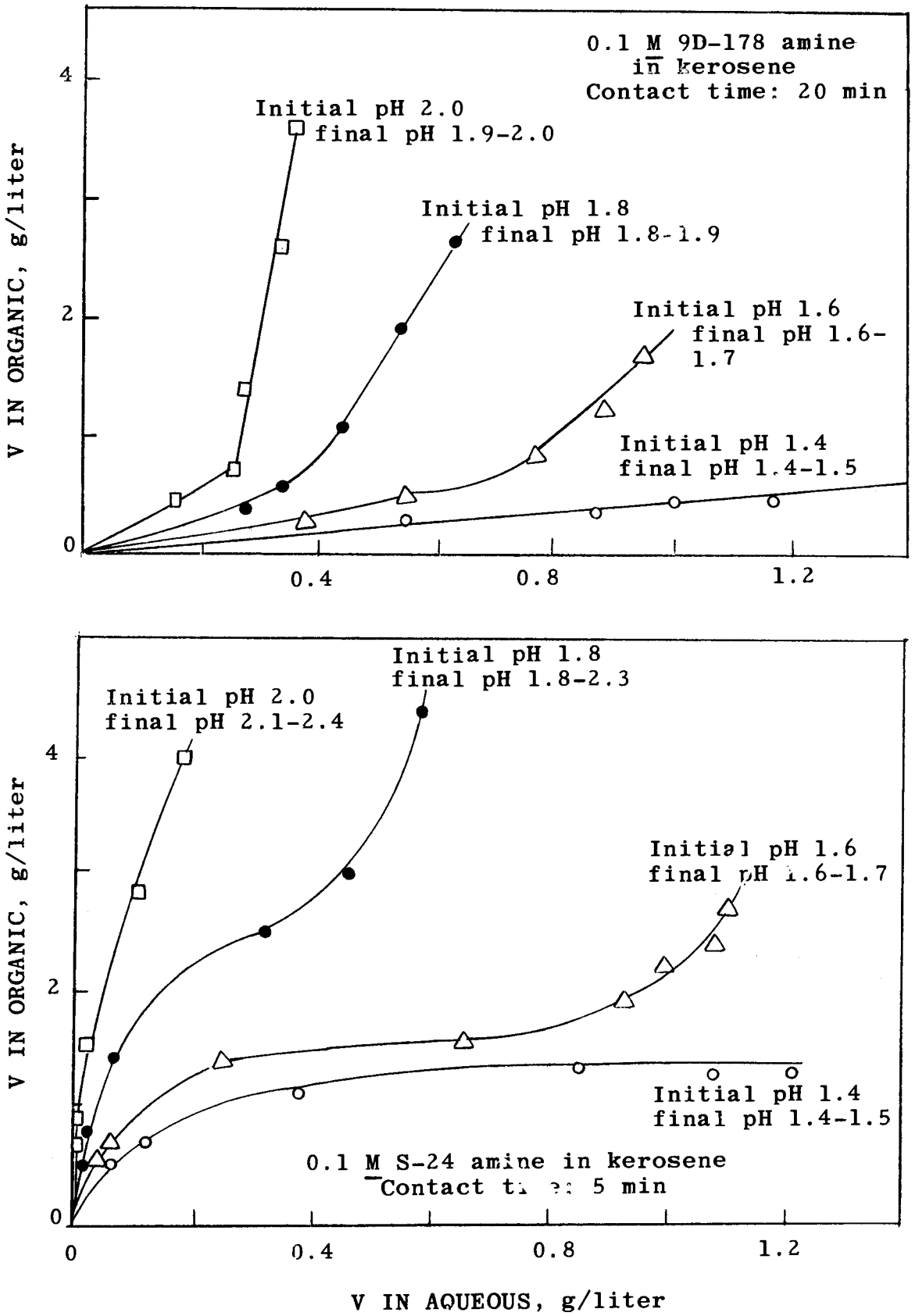

Fig. 2.1 Effect of pH on Vanadium Extraction

Aqueous: 1.5 g V(V)/liter, 0.5 M SO_4
Temperature: 27°C

The isotherms for the two amines are markedly different, and both are unconventional in shape. The curves for 9D-178 have a low initial slope followed by a sharp change to a steeper slope, which appears to occur at a definite vanadium loading, i.e., 0.6-0.8 g V/liter. Isotherms for 0.2 M 9D-178 solutions (results not shown) have the same general shape with the change of slope occurring at approximately the same vanadium/amine ratio, i.e., 1.4 g V/liter.

With S-24 amine the slope of the isotherms is fairly high initially, even at the lower pH levels. At pH 1.4, 1.6, and 1.8 the slope changes to a low value, and, in the case of the latter two curves, again to a high value as the vanadium loading is increased. At pH 2, on the other hand, the slope is uniformly high and without a plateau region.

Effect of Sulfate Concentration. Increasing the sulfate concentration from 0.1 M to 0.5 M appreciably decreased the vanadium extraction efficiency (Fig. 2.2). Further increase in sulfate to 1.0 M had only a minor added depressing effect.

Extraction Isotherms. Complete isotherms are presented in Fig. 2.3 for extraction of vanadium(V) from 0.5 M sulfate solutions by 0.1 M solutions of 9D-178 and S-24 amines in kerosene and tri(iso-octyl)amine in 97% kerosene--3% tridecanol at pH 1.8. Although the general shape of the isotherm for tri(iso-octyl)amine is similar to that for 9D-178 amine, the extraction power of the former amine is higher, particularly in the dilute vanadium region.

The amines showed a very high capacity for vanadium(V). Tri(iso-octyl)amine was loaded to slightly over 13 g V/liter (23 g V_2O_5/liter) or about 2.6 moles V/mole amine. The maximum loading of 9D-178 amine was somewhat lower (~11.5 g V/liter). Attempts to load S-24 amine higher than 10.5 g V/liter resulted in some precipitation of an amine-vanadium complex from the solvent. This precipitate, which contained 2.4 moles V/mole amine, redissolved readily when a small amount of tridecanol was added to the system and presumably could have been avoided by using kerosene diluent modified with alcohol. The sulfate content of the organic phase decreased to a negligible value as the concentration of extracted vanadium was increased to its maximum.

The anomalous shape of the vanadium extraction isotherms, showing in certain regions increased rather than constant or decreasing extraction coefficients with increasing vanadium loading, suggests that some change in the chemical form of the vanadium occurs after extraction into the organic phase. This is further suggested by observation that the extraction reaction is not readily reversible. For example, although extractions from solutions of pH <1 are very weak, fairly strong sulfuric acid solutions, e.g., 2 M, are ineffective stripping agents.

Interpretation of the extraction isotherms (Fig. 2.3) in terms of process operation of a countercurrent extraction system shows that, when using tri(iso-octyl) or 9D-178 amines, the ex-

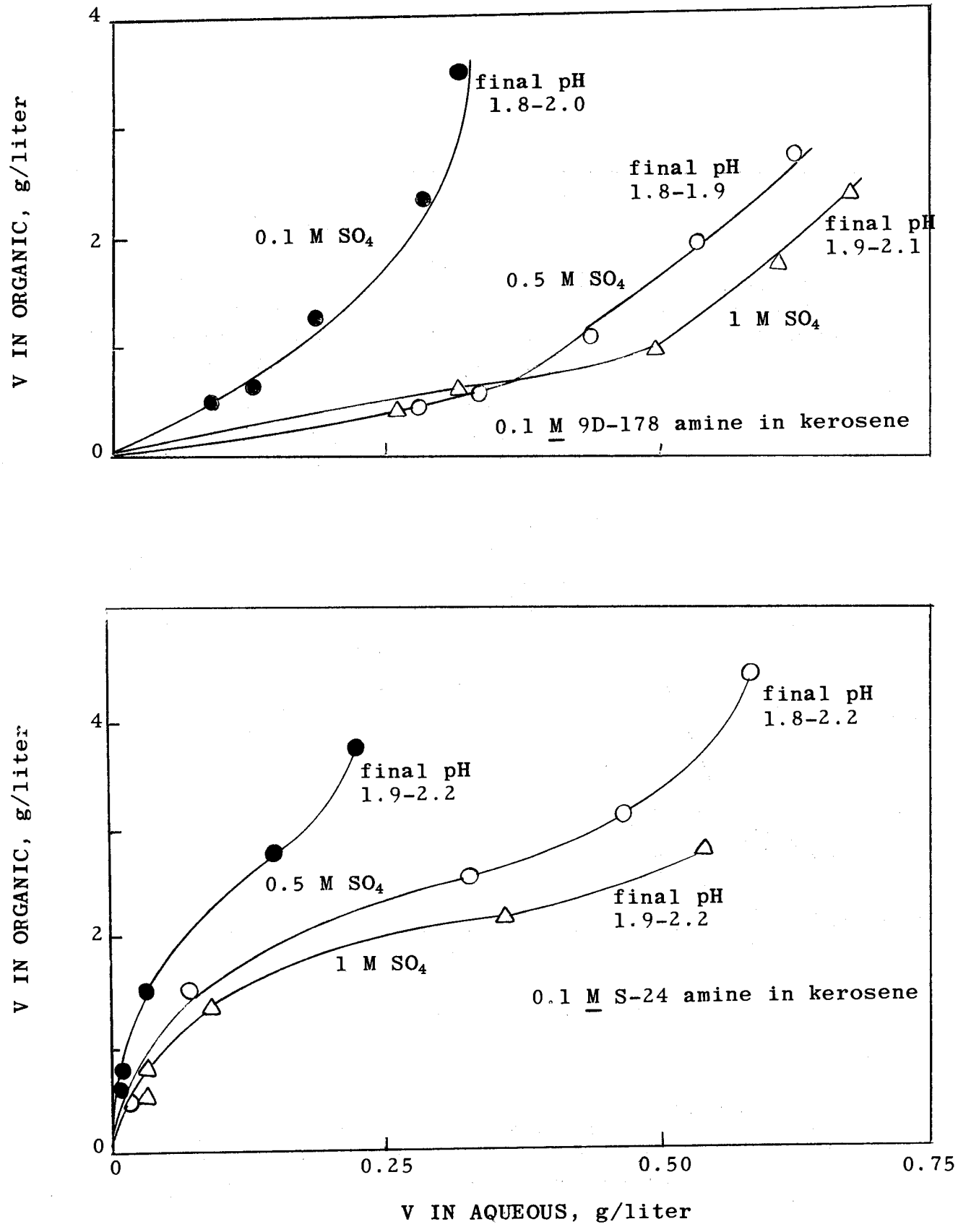

Fig. 2.2 Effect of Sulfate Concentration on Vanadium Extraction
Aqueous: 1.5 g V(V)/liter, pH 1.8, Indicated SO_4
Contact time: 5 min at 27°C

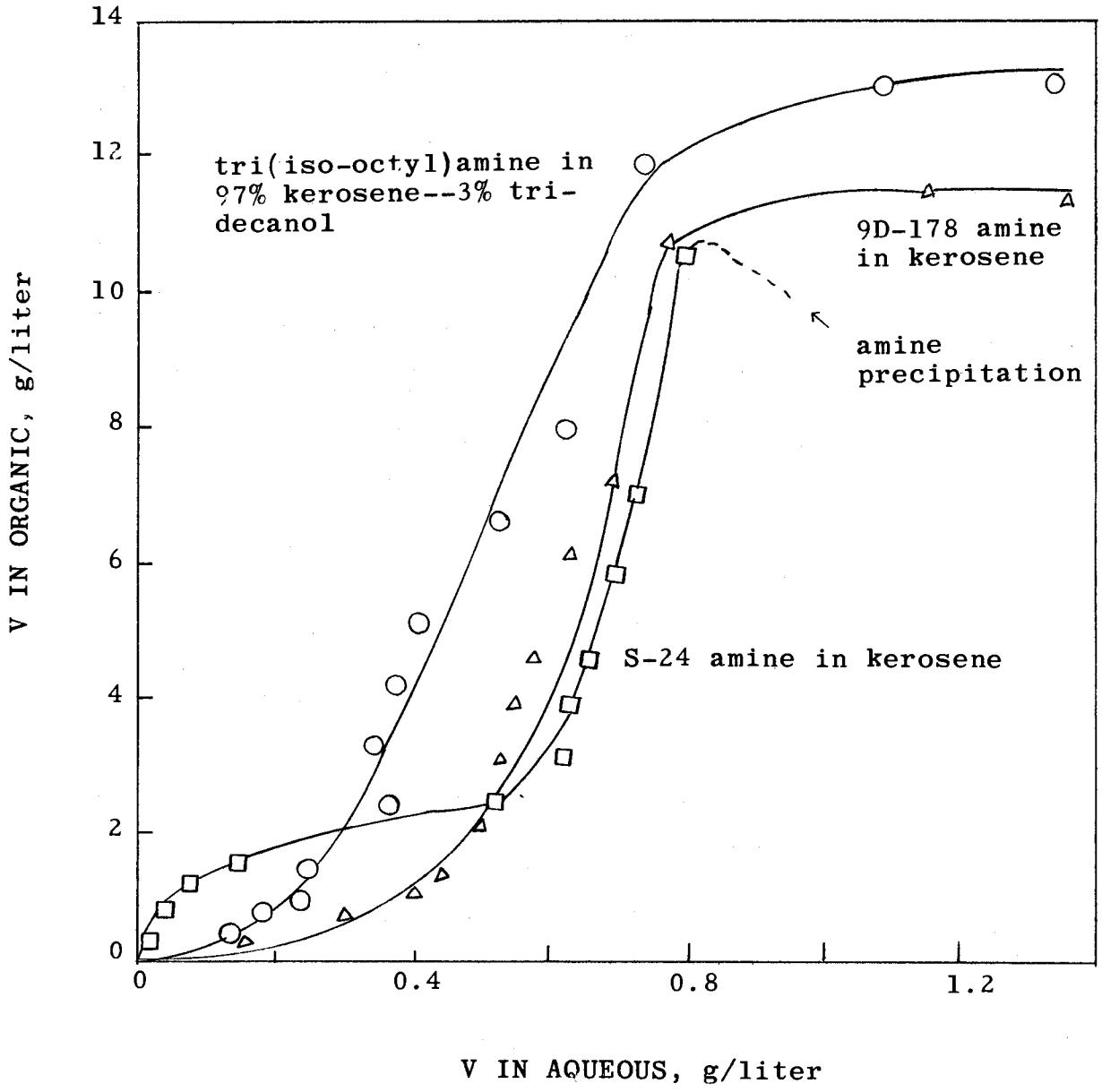

Fig. 2.3 Vanadium Extraction Isotherms

Amine Conc.: 0.10 M
Head Aqueous: 1.4 g V(V)/liter, 0.5 M SO_4, pH 1.8
Procedure: organic cascaded against fresh volumes of aqueous; 2 min contact per stage
Final pH: ~1.8

traction efficiency would be poor in the lower stages of the system owing to the severe "pinch" between the operating line and the equilibrium line in the dilute vanadium region. Thus, although 80-90% of the vanadium can be recovered easily at pH 1.8 from a liquor containing 2-3 g V/liter, recoveries greater than 95% can be achieved only with comparative difficulty. The pinch is more severe for 9D-178 than for tri(iso-octyl)amine. A still different performance pattern would be predicted for S-24 amine. Here the vanadium concentration in the aqueous phase would be reduced rapidly to 0.5-0.6 g/liter, where a pinch would be encountered and the efficiency would then be low. Once the region of the pinch was passed, the extraction efficiency would again be relatively high.

The severity of the pinch between the equilibrium and operating lines can, of course, be minimized by increasing the solvent flow, i.e., accepting lower vanadium loadings, although this is done at the expense of increasing the consumption of stripping chemicals.

It is apparent from Fig. 2.1 that the region of low slope, i.e., region of low extraction efficiency, can be nearly eliminated by operating the extraction system at a pH of 2.0 or slightly higher. This, however, may not be practical in process operation* since oxidized vanadium liquors (particularly those of relatively high vanadium and iron content) are quite unstable in this pH region, tending to precipitate ferric vanadate and vanadium "red cake". These precipitates in some cases have caused formation of slow-breaking emulsions in subsequent solvent extraction operations. In order to avoid precipitate formation even when operating at pH 1.8, it has been necessary with many vanadium liquors to use special procedures in adjusting the vanadium oxidation state and liquor pH. The most favorable results have been obtained by oxidizing the liquor with sodium chlorate at room temperature and at a pH <1.5 and making the final pH adjustment to 1.8-2.0 with ammonia on a continuous basis immediately before the liquor enters the extraction system. Using this procedure, a liquor from Plant D (the liquor was prepared by the "acid cure" process) and synthetic liquors of similar composition have been processed in bench-scale countercurrent tests without operational difficulty.

For treating very dilute vanadium liquors (<0.6 g V/liter, for example, those obtained in processing uranium ores where no attempt is made to encourage vanadium dissolution), it is apparent (Fig. 2.1 and 2.3) that good recoveries with reasonable solvent loadings would

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*The pH rise which occurs naturally in the bottom extraction stage (the extractant returns from the stripping circuit in the free amine form) also imposes some limitation on choice of the feed liquor pH since the liquor pH in this stage must be maintained below the point of precipitation of hydrolyzable metals, e.g., iron and aluminum. This pH rise can, of course, be prevented if desired by feeding sulfuric acid equivalent to the amine to the last stage or by converting the amine to the salt form prior to its return to the extraction system.

be possible only by operating at a pH > 1.8. The low vanadium liquors are less susceptible to precipitation than the relatively concentrated "acid cure" liquors and probably could be processed at higher pH levels, e.g., 2.0-2.3, with less difficulty.

2.2 Recovery of Thorium from Amex Carbonate Strip Solutions (W. D. Arnold)

In previous tests (ORNL-1859, -2173) thorium was stripped effectively from amines with sodium carbonate solutions. The thorium reports to the aqueous phase as a soluble carbonate complex when the carbonate excess is relatively large, but, with smaller amounts of carbonate, some thorium precipitates in the stripping system. The stripped thorium was essentially completely precipitated under certain test conditions. In batch tests, this precipitate has settled rapidly in the aqueous phase and did not cause emulsions, suggesting that operation with a low carbonate excess, i.e., allowing thorium precipitation, may be possible. This possibility is being studied in continuous contacting equipment. If operational feasibility can be established, this reaction would provide a direct and economical method of recovering thorium from the solvent.

If operational difficulties are encountered, it may prove necessary to strip with excess carbonate and avoid thorium precipitation in the stripping system, and therefore some studies have recently been made of thorium precipitation from carbonate strip solutions. Thorium recovery was effective when caustic was added to pH 12-13 or when sulfuric acid was added to pH 5-6.

The pregnant strip solution (18.5 g Th, 0.07 g U, 46 g CO_3 and 40 g SO_4 per liter) used in the precipitation tests was produced in a continuous run in which a monazite liquor was extracted with Primene JM-T--kerosene and the thorium was stripped with 1 M Na_2CO_3 solution, using a sufficient excess of carbonate to avoid thorium precipitation.

Precipitation by Addition of Caustic. Approximately 93% of the thorium was precipitated when caustic was added to the solution to pH 11.9 (1.1 lb NaOH/lb ThO_2) and the solution was digested for 0.5 hr (Table 2.1). Thorium recovery decreased to 87% when the digestion time was extended to 18 hr. At pH > 13 (1.3 lb NaOH/lb ThO_2), recovery in all tests was >99.9%. Filtration of the rather gelatinous precipitates was extremely slow.

The thorium product, precipitated at pH 11.9 and digested for 0.5 hr, apparently was principally the basic carbonate salt, analyzing 72% ThO_2 and 16% CO_3. The carbonate content decreased to 12% with increase in digestion time to 18 hr. Thorium was almost completely separated from uranium, the U_3O_8 content of the product being <0.01%. Products precipitated at pH > 13 contained 80-84% ThO_2 and 9-11% CO_3. The U_3O_8 content of the product was 0.12-0.18%. In all tests the sulfate content of the products was low (1% or less). Thorium was very favorably separated from uranium (<0.01% U_3O_8 in product) at pH 11.8.

Table 2.1 Precipitation of Thorium from Carbonate Strip Solutions with Sodium Hydroxide

Carbonate strip solution: 18.5 g Th, 0.07 g U, 46 g CO_3, and 48 g SO_4 per liter at pH 9.0

Procedure: thorium precipitated with 10% NaOH from three portions of the strip solution by addition of 0.21, 0.26, and 0.30 lb NaOH/lb ThO_2, respectively; samples of precipitate slurries withdrawn after 0.5, 2, and 18 hr, filtered, washed with water, dried at 110°C, and analyzed

lb NaOH Added per lb ThO_2	Digestion Time, hr	pH of Filtrate	Th precipitated, %	Dried Product, %			
				ThO_2	U_3O_8	SO_4	CO_3
1.1	0.5	11.9	93.4	72	-	1.0	16
	2	11.8	92.6	76	<0.01	<0.2	14
	18	11.7	86.9	80	0.01	<0.2	12
1.3	0.5	>13	>99.9	80	0.12	<0.2	11
	2	>13	>99.9	82	0.12	<0.2	11
	18	>13	>99.9	84	0.17	<0.2	9
1.5	0.5	>13	>99.9	82	0.17	<0.2	11
	2	>13	>99.9	82	0.18	<0.2	10
	18	>13	>99.9	81	0.17	<0.2	10

In use of the caustic precipitation method some recycle of the barren filtrate would, of course, be possible after conversion of the excess NaOH to Na_2CO_3 by addition of $NaHCO_3$. The amount of recycle, however, would be limited by sodium sulfate build-up in the system.

Precipitation by Neutralization with Sulfuric Acid. Greater than 99.9% of the thorium was precipitated by adjusting the strip solution pH to 6.0 with sulfuric acid (1.7 lb H_2SO_4/lb ThO_2) and digesting for 0.5 hr (Table 2.2). As the digestion period was lengthened, the solution pH rose (owing to evolution of CO_2) and thorium recoveries decreased. When the solution was adjusted initially to pH 5.3 (2.1 lb H_2SO_4/lb ThO_2) or pH 4.5 (2.3 lb H_2SO_4/ lb ThO_2), recoveries were not sensitive to the digestion time, being in all cases greater than 99.9%. In contrast to the very poor filtration characteristics of the precipitates obtained by caustic addition, the precipitates in these tests were granular and filtered readily.

Table 2.2 Precipitation of Thorium from Carbonate Strip Solutions by Neutralization with Acid

Carbonate strip solution: 18.5 g Th, 0.07 g U, 46 g CO_3, and 48 g SO_4 per liter at pH 9.0

Procedure: three portions of strip solution adjusted to pH 6.0, 5.3, and 4.5, respectively, with 10% H_2SO_4 to precipitate thorium; samples of precipitate slurries withdrawn after 0.5, 2, and 18 hr digestion, filtered, washed with water, dried at 110°C, and analyzed

lb H_2SO_4 Added per lb ThO_2	Digestion Time, hr	pH		Th Precipitated, %	Dried Product, %			
		Slurry	Filtrate		ThO_2	U_3O_8	CO_3	SO_4
1.7	0	6.0	-	-	-	-	-	-
	0.5	6.7	7.2	>99.9	73	<0.01	19	<0.2
	2	7.8	7.8	98.9	73	<0.01	19	<0.2
	18	8.9	8.9	93.8	68	0.02	19	2.7
2.1	0	5.3	-	-	-	-	-	-
	0.5	5.9	6.2	>99.9	79	0.16	12	<0.2
	2	6.9	7.4	>99.9	77	0.14	15	<0.2
	18	7.6	7.6	>99.9	77	0.09	13	<0.2
2.3	0	4.5	-	-	-	-	-	-
	0.5	5.2	6.0	>99.9	78	0.15	8	7.2
	2	6.0	6.5	>99.9	78	0.19	7	7.5
	18	6.8	6.8	>99.9	77	0.18	7	6.9

The ThO_2 content of the products was 68-79%. At the higher pH levels, the precipitates were principally the basic carbonate salt and contained little or no sulfate. The carbonate content decreased with increasing acid addition. At the lowest pH levels, the products contained approximately 7% CO_3 and 7% SO_4. The thorium was separated

very effectively from the uranium in the test in which the pH was adjusted initially to 6.0, the U_3O_8 content of the product being <0.01-0.02%.

2.3 Oxidation of Iron(II) by Air in the Dapex Systems (F. J. Hurst)

In the Dapex vanadium process, a relatively high extraction pH (1.5-2.2) and extractant concentration (0.2-0.4 M) are used to achieve efficient vanadium extraction. Since ferric iron is extracted very readily under these conditions, nearly all the iron must be reduced (with metallic iron) to the nonextractable ferrous state prior to the extraction. This provides an adequate solution to the problem provided appreciable amounts of iron are not oxidized as the liquor passes through the extraction system.

Appreciable air oxidation of Fe(II) to Fe(III) in the acidic sulfuric acid liquors would not be expected under ordinary circumstances. However, experiments conducted some time ago (ORNL-1903) suggested that oxidation was more liable to take place in a solvent extraction system comprised of the liquor and a solvent containing an organophosphorus acid extractant dissolved in kerosene. In view of these tentative results, further studies have been made to determine whether air oxidation of iron(II) is an important process consideration in the Dapex vanadium extraction system. In process practice, some contact with air would occur during mixing of the phases and in their transfer between stages, particularly if air lifts are utilized.

In the first test, a synthetic liquor (2.6 g Fe(II), 0.01 g Fe(III), 2.5 g Al, and 50 g SO_4 per liter, pH 2.2) was placed in a baffled beaker equipped with a stirrer, bottom air inlet tube, and heating jacket. Air was bubbled up through the solution at a fairly rapid rate while it was being stirred vigorously at room temperature. Evaporation losses were kept below 1% by presaturating the air with moisture. Analyses of the liquor after 10 and 30 min showed essentially no oxidation (<1%) of the ferrous iron under these conditions.

Aeration Time, min	Temp, °C	Fe(III) in aerated sol'n, g/liter	Fe Oxidized, %
10	25	0.02	<1
30	25	0.02	<1

Similar tests were then performed in which organic was added to the mixer along with the liquor. Both kerosene alone and 0.25 M D2EHPA-kerosene solutions were examined, the volume of organic added being half that of the aqueous. For comparison, tests were also included wherein the phases were contacted by vigorous shaking in a separatory funnel under an argon atmosphere.

Organic	Phases Aerated?	Contact Time, min	Temp, °C	Fe(III), g/liter Aqueous	Fe(III), g/liter Organic	Fe Oxidized, %
Kerosene	Yes	10	45	<0.01	-	<1
0.25 M D2EHPA in kerosene	Yes	10	25	<0.01	0.22	4.1
		10	45	<0.01	0.34	6.5
		30	45	<0.01	0.38	7.3
0.25 M D2EHPA in kerosene	No*	30	25	0.02	0.07	1.7
		30	45	<0.01	0.10	1.9

*Contact made in a separatory funnel under an argon atmosphere.

Iron was <1% oxidized when air was mixed with the liquor and kerosene for 10 min at 45°C. However, with di(2-ethylhexyl)phosphoric acid (D2EHPA) added to the system, oxidation was appreciable. In this case, the oxidized iron transferred to the organic phase and analyses confirmed that the extracted iron was in the ferric state. The rate of oxidation increased with increase in temperature. In 10 min, 4.2% of the iron was oxidized at 25°C and 6.3% at 45°C. At the latter temperature, extending the contact time to 30 min increased the amount of oxidation to 7.3%. Contacting of D2EHPA-kerosene with the liquor under an argon atmosphere for 30 min at 25°C or 45°C resulted in some oxidation although the amount was relatively small (1.7-1.9%) and might be attributed to the presence of oxygen impurity in the argon or to incomplete purging of the contacting vessel.

The above data cannot be interpreted quantitatively in terms of a process operation. Air was fed directly to the mixer, and it is safe to assume that the contact with air was more extensive than would occur in a properly designed process mixer and that the amount of oxidation observed therefore represents an extreme. Contact with air was also much more intimate than would be expected in intrastage transfer (from mixer to settler) of the mixed phases with air lifts.

3.0 ENGINEERING STUDIES

In addition to the studies described below, engineering studies during the month have included: (1) measurement of the stage efficiency of the baffled tank mixer for uranium extraction in the Dapex process, (2) phase separation tests in a scale model mixer-settler unit, and (3) recovery of entrained organic in a gravity settling tank.

3.1 Batch Kinetic Studies of Vanadium and Iron Extraction in the Dapex Process (F. L. Daley)

The kinetics of uranium extraction from different leach liquors were reported previously (ORNL-2388). Below are reported the results

of survey tests for the extraction of vanadium(IV) and iron(III) by Dapex-type solvent from a uranium-barren liquor. Rates of extraction were measured as a function of power input in 6- and 12-in-dia mixers.

All tests were made in the same mixer tanks described in ORNL-2269, and the impellers were flat-bladed turbines with six blades. The organic solvent was 0.24 M di(2-ethylhexyl)phosphoric acid in kerosene containing 50 g of tributylphosphate per liter and the composition of the aqueous feed, g/liter, was 0.94 V(IV), 0.22 Fe(III), 3.0 Al, 50 SO_4, and 1.9 PO_4 at pH 1.8.

The rate constant, K', was calculated from the vanadium (or iron) concentrations in the aqueous phase in the same way as described for uranium extraction in ORNL-2269. Test data are shown in Table 3.1. For comparison of the rate of extraction at different phase ratios, the rate constant was multiplied by the fraction of aqueous phase present in the mixer, yielding K'R/V, where R was the volume of aqueous and V was total volume of the mixer. The rate constants for the 6-in. mixer and 3-in. turbine were adjusted for D/T effect so that all of the values of K'R/V in Table 3.2 and Fig. 3.1 are at a D/T ratio of 1/3.

Correlation of the rate constants with power input (Fig. 3.1) shows very similar curves for uranium, vanadium, and iron. The slope of each curve is about 1/3, showing that the rate of extraction is dependent on the cube root of power input for both 6- and 12-in. mixers. The relative position of the curves shows that the rate of vanadium extraction is lower than that of uranium and that the iron rate is about one order of magnitude lower. For example, at a power input of 30 hp per 1000 gal, the values of K'R/V are 1.62 for uranium, 0.95 for vanadium, and 0.11 for iron.

Direct comparison of the rate constants at a phase ratio (aq/org) of 1/1 vs 4/1 shows that the rates of vanadium and iron extraction are 10% greater at 1/1. The rate of extraction was not affected by the type of dispersion, being the same for both oil-in-water and water-in-oil dispersions at a phase ratio of 1/1. These results are in agreement with the previously reported kinetics of uranium extraction (ORNL-2269 and -2388).

The batch values of K'R/V can be used to calculate the stage efficiency* of the mixer operated with continuous countercurrent flow. With the mixing conditions recommended for uranium extraction, 30 hp per 1000 gal and 2 min residence time for an aqueous/organic ratio of 1/1 or 3.2 min for an aqueous/organic ratio of 4/1, the calculated stage efficiency is 87% for uranium, 79% for vanadium, and 31% for iron. Increasing the power input and/or the residence time will increase the stage efficiency for each metal.

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*$K'R/V = \frac{E}{1-E} \frac{1}{\theta} \frac{R}{V}$ where E is stage efficiency, θ is residence time of dispersion in the mixer, and R/V is the volume fraction of aqueous in the mixer.

Table 3.1 Vanadium and Iron Concentrations in Raffinates VS. Mixing Times

Test No.	0 sec	5 sec	10 sec	20 sec	30 sec	45 sec	60 sec	120 sec	240 sec	480 sec	960 sec	K', min^{-1}
Vanadium Concentration, g/liter												
151	0.94	0.91	0.89	0.85	0.81	0.76	0.71	0.60	0.49	0.43	-	0.536
153	0.94	0.81	0.78	0.74	0.70	0.65	0.60	0.48	0.43	0.44	-	0.952
155	0.94	0.77	0.72	0.66	0.60	0.54	0.51	0.46	0.46	0.50	-	1.89
159	0.94	0.77	0.76	0.70	0.66	0.59	0.55	0.46	0.42	0.44	-	1.11
161	0.94	0.75	0.71	0.65	0.59	0.55	0.50	0.43	0.42	0.45	-	1.50
177	0.99	0.70	0.62	0.49	0.40	0.31	0.26	0.18	0.17	0.20	-	1.93
179	1.00	0.59	0.55	0.46	0.39	0.31	0.26	0.19	0.18	0.20	-	1.93
Iron(III) Concentration, g/liter												
151	0.22	-	0.215	0.210	0.210	0.200	0.200	0.188	0.171	0.151	0.132	0.087
153	0.22	-	0.205	0.200	0.200	0.200	0.190	0.175	0.159	0.133	0.110	0.115
155	0.22	-	0.200	0.188	0.186	0.180	0.168	0.156	0.133	0.105	0.074	0.182
177	0.22	-	0.198	0.192	0.177	0.163	0.157	0.122	0.082	0.041	0.012	0.228
179	0.22	-	0.189	0.181	0.175	0.164	0.154	0.122	0.080	0.039	0.013	0.228

Table 3.2. Vanadium and Iron Extraction Rates

Run No.	Phase Ratio (a/o)	Mixer-Dia, in.	Turbine Dia, in.	Turbine Speed, rpm	Power Input, hp/1000 gal	K', min^{-1}, x R/V Vanadium[a]	K', min^{-1}, x R/V Iron[a]
151	4/1	6	3	262	2.5	0.47	0.077
153	4/1	6	3	524	20	0.84	0.102
155	4/1	6	3	1170	220	1.66	0.160
177	1/1	6	3	524	20	1.06	0.126
179[b]	1/1	6	3	524	20	1.06	0.126
159	4/1	12	4	647	20	0.89	-
161	4/1	12	4	970	67	1.20	-

[a] Calculated at D/T = 1/3.

[b] Water-in-oil dispersion.

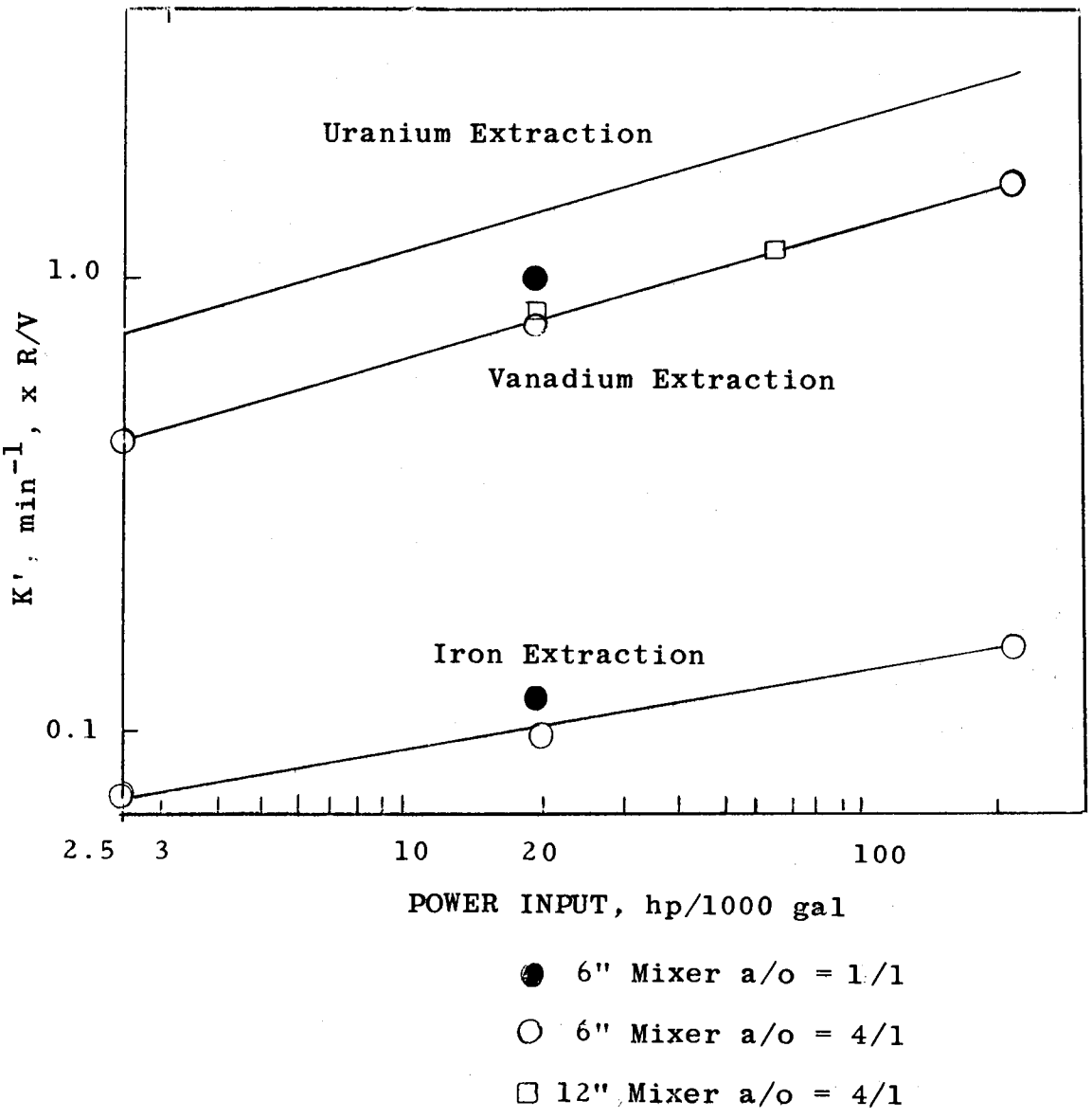

Fig. 3.1 Rate Constants in Dapex Process Batch Extractions

4.0 FUNDAMENTAL STUDIES

In addition to the work described below, fundamental studies during the month have included (1) measurements of aggregation of amine salts and uranyl-amine salt complexes by light scattering, (2) measurement of dielectric constants of organic solutions of amine salts, (3) measurement of uranium and water distribution between aqueous sulfate solutions and synergistic extractants, and (4) examination of dialkylphosphoric acid--phosphine oxide association by isopiestic measurements.

4.1 Interaction Between the Components of Synergistic Extractants (H. T. Baker, C. F. Baes, Jr.)

As previously described (ORNL-2346, p. 4), the synergistic enhancement of U(VI) extraction by a dialkylphosphoric acid on addition of an organophosphorus ester or a phosphine oxide goes through a maximum as the concentration of the neutral component is increased. From this behavior it has been assumed that at least two equilibria involving the neutral additive occur, one leading to a complex with both U(VI) and $(RO)_2PO_2H$, and the other to competing complex with the $(RO)_2PO_2H$ only. The first is being studied by means of uranium extraction measurements, and the second by infrared spectrophotometry.

Di(2-ethylhexyl)phosphoric acid (D2EHPA), in n-octane solution, is the acid component used in the infrared measurements to date. In previous tests, isopiestic molecular weight measurements showed that D2EHPA is dimerized in n-hexane solutions, at least in the concentration range 0.025-2 M. Similar measurements confirmed that it is also dimerized in the n-octane solutions. Infrared absorption by the phosphoryl band at 1233 cm^{-1} was found to conform to Beer's law over the concentration range 0.001-0.1 M. The experimental error was estimated to be around ±10% at 0.001 M, and not more than ± 1% at concentrations above 0.005 M. Since dissociation of the D2EHPA dimers on dilution would be expected to cause a shift of this band to higher frequencies, these results indicate that there is probably less than 20% dissociation at 0.001 M and less than 2% at 0.005 M.

Comparison of the infrared spectra of water-free octane solutions of the components alone and intermixed showed evidence of some interaction between D2EHPA and TBP (Fig. 4.1) and of considerable interaction between D2EHPA and tri-n-octylphosphine oxide (TOPO) (Fig. 4.2). All solute concentrations were 0.5 M. The dashed curve in each figure shows the calculated combined absorption that would be expected if no interaction occurred, for comparison with the curve actually found. While the differences between the curves for D2EHPA-TBP were small, differences between the curves for D2EHPA-TOPO were large enough to permit quantitative measurements.

Investigation of the D2EHPA-TOPO interaction by the method of continuous variations (Fig. 4.3) indicated an association product

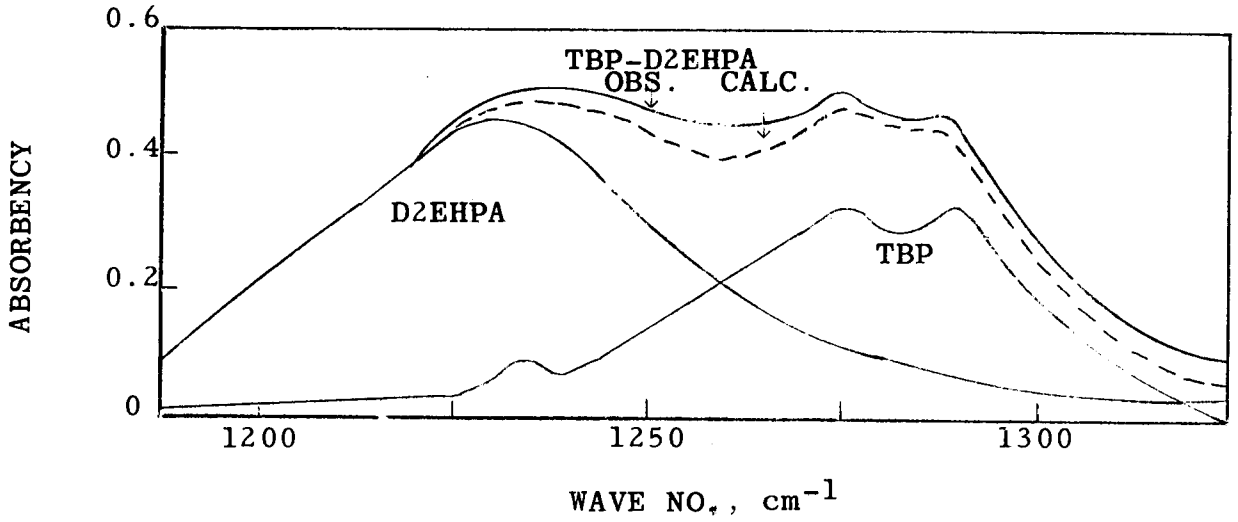

Fig. 4.1 Infrared spectra of di(2-ethylhexyl)phosphoric acid, tributylphosphate, and mixture, each solute at 0.5 M in n-octane.

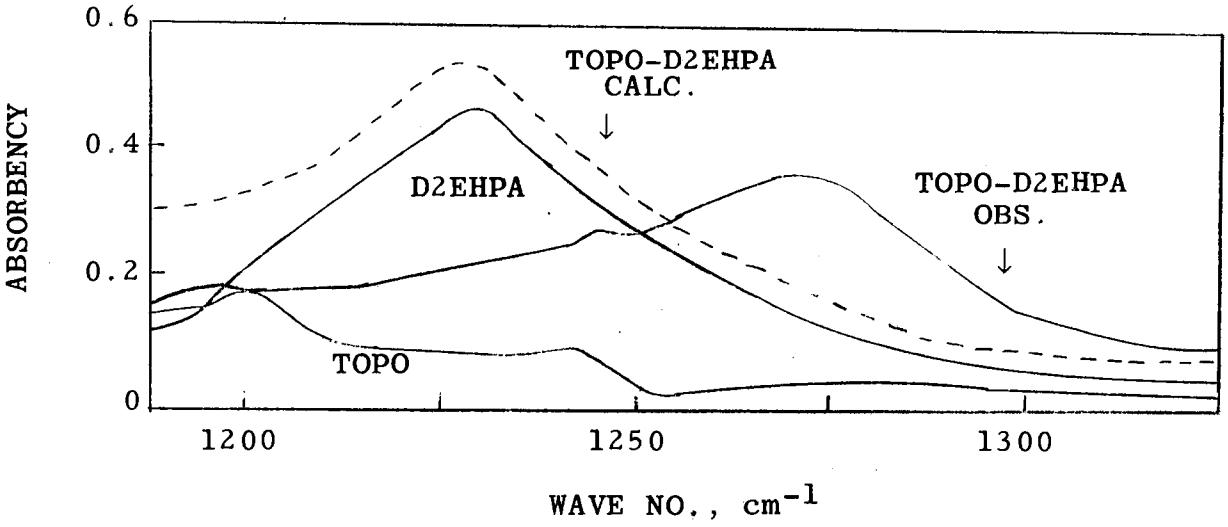

Fig. 4.2 Infrared Spectra of di(2-ethylhexyl)phosphoric acid, tri-n-octylphosphine oxide, and mixture, each solute at 0.5 M in n-octane.

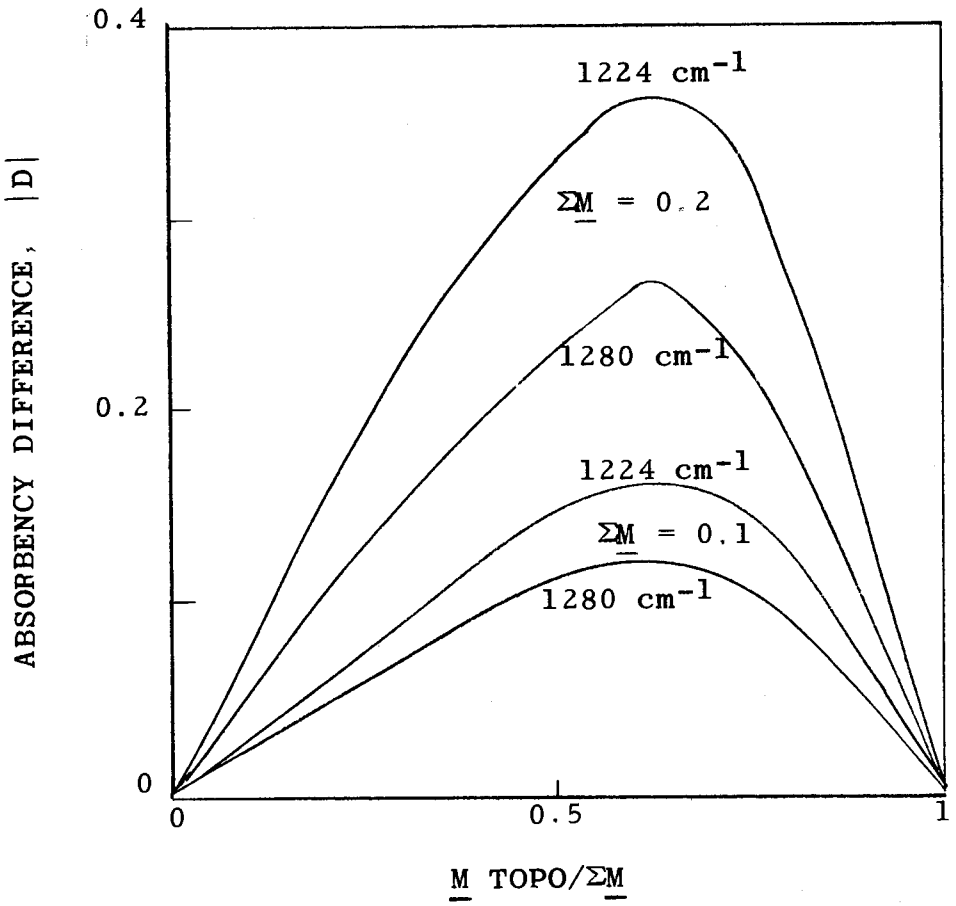

Fig. 4.3 Continuous Variation Plots for TOPO + D2EHPA in n-octane at 25°C, absolute value of difference between calculated and measured absorbency vs mole fraction TOPO, with total molarity ΣM = [TOPO] + [D2EHPA dimer] held constant.

at a TOPO/(D2EHPA dimer) mole ratio of 2/1, or TOPO/D2EHPA = 1/1. In these tests, the difference, D, between observed and calculated absorbency was plotted as a function of the mole fraction, M, TOPO/(M dimer + M TOPO), the total concentration, M dimer + M TOPO, being held constant. D should be maximum at the mole ratio corresponding to the stoichiometry of the association product, provided only one association product is formed. The similarity between the curves at 0.2 and 0.1 M total concentration, and in each series between the results at 1224 cm^{-1} (phosphoryl band of the D2EHPA dimer) and at 1280 cm^{-1} (the new band), support the assumption that only one association product is formed in appreciable amounts.

If the 1/1 interaction product contains only one molecule of each component, it is reasonable to assume tentatively that it is formed by hydrogen bonding between the hydroxyl of the acid and the phosphoryl oxygen of the phosphine oxide: $(RO)_2\overset{O}{P}\text{-}OH\text{--}O{=}PR_3$. Here the phosphoryl bond not involved in the hydrogen bonding would be expected to absorb at a frequency higher than the 1233 cm^{-1} found for the hydrogen-bonded phosphoryl groups in the D2EHPA dimer. Hence, the appearance of the new band at ~1280 cm^{-1} appears consistent with this tentative structure.

4.2 Determination of Molecular Weights of Amine Species in Benzene Solution by Light Scattering (K. A. Allen)

In continuation of the light-scattering measurements as previously described (ORNL-2380, -2399), average molecular weights were found indicating aggregation numbers of 2 for tri-n-octylamine bisulfate, ~11 for 1-(3-ethylpentyl)-4-ethyloctylamine normal sulfate, and 15-20 for N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine normal sulfate (Fig. 4.4 and Table 4.1).

The existence of tri-n-octylamine bisulfate in as small a group as a dimer instead of in a larger aggregate is consistent with the existence of its normal sulfate as a monomer (determined by light scattering and confirmed by isopiestic measurement, ORNL-2399). As in the measurements with the normal sulfate, the correction for depolarization of the scattered light was unusually large; however, its reproducibility was good, and it is estimated to have contributed less than 20% uncertainty to the molecular weight. Measurements with tri-n-octylamine sulfate and bisulfate in an aliphatic diluent are planned, but relatively more experimental difficulty is expected because of the smaller difference in refractive index between solute and solvent.

Depolarization ratios with the other two amine sulfates (Table 4.1) were too low to be measured, so that no correction was required. The rather wide range of uncertainty for the last solute resulted from the small but relatively important uncertainty in the very small slope of the scattering vs. concentration curve (Fig. 4.4).

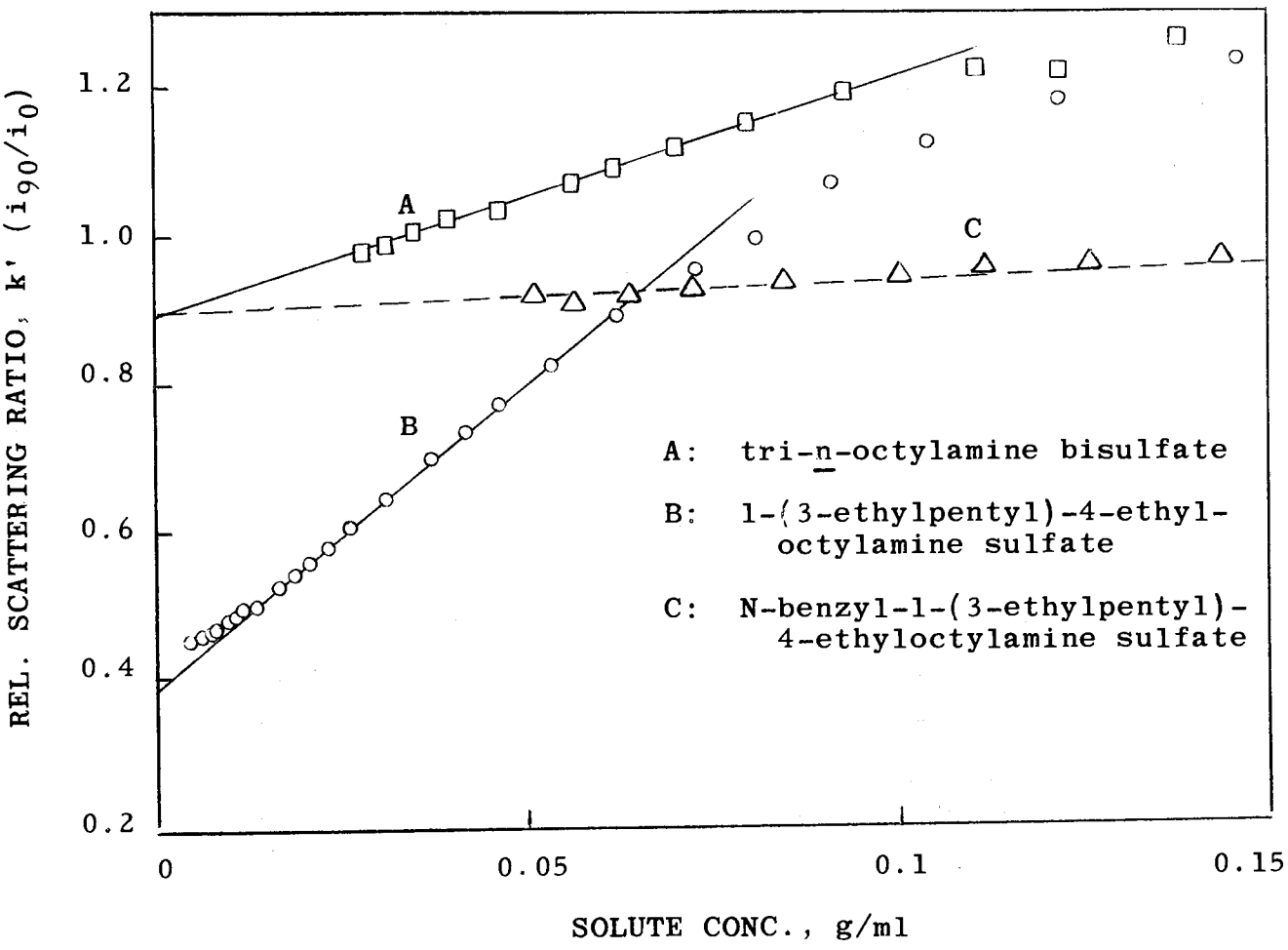

Fig. 4.4 Change of relative light scattering ratio with change of solute concentration. Slope (a) and intercept (b) used in Table 4.1.

Table 4.1 Molecular Weights of Amine Species in Benzene Solution

From light scattering at 546 mμ

$$M = \left(\frac{2.68 \times 10^{-4}}{H}\right)\left(\frac{a}{b}\right)\left(\frac{6-7\rho}{6+6\rho}\right)$$

Solute[a]	A	B	C
Formula Weight	452	608	792
Refr. Index Incr. $(\partial n/\partial c)$	-0.0462	-0.0768	-0.00524
Optical Const. (H)[b]	2.98×10^{-7}	8.20×10^{-7}	7.28×10^{-9}
Slope (a)[c]	3.2	8.2	0.33 - 0.39
Intercept (b)[c]	0.89	0.39	0.91 - 0.90
Depol. Ratio (ρ)[d]	0.5 ± 0.05	negl.	negl.
Mol. Wt. (M)	750-1050	6800	13,000-16,000
Aggregation Number (n)[e]	2	~11	15-20

[a]Solutes: A, tri-n-octylamine bisulfate
B, 1-(3-ethylpentyl)-4-ethyloctylamine sulfate
C, N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine sulfate

[b]$H = (5.49 \times 10^{-22}/\lambda^4) n^2_{solv} (\partial n/\partial c)^2$

[c]Slope (a) and intercept (b) from plots of relative scattering ratio vs. concentration, Fig. 4.4.

[d]Ratio of horizontally to vertically polarized components of the 90°-scattered light.

[e]Average number of monomeric units per aggregate, M/formula weight.

5.0 RARE EARTH SEPARATIONS

(Boyd Weaver, F. A. Kappelmann)

The rare earth separation program has recently been transferred from the former Stable Isotopes Division. It originated from the need for unusual amounts of several of the rare earths of high purity as charge materials for the separation of their isotopes by the electromagnetic process. It has also supplied numerous and various rare-earth materials to other programs of the laboratory. Progress has been reported in unclassified periodic reports of the Stable Isotopes Division (ORNL-1617, p. 29; ORNL-2028, p. 39; ORNL-2114, p. 34; ORNL-2236, p. 15), topical reports (ORNL-1408, -1409, and -1811), and a publication (J. Am. Chem. Soc. 75, 3943 (1953)). Most of the effort has been applied to investigation of the behavior of rare-earth nitrates in nitric acid--tributyl phosphate systems and the use of multistage liquid-liquid extraction equipment for the separation of kilogram quantities of several of the rare earths.

Results of experience in this laboratory and elsewhere are summarized in the following qualitative statements as background to this and subsequent reports.

1. Distribution coefficients (E_a^o) of dilute individual rare-earth nitrates increase with HNO_3 concentration.

2. With low acidities the order of extractability varies with the acidity. The distribution coefficients increase with increasing atomic number to a maximum and then decrease. The element of maximum extractibility appears to be gadolinium in neutral solutions, holmium in ~4 M HNO_3. With acidities above ~6 M HNO_3, the point of maximum extractability reaches the end of the series, i.e., the distribution coefficients increase in the order of increasing atomic number throughout.

3. With high acidities, distribution coefficients of individual rare earths decrease with increasing salt concentration. This effect increases with atomic number. The practical effect is that constant operating lines cannot be set up for multistage extraction separators without external reflux. In practice, kilogram quantities of neodymium, samarium, and gadolinium oxides with reasonable degrees of purity were produced without too much labor. The increased difficulty of purifying dysprosium and the heavier elements cannot be accounted for solely by their relatively lesser abundances.

4. Addition of external reflux devices to extraction equipment makes it possible to maintain essentially constant salt and acid concentrations throughout the system. Therefore, with a given solvent flow ratio there is uniform separation in all stages. External reflux also makes it possible to operate extraction systems with salt concentrations near the saturation point, thus attaining maximum throughput.

5. The high separation factors characteristic of saturated solutions can be maintained in multistage systems with double external reflux.

6. The separation factor between a pair of elements at saturation in a highly acid system appears to be well represented by the ratio of the individual distribution coefficients measured at very low salt concentrations.

Single-Stage Separations. Distribution and separation of the gadolinium-samarium pair have been studied by analysis of the contents of both phases in equilibrium when the aqueous phase is saturated with a mixture of the two nitrates. Acidity was varied from zero to 16 M HNO_3. Samples were converted to oxide and analyzed spectrographically. Separation factors calculated from the ratios of gadolinium to samarium in the two phases (Fig. 5.1) indicate that gadolinium is extracted preferentially from saturated neutral nitrate solutions with a separation factor of about 1.1 and that the separation factor increases gradually to nearly 3 at 16 M HNO_3. Above this point the mutual miscibility of the two phases decreases the separation factor.

Pilot-Plant Developments. Systems with double external reflux have been developed in which the rare-earth content of the aqueous effluent is concentrated by evaporation and returned to the system by extraction by the entering organic phase, while the rare earth content of the organic effluent is stripped out, concentrated by evaporation, and returned in the entering aqueous phase. Distribution of the constituents of an yttrium-earth mixture between the two ends of a 17-stage mixer-settler system at total reflux was:

	Composition of End Stages, %	
	Aqueous Effluent	Organic Effluent
Y_2O_3	95	4.2
Er_2O_3	2.1	-
Tm_2O_3	0.4	0.4
Yb_2O_3	2.7	75
Lu_2O_3	-	20

The system was operated at near saturation in 14 M HNO_3 with relative flow rates adjusted so as to split the mixture between erbium and ytterbium.

A separations pilot plant has been constructed which consists of 81 pump-mixer-settler separation stages with auxiliary pumps, evaporators, and flow lines for double external reflux. This system, loaded with rare earths at saturation in 14 M HNO_3 and undiluted tributylphosphate, was operated at total reflux until equilibrium was attained. After 150 hr, analyses of the aqueous phase at 10-stage intervals showed the following distribution:

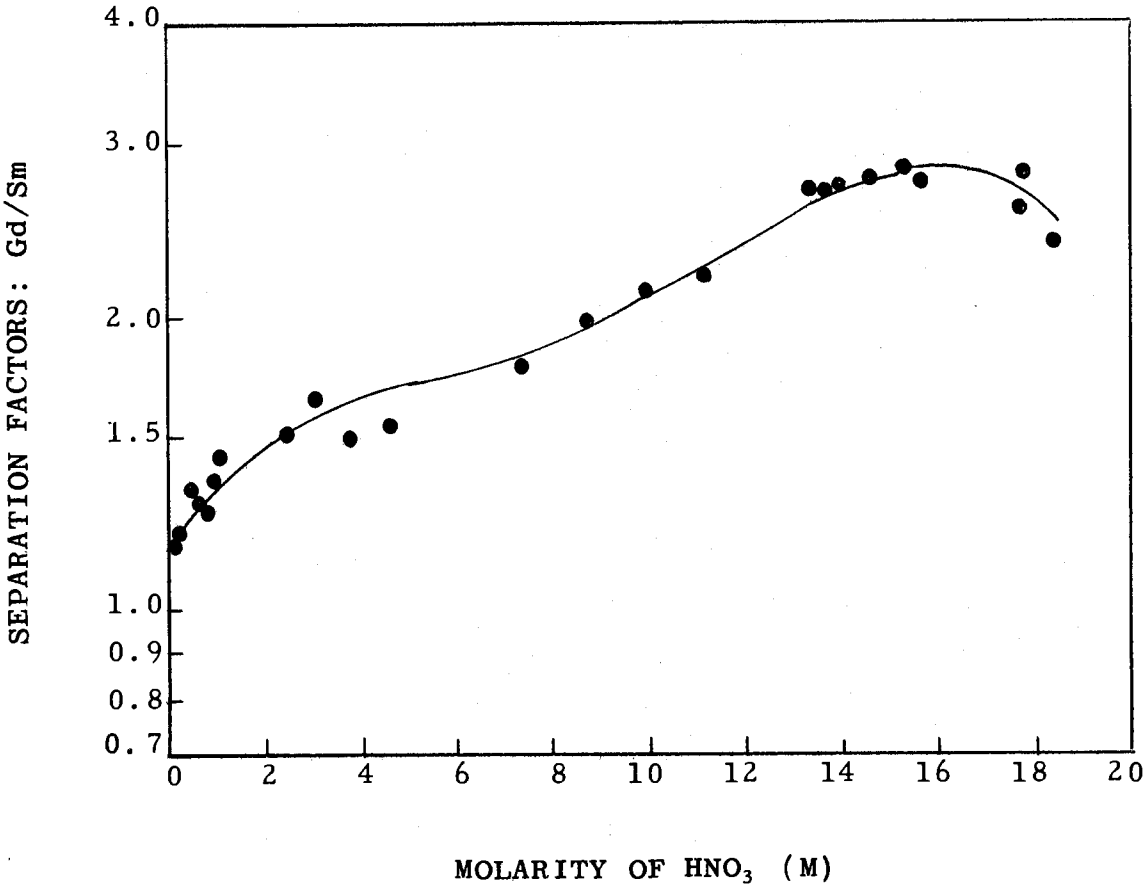

Fig. 5.1 Gadolinium-Samarium Separation in Saturated Solutions

Stage No.	Composition, %							
	Gd_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Y_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3
1	3.1	3.5	0.8	4.5	85	2.2	0.4	
11				2.6	91	5.2	1.7	
21					20	12	68	
31					T	1.9	98	T
41							99	1
51							97	2.9
61							92	8.2
71							76	24
81							43	57

Single-stage separation factors calculated from these data are: Lu/Yb, ~1.2; Yb/Tm, ~1.3; Tm/Y, 1.08; and Y/Er, 1.08. This places yttrium, which is not a lanthanon, midway between erbium and thulium.