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PROGRESS REPORT ON RAW MATERIALS

FOR AUGUST, 1957

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

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CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT ON RAW MATERIALS

FOR AUGUST, 1957

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

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

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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.

OTHER REPORTS IN THIS SERIES

Preliminary, ORNL-2268 (20¢)
February, ORNL-2269 (25¢)
March, ORNL-2306 (25¢)
April, ORNL-2346 (25¢)
May, ORNL-2366 ($0.25)
June, ORNL-2380 ($1.00)
July, ORNL-2388 (75¢)

ABSTRACT

Systematic Studies. A mixture of 0.1 M dibenzylamine and 0.1 M bis(1-isobutyl-3,5-dimethylhexyl)amine in benzene extracted uranyl sulfate from 1 M sulfate solution, pH 1, with an extraction coefficient of 250, in comparison with coefficients of <0.3 and 20, respectively, by 0.1 M solution of the separate amines. None of several other related amine mixtures showed similar enhancement.

Some changes in the method for preparing tri-n-octylphosphine oxide shortened the time of preparation and improved the overall yield, with perhaps some improvement in purity. These included oxidation of certain impurities with cold neutral permanganate instead of with air at high temperature, removal of acidic impurities with activated alumina instead of with alkaline aqueous solution, and elimination of vacuum distillation.

Process Development. A new tertiary amine, tris(tridecyl)amine, was shown to be an extractant of potential use in Amex processing. Uranium extraction coefficients for the amine in kerosene diluent were higher by a factor of 2 than those obtained in 97% kerosene--3% tridecanol diluent.

Several methods were briefly studied for limiting the phosphate content of Dapex vanadium products to the specification limit of 0.05% phosphorus. Most favorable results were obtained by precipitating the vanadium as "red cake." In addition, limited success was noted in scrubbing the extract prior to stripping and in precipitating phosphate from the pregnant strip solution with zirconium prior to precipitation of vanadium with ammonia.

Engineering Studies. Scaleup factors for gravity settlers were determined for the extraction section of the Dapex uranium process. Correlation of the flow capacity of 6-, 22-, and 48-in.-dia settlers showed that the aqueous flow rate per unit cross-sectional area was

virtually independent of settler diameter when wall effects in the 6-in. settler were minimized. For water-in-oil type dispersions the aqueous flow capacity was 1.1 gpm/sq ft and for oil-in-water type dispersions the aqueous flow was 1.4 gpm/sq ft at an aqueous/organic phase ratio of 1/1 and was 4.5 gpm/sq ft at a phase ratio (aq/org) of 4/1. The flow capacity increased with increasing temperature. Wire mesh packing increased the settler capacity four-fold for water-in-oil type dispersions, but had virtually no effect on oil-in-water type dispersions.

Fundamental Studies. Molecular weight determinations by light scattering indicated that tri-n-octylamine normal sulfate is monomeric in benzene solution at concentrations up to 0.1 M, whereas acid extraction and uranium extraction equilibria had previously been interpreted as indicating aggregation at concentrations above 0.02 M. The monomeric molecular weight was confirmed by isopiestic measurements at 0.12 M.

With chloroform as the diluent, the uranium extraction coefficient varied with the square of tri-n-octylamine sulfate concentration, instead of with the first power as with the hydrocarbon diluents which have been examined.

Tri-n-octylamine extracted sulfuric acid more strongly to form the normal sulfate salt when in chloroform than when in benzene solution, although still not so strongly as does di-n-decylamine in benzene solution. The tri-n-octylamine normal sulfate extracted additional acid to form the bisulfate less strongly when in chloroform than when in benzene solution.

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) comparison of base strengths of amine-diluent combinations, (3) extraction of thorium from sulfate liquor with dialkylphosphoric acid, (4) tracer phosphorus determination of organophosphorus extractant losses and of inorganic phosphate extraction, and (5) comparative testing of phosphine oxide reagent batches.

1.1 Screening of Organonitrogen Compounds (J. G. Moore)

The uranium extraction power of several new compounds (Table 1.1) was examined as previously described (ORNL-1734, p. 6; cf. ORNL-2269). Of these, only di(2-propyl-4-methylpentyl)amine gave good extraction coefficients and phase separations, and this compound showed excessively high loss rate (> 240 mg/liter) from kerosene into a sulfate liquor. Dilauryl(2-hydroxypropyl)amine showed fair uranium extraction power in benzene but low in kerosene, and gave poor phase separation. Direct and differential titrations (Table 1.2) indicated that the secondary amine was of good and the tertiary amine of fair purity.

Table 1.1 Preliminary Tests of Uranium Extractions from Sulfate Solutions

Compound	Batch No.	Conc., M	U Extracted and Extraction Coefficient (o/a) Kerosene %	Kerosene E_a^o	Benzene %	Benzene E_a^o	Benzene Prewashed %	Benzene Prewashed E_a^o	Phase Separation
Di(2-propyl-4-methyl-pentyl)amine	311A	0.01	36	-	43	-	39	-	Good
		0.1	99	110	99	130	99	75	
Propomeen 2/12-11	313A	0.1	66	2	94	16	93	12	Very poor
Arquad 18	291A	0.1	Insol.		Insol.		Insol.		
Arquad 2C	105B	0.1	ppt		39	0.65	37	0.59	Poor
Arquad 2T	290A	0.1	Insol.		37	0.58	16	0.19	Emulsions in aqueous
Di(1-aminocyclohexyl-methyl)amine	312A	0.1	nil	-	nil	-	nil	-	Kerosene slow
O.C. No. 8[a]	314A	50 g/l	Insol.		Insol.		Insol.		
O.C. No. 30[b]	315A	50 g/l	Insol.		Insol.		Insol.		

[a]Ethoquad C/25, $[R\text{-}\overset{(CH_2CH_2O)_xH}{\overset{|}{N}}(CH_3)C_3H_6\text{-}\overset{(CH_2CH_2O)_yH}{\overset{|}{N}}(CH_3)\text{-}(CH_2CH_2O)_zH]Cl_2$, $x + y + z = 15$

[b]Arquad C - Urea Complex 30% A.I.

Table 1.2 New Organonitrogen Compounds, Assay by Direct and Differential Titration

Compound	Batch No.	Source[a]	% by Differential Titration			Equivalent Weight	
			Primary	Secondary	Tertiary	Theo.	Found
Di(2-propyl-4-methyl-pentyl)amine	311A	E	2	97	<1	270	275
Propomeen 2/12-11 $(C_{12}H_{25})_2NCH_2 \cdot CH(OH)-CH_3$	313A	A	3	9	87	412	408
Arquad 18	291A	A	-	-	-	-	343
Arquad 2C	105B	A	-	-	-	-	429
Arquad 2T	290A	A	-	-	-	-	647
Di(1-aminocyclohexyl-methyl)amine	312A	D	-	-	-	239	259

[a]A = Armour Chemical Division, Chicago
D = E. I. du Pont de Nemours and Company, Wilmington
E = Eastman Chemical Products, Kingsport, Tenn.

1.2 Uranyl Sulfate Extraction by Amine Mixtures (J. G. Moore)

In connection with the comparison of uranium extractions by amines related to N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine (ORNL-1922, p. 21; -2099, p. 2; -2380), extraction by a mixture of 0.1 M dibenzylamine and 0.1 M Amine S-24 in benzene was found to be considerably higher than by a 0.1 M solution of either amine alone (Table 1.3). This enhancement may be due to a synergistic simultaneous complexing with the two amines, or it might indicate that dibenzylamine has inherently high complexing power, not shown when alone because of high distribution to the aqueous phase. While the enhanced extraction coefficient (250) is still not strikingly high, and the dibenzylamine is lost to aqueous solutions too rapidly for this particular mixture to be of process interest, the occurrence of such an enhancement suggests both that practicable mixtures might be found and that information might be obtained to aid in the understanding of the high extraction power of particular amines. Mixtures of Amine S-24 with several other readily available benzyl amines did not show a similar large enhancement of extraction. Mixtures with the strong extractants N-benzyllauryl- and N-benzyl-n-tetradecylamine gave extraction coefficients similar to those obtained with the latter two amines alone, and mixtures with the weak extractants N-benzylisopropyl-, tribenzyl-, and N,N-dibenzyllaurylamine increased the extraction coefficient by at most a factor of 2. Mixtures of dibenzyl-, tribenzyl-, and N,N-dibenzyllaurylamine with the primary branched Amine 21F81 also gave at most a doubling of the coefficient (Table 1.4). Mixtures with related amines, e.g., di(p-alkylbenzyl)amines, will be examined similarly if they become available.

1.3 Preparation of Trioctylphosphine Oxide (W. T. Rainey, J. M. Schmitt)

During the preparation of a supply of tri-n-octylphosphine oxide reagent, some changes in the procedure were tested which shortened the time of preparation, improved the overall yield, and may have given some improvement in product purity.

The previous procedure (ORNL-1964 and ORNL-2161*) involved reaction of $POCl_3$ with excess Grignard reagent, alkaline extraction of acid by-products, hot air oxidation of "combined acid" impurities (ORNL-1964, pp. 4, 106) to free acid followed by further alkaline extraction, vacuum distillation, and recrystallization. The repeated extractions, typically giving slow-breaking emulsions, accounted for most of the handling time and for considerable reagent loss. The beneficial changes included (1) increasing the Grignard reagent excess to minimize dialkyl products, (2) oxidation by dilute neutral permanganate solution at room temperature instead of by air at ~100°C, (3) removal of acid impurities by treatment with

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*J. C. White, "The Use of Trialkyl Phosphine Oxides as Extractants in the Fluorometric Determination of Uranium," ORNL-2161, Nov. 1, 1956.

Table 1.3 Uranyl Sulfate Extraction by Mixtures of Amine S-24[a] with Benzyl Amines in Kerosene

Initial aq soln: 0.004 M U, 1 M SO_4, pH 1
Phase ratio, a/o = 1/1

Benzyl Amine	Uranium Extraction Coefficient (o/a)				
	Benzyl Amine alone, 0.1 M	0.1 M Amine S-24 + Benzyl Amine at			
		0	0.02 M	0.06 M	0.1 M
Dibenzyl	<0.3	20	40	75	250
N-Benzylisopropyl	<0.01	20	30	35	40
N-Benzyllauryl	130	20	70	150	130
N-Benzyl-n-tetradecyl	350	20	90	200	330
Tribenzyl	<0.1	20	25	20	20
N,N-Dibenzyllauryl	1.5	20	25	30	35

[a]Amine S-24 = bis(1-isobutyl-3,5-dimethylhexyl)amine

Table 1.4 Uranyl Sulfate Extraction by Mixtures of Amine 21F81[a] with Benzyl Amines in Benzene

Initial aq soln: 0.004 M U, 1 M SO_4, pH 1
Phase ratio, a/o = 1/1

Benzyl Amine	Uranium Extraction Coefficient (o/a)				
	Benzyl Amine alone, 0.1 M	0.1 M Amine 21F81 + Benzyl Amine at			
		0	0.02 M	0.06 M	0.1 M
Dibenzyl	<0.3	30	40	60	50
Tribenzyl	<0.1	30	35	45	45
N,N-Dibenzyl-lauryl	1.5	30	60	70	50

[a]Amine 21F81 = 1-(3-ethylpentyl)-4-ethyloctylamine

activated alumina instead of by extraction with alkaline solution, thus avoiding emulsions, and (4) elimination of the vacuum distillation, which may cause formation of some pyrolytic by-products. No difference was found whether reagent grade or redistilled $POCl_3$ was used, or whether the cooled reaction mixture was worked up immediately or allowed to stand overnight.

The procedure incorporating these improvements is as follows:

(1) Reflux ~5 g of 1-bromooctane with 3 moles (73 g) of magnesium, just covered with anhydrous ether, until reaction starts, then add ether to a total of 2 liters. Add the remainder of 3 moles (579 g) of 1-bromooctane dissolved in 500 ml of ether over a period of ~2 hr, maintaining reflux and vigorous stirring. Continue reflux for 1/2 hr. Decant from any solid residue.

(2) Add 0.6 mole (92 g) of $POCl_3$ in 500 ml of ether to the refluxing Grignard reagent solution over a period of ~1 hr, and continue refluxing for 1 hr. Hydrolyze the excess reagent slowly with ~200 ml of water. Filter the supernatant solution through Cellite and then wash it with dilute HCl and water to give a completely clear solution.

(3) Evaporate the ether and take up the residue in 500 ml of petroleum ether. Mix with 800 ml of 1 M neutral $KMnO_4$ solution for 1/2 hr at room temperature; then destroy excess permanganate and manganese dioxide with excess oxalic acid. Wash with dilute HCl and water, dry with Na_2SO_4, and determine the free acid content.

(4) Make up to 1 liter with petroleum ether, agitate with ~1.5 g of activated alumina for each gram of free acid (calculated as dioctylphosphinic acid, mol wt 290) for ~1 hr, and filter through Cellite. If a small amount of free acid remains, it can be extracted with 2% NaOH solution without emulsion trouble.

(5) Treat with decolorizing charcoal, and recrystallize twice from petroleum ether at -10°C.

The yield (based on $POCl_3$) obtained with this procedure was ~60% crude, and ~50% recrystallized product containing 0.2% free acid and 0.05% combined acid (for method of analysis see ORNL-1964, p. 106 or ORNL-2161, p. 23), m.p. 52°C. The elapsed time was about 2 days, operating time about 1/3 of that.

The foregoing procedure has by no means been brought to optimum conditions. Some of the possibilities for further improvement are (1) with the improved means of acid removal, a lower excess of Grignard reagent over $POCl_3$ may be suitable, (2) hydrogen peroxide might be suitable for the oxidative purification, and (3) vacuum stripping (without distillation of the phosphine oxide) might remove some significant impurities.

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 stripping method for recovering uranium from amines, (2) continued study of the compatibility of amines with liquors containing molybdenum, (3) further evaluation of the Amex process for vanadium recovery, (4) dissolution of uranium from ores by a sodium carbonate pugging treatment, (5) recovery of vanadium by adsorption on activated zirconium oxide, and (6) recovery of thorium from Amex process carbonate strip solutions.

2.1 Extraction of Uranium with Tris(tridecyl)amine (W. D. Arnold)

In previous tests (ORNL-2388) of tris(tridecyl)amine, a new amine submitted by the Union Carbide Chemicals Company, the amine distribution loss to acidic sulfuric acid leach liquors was less than 5 ppm. In contrast to most tertiary amines, this amine could be used in kerosene without addition of alcohol.

Further evaluation of the tris(tridecyl)amine as a possible Amex process extractant have now been made by measuring isotherms for the extraction of uranium from a synthetic sulfuric acid leach liquor. Kerosene, both with and without alcohol, was used as the diluent.

As shown in Table 2.1, the amine has the high uranium extraction power, relatively high uranium loadings (~5 g U/liter) and excellent selectivity with respect to ferric iron that are typical of the tertiary amines. Thus in 97% kerosene--3% tridecyl alcohol diluent, its extraction performance was nearly identical to that shown previously (ORNL-1959, -2099, -2380) by other tertiary amines in the same diluent, including tri-n-octyl, tri(iso-octyl), didodecenyl-n-butyl, mixed tertiary (n-octyl and n-decyl), and trilauryl. In kerosene diluent the uranium extraction coefficient at low uranium loading was 750, or approximately twice that with kerosene-alcohol diluent. Phase separations were rapid (<1 min) in all tests.

The initial request for a sample of the tris(tridecyl)amine was made on the basis that the long highly branched chain might provide an extractant having better compatibility with molybdenum-bearing liquors than observed with tertiary amines of shorter, less branched chains. In preliminary tests tris(tridecyl)amine was somewhat more compatible than tri-iso-octyl or the mixed octyl-decyl fatty tertiary amine, but did not seem to be as compatible as trilaurylamine. The tests are continuing.

2.2 Phosphate Content of Dapex Vanadium Products (F. G. Seeley, W. D. Arnold, A. D. Kelmers)

In the Dapex process for vanadium recovery, vanadium(IV) is extracted with 0.2-0.4 M di(2-ethylhexyl)phosphoric acid (D2EHPA) in kerosene-TBP diluent and stripped with sulfuric acid. Vanadium is then recovered from the strip solution either by neutralization with ammonia to precipitate hydrated vanadyl oxide or by oxidation with sodium chlorate to precipitate a product similar to the conventional "red cake."

Table 2.1. Uranium Extraction Isotherms for Tris (tridecyl) Amine

Initial aq soln: Synthetic Marysvale liquor - 0.15-3.0 g U, 5.8 g Fe(III), 3.3 g Al, 50 g SO_4, 2.0 g PO_4, and 1.7 g F per liter at pH 0.9

Initial org soln: 0.10 M tris (tridecyl) amine in kerosene or 97% kerosene--3% tridecanol diluent

Phase ratio, a/o = 2/1

Contact time: 5 min

Temperature: 27°C

Diluent	U, g/liter Head Liquor	U, g/liter Org	U, g/liter Aq	Fe in Organic g/liter	U Extraction Coefficient (E_a^o)
Kerosene	0.15	0.3	0.0004	0.017	750
	0.30	0.6	0.0009	0.015	670
	0.60	1.3	0.003	0.012	430
	1.0	2.0	0.005	0.009	400
	1.25	2.5	0.008	0.007	310
	1.5	3.1	0.012	0.005	260
	2.0	4.0	0.035	0.002	110
	3.0	4.9	0.52	0.001	9
97% kerosene--3% tridecanol	0.15	0.3	0.0008	0.006	370
	0.30	0.6	0.002	0.004	300
	0.60	1.2	0.004	0.003	300
	1.0	1.9	0.009	0.002	210
	1.25	2.3	0.018	0.002	130
	1.5	3.0	0.027	0.002	110
	2.0	3.9	0.084	0.001	46
	3.0	4.7	0.56	0.001	8

The latter products, in almost all known cases, have met market specifications with regard to vanadium grade and impurity content provided the precipitate is washed sufficiently to remove sulfate. In a few cases the phosphate content was greater than allowable, i.e., 0.05% P based on contained V_2O_5. However, in the ammonium precipitation method, products containing more phosphate than the specified limit have been the rule rather than the exception. This has been found in tests by the Kerr-McGee Oil Industries* and the Climax Uranium Company*, and has been confirmed by more recent studies in this laboratory.

Since the ammonium precipitation method, without the handicap of phosphate contamination, could have advantages in some process schemes from the standpoint of operation and product marketing, studies have been initiated at Oak Ridge National Laboratory to determine the mechanism by which phosphate enters the product and, if possible, to devise methods for controlling the phosphate content. The red cake precipitation method already seems to be an acceptable operating procedure. However, some further studies are also being made of this method to better establish its dependability in meeting phosphorus decontamination requirements under a variety of operating conditions.

2.2.1 Sources of Phosphate Contamination

Both organic phosphate derived from the extraction reagents and inorganic phosphate in the leach liquor may contribute phosphate to the product.

Organic Phosphate. The strip solution may become contaminated with phosphate during stripping as a result of physical entrainment of the solvent in the aqueous phase or of solubility distribution of the organophosphorus components from the solvent to the strip liquor. These organophosphorus components could be the D2EHPA extractant, the TBP additive, lower molecular weight organophosphorus components present as impurities in the original reagents,** or hydrolysis products of the D2EHPA and TBP.

Available information on the chemistry of reagents and on the system in which they are used suggests that the most important source of phosphate contamination would be the low molecular weight impurities. On the other hand, only a small amount of phosphorus is required to exceed the specification limit and the sum of several small contributions could be an important contribution.

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* Personal communications.

**The various shipments of D2EHPA received from the vendor (Carbide) have contained 2-10% monalkylphosphoric acid. The mono-compound has a relatively high distribution loss to acid solutions and can introduce phosphate into the vanadium strip solution far in excess of the allowable limit. In process use, it would be lost from the organic phase after a few cycles as a natural result of the extraction-stripping operations. For batch or limited cycle laboratory tests, however, it is important that the solvent be thoroughly scrubbed prior to use. Sodium carbonate solution (5-10%) is an effective scrubbing agent.

Trace studies with labeled P^{32} compounds have been started to better evaluate the importance of the organophosphorus contribution from each potential source. In the meantime, products derived from a series of bench-scale continuous tests have given a gross indication of the importance of organic phosphate as a contamination source.

In these tests, vanadium and uranium were co-extracted from several synthetic leach liquors with 0.3 M D2EHPA in kerosene + 5 w/v % TBP. The vanadium was selectively stripped with 0.75-1.0 M H_2SO_4 and the uranium stripped with sodium carbonate solution. The vanadium was precipitated from the pregnant strip solution with ammonia at pH 7, washed with water, and calcined at 600°C. None of the synthetic liquors contained inorganic phosphate, and phosphate in the products therefore must have been of organic phosphate origin. The vanadium content of the products ranged from 93 to 99% V_2O_5. The phosphorus contents were:

Run	Preg. Strip Solution, g/liter		% P in Calcined Product (based on V_2O_5)
	V_2O_5	PO_4	
1	17	-	0.05
2	22	-	0.03
3	19	-	0.03
4	21	-	0.03
5	25	-	0.03
6	61	0.036	0.02[a]

[a] Calculated on the basis of the strip solution analysis, assuming (probably incorrectly) that all the phosphate would report to the product.

The products contained 0.02-0.05% phosphorus, with the lowest value in Run 6 where loading of the strip solution was highest, i.e., 61 g V_2O_5/liter. A decrease in the P/V_2O_5 ratio would be expected with increase in loading of the strip solution since distributions of organic phosphates to the aqueous phase and entrainment of solvent in the aqueous phase should be virtually independent of vanadium loading. Loading of a 1 M H_2SO_4 strip solution to approximately 60 g V_2O_5/liter is considered typical for the Dapex process when treating liquors of high vanadium content, i.e., 5-6 g V_2O_5/liter. Appreciably lower loadings might be anticipated with dilute vanadium liquors.

Although all the products met the specification of 0.05% P, it is evident that phosphate of organic origin is an important consideration. The solvent had been scrubbed with 10% Na_2CO_3, but not thoroughly. It is likely that mono(2-ethylhexyl)phosphate was an important contributor.

Inorganic Phosphate. Inorganic phosphate may be transferred to the stripping system by entrainment of leach liquor in the extract or by actual extraction of orthophosphate combined with extractable metals in the form of a cationic metal complex. The

possible importance of metal-phosphate complexing was studied by extracting vanadium(IV), iron(III), and aluminum from 0.5 M sulfate solutions containing 0-4 g of phosphate per liter. The extraction was made with 0.25 M D2EHPA in kerosene that had been scrubbed thoroughly with 10% Na_2CO_3 and 6 M HCl to eliminate readily soluble organophosphorus impurities. The amounts of extracted phosphate were determined by stripping the extracts (after filtering to remove any entrained aqueous) with 6 M HCl and analyzing the strip solutions. Removal of the metals from the solvent was complete. To permit correction for any organic phosphate that might have been present, despite the precautions taken, a sample of solvent that had not been contacted with one of the aqueous solutions was stripped with 6 M HCl which was subsequently analyzed for phosphorus content. The test conditions were: Phase ratio, aq/org = 2/1; 10 min contact for V(IV) and Fe(III) tests, 30 min contact for Al tests; final pH 1.5-1.7. The results were:

Metal	PO_4 in Head Aqueous g/liter	g/liter of Metal			Extraction Coefficient (E_a^o)	Extracted PO_4, g/liter of organic
		Head	Organic	Aqueous		
V(IV)	0	3.1	4.3	1.1	3.9	0.003
	1	3.1	4.2	1.1	3.8	0.003
	4	3.1	4.3	1.1	3.9	0.003
Fe(III)	0	0.41	0.6	0.13	4.6	<0.002
	1	0.41	0.8	0.008	100	<0.002
	4	0.41	0.8	0.001	800	<0.002
Al	0	5.3	0.6	4.9	0.12	<0.002
	1	5.3	1.0	4.8	0.21	0.015
	4	5.3	1.1	4.7	0.23	0.060

According to the results, extractions of phosphate with vanadium(IV) and iron(III) were negligible. Aluminum, on the other hand, carried appreciable amounts of phosphate into the solvent, i.e., 0.015 and 0.06 g PO_4/liter, respectively, in extractions from head liquors containing 1 and 4 g PO_4/liter. These amounts of phosphate are sizeable in relation to the small amounts allowable. For example, assuming a loading of 5 g V_2O_5 in the solvent, 0.015 g PO_4/liter corresponds to 0.1% P based on V_2O_5 and 0.061 g PO_4/liter to 0.4% P.

Vanadium extractions were unaffected by the presence of phosphate. Both iron(III) and aluminum extractions, however, were appreciably enhanced. The extractions of iron and aluminum are ordinarily slow in this system, and the 10-30 min contact time used is ordinarily not sufficient to reach equilibrium. The enhancement of extraction might have been due, in these cases, to an increase in the extraction rate of the metals in the presence of phosphate.

2.2.2 Separation of Inorganic Phosphate from Vanadium

The separation of phosphate from vanadium has been examined by the Dow Chemical Company* in their studies on ion-exchange recovery of vanadium from commercial phosphoric acid. Best results were obtained by precipitating the vanadium from the resin eluate as "red cake," agreeing with the more recent studies on solvent extraction strip solutions. Results were also favorable for the ammonium precipitation method when phosphate had been precipitated from solution with zirconium prior to precipitation of vanadium.

In the studies at ORNL, zirconium phosphate precipitation is being evaluated with respect to its effectiveness on Dapex strip liquors. Studies are also being made on the possibility of scrubbing phosphate from the organic extract prior to stripping and on the possibility of treating the ammonium precipitate to remove phosphate.

Scrubbing the Extract Prior to Stripping. Partial removal of extracted phosphate was achieved by scrubbing a Dapex vanadium-loaded solvent with ammonium sulfate solution or with dilute sulfuric acid. The loaded solvent was prepared for these tests by contacting 0.3 M D2EHPA in kerosene (thoroughly scrubbed with sodium carbonate and hydrochloric acid solutions prior to use to remove impurities) with a synthetic vanadium leach liquor containing 4 g PO_4/liter. After being filtered to remove any entrained aqueous liquor, the solvent (4.1 g V_2O_5, 0.5 g Fe, and 0.5 g Al per liter) was divided into three portions. One portion was scrubbed twice (5 min per contact) at org/aq = 5/1 with 1 M $(NH_4)_2SO_4$ (in a process plant ammonium sulfate would be available in the filtrate after precipitation of vanadium(IV) with ammonia). A second portion was scrubbed in the same way with dilute sulfuric acid (pH 2). The scrubbed and unscrubbed extracts were then stripped twice with 6 M HCl at org/aq = 1/1, and the phosphate contents of the strip solutions were compared.

Scrub Solution	% P (based on V_2O_5) in 6 M HCl Strip Solution[a]	% Removed by Scrubbing	
		V_2O_5	Extracted Phosphate
None	0.5-0.6	-	-
1 M $(NH_4)_2SO_4$, pH 3	0.2	0.3	60-70
H_2SO_4, pH 2	0.3	0.7	40-50

[a] Does not include phosphate contributed by dissolved organic phosphate, which was estimated by carrying an organic blank, i.e., organic solution which had not been contacted with the liquor, through the test sequence.

The ammonium sulfate solution was the more effective of the scrub solutions, removing approximately 2/3 of the extracted phosphate and only 0.3% of the vanadium. The remaining phosphate (0.2% P) was still considerably above the specification limit. However, the phosphate concentration of the liquor was higher than is usually encountered, and the amount of extracted phosphate was

*Dow progress reports for 1950; Dow-23, January; Dow-25, February; Dow-26, March; Dow-31, June; Dow-34, August.

therefore probably extreme. For processing liquors more dilute in phosphate, the treatment may be sufficiently effective to be useful. In addition to removing extracted phosphate, the scrub would also remove leach liquor that had been entrained in the solvent, thus minimizing phosphate transfer to the stripping system by this mechanism.

Fractional Precipitation of Vanadium. Attempts to achieve a favorable separation of phosphate from the bulk of the vanadium by stepwise precipitation of vanadium with ammonia were not successful.

Synthetic strip solutions (56 g V_2O_5, 0.5 g Fe(III), 0.5 g Al, 98 g SO_4, and 0.45-1.0 g PO_4 per liter) were used for the tests. The pH of the solution was raised with ammonia gas until some precipitate formed. After a 1-hr digestion, the slurry was filtered and the precipitate washed with water and analyzed. The balance of the vanadium was precipitated from the filtrate in two more steps, allowing a 1-hr digestion after each adjustment of pH. In each case the phosphate content of the third fraction was approximately half that of the first two fractions but still considerably above the specification limit:

g PO_4/liter in the Synthetic Strip Solution	Precipitate	P/V_2O_5, wt %	Vanadium Distribution, % of total
0.45	1st fraction, pH 3.4	0.30	19
	2nd fraction, pH 3.7	0.32	44
	3rd fraction, pH 7.3	0.17	37
1.0	1st fraction, pH 3.4	0.77	17
	2nd fraction, pH 3.6	0.77	40
	3rd fraction, pH 7.6	0.39	43

It is obvious from the above data that no useful separation of phosphate and vanadium was achieved by this procedure.

In the hope that vanadic phosphate would precipitate at a lower pH than vanadyl phosphate, a similar test was made with a solution that had been spiked with vanadium(III). The V(III)/V(IV) ratio in the head solution was approximately 0.1. The precipitation was performed in two steps, again with no useful separation:

g PO_4/liter in the Synthetic Strip Solution	Precipitate	P/V_2O_5, wt %	Vanadium Distribution, % of total
0.45	1st fraction, pH 3.3	0.30	45
	2nd fraction, pH 7.0	0.20	55

Precipitation of Phosphate with Zirconium and Titanium. Elimination of phosphate from the pregnant strip solution by precipitation with zirconium or titanium was studied briefly. The metal, in 1 M

H_2SO_4, was added to a synthetic strip solution in quantities equivalent to 190 and 350% of the stoichiometric amount for precipitating the phosphate as $M_3(PO_4)_4$. After 15 min digestion the solution was filtered and a portion of the filtrate was analyzed for vanadium and phosphate. The balance of the filtrate was adjusted to pH 2.1-2.3 (below the point of vanadium precipitation) with ammonia gas, digested 15 min, filtered, and analyzed. The results show precipitation of phosphate with both zirconium and titanium, but only in one test was the phosphate concentration reduced to the specification limit:

Metal Added	Amount, % of Stoichiometric	pH	P/V_2O_5 in Filtrate, wt %	Phosphate Precipitated, %
Zr	190	0.4	0.07	75
		2.3	0.05	80
	350	0.4	0.21	20
		2.2	0.11	60
Ti	190	0.4	0.26	<5
		2.1	0.15	40
	350	0.4	0.26	<5
		2.2	0.08	70

Synthetic strip solution: 55 g V_2O_5, 0.45 g PO_4, 0.5 g Fe(III), 0.5 g Al, and 98 g SO_4 per liter.

In all cases precipitation was more complete at the higher pH. The first test (190% of stoichiometric zirconium) was different from the others in that the solution was filtered through No. 50 filter paper. Owing to the colloidal nature of the precipitate, the filtration was very slow. In the last three tests, the solutions were filtered through relatively coarse, No. 42, paper and filtration was rapid. The poorer results achieved with the larger amounts of zirconium suggest that a considerable portion of the precipitate passed the coarse filter. Further study of the system is being made to define the optimum precipitation conditions.

Leaching of Phosphate from the Ammonium Precipitate of Vanadium (IV). Treatment of a vanadium(IV) precipitate with dilute sodium or ammonium hydroxide removed only a fraction of the phosphate.

A vanadium precipitate was prepared for these tests by neutralizing a synthetic strip solution (55 g V_2O_5, 0.45 g PO_4, 0.5 g Fe(III), 0.5 g Al, and 98 g SO_4/liter at pH 0.4) with ammonia gas. Samples of the wet precipitate were digested with hydroxide solutions, filtered, washed, and analyzed. The phosphate contents of the treated precipitates are compared below with that of a sample which received no treatment.

Leach Solution	lb Leaching Agent/lb V_2O_5	Digestion Time, hr	pH	% in Filtrate V_2O_5	% in Filtrate PO_4	P/V_2O_5 in the Leached Precipitate wt %
Untreated	-	-	-	-	-	0.26
Water	-	4	7.5	3	2	0.26
1% NaOH	0.08	0.5	9.5	5	15	0.23
1% NaOH	0.08	4	9.6	6	19	0.23
3% NaOH	0.25	0.5	11.1	21	56	0.17
3% NaOH	0.25	4	11.2	26	62	0.13
4% NH_3	0.34	4	10.1	5	24	0.21

Of the solutions tried, only 3% NaOH reduced the phosphate content of the vanadium by more than 50%. However, a considerable portion of the vanadium was removed with the phosphate owing to the tendency of the precipitate to peptize and also to oxidize during the digestion.

Precipitation of Vanadium "Red Cake." With two different synthetic strip solutions, a series of "red cake" precipitation tests was made to determine the effect of precipitation conditions on the phosphate content of the product. Precipitation was accomplished by adding sodium chlorate, (10-35% in excess of the stoichiometric quantity shown by the reaction)

$$6VO^{++} + NaClO_3 + 3H_2O \rightarrow 6VO_2^{+} + 6H^{+} + NaCl$$

and heating to 90°C. A granular red precipitate, presumably a hydrated polymer of V_2O_5, was readily formed and easily filtered.

$$2x(VO_2^{+}) + (x + y)(H_2O) \rightarrow (V_2O_5)_x(H_2O)_y + 2x(H^{+})$$

As shown by the equations the oxidation-precipitation is accompanied by a large drop in pH. In some tests the pH was adjusted to 1.1 or 2.0 with ammonia gas prior to the addition of sodium chlorate in order to increase the precipitation efficiency. After digestion at 90°C for 1 hr, the precipitates were filtered, washed with water, and calcined at 600°C. The calcined products contained 97-99% V_2O_5 and 0.2-0.6% Na:

g PO_4/liter in the Strip Soln.	Excess $NaClO_3$, %	Init. pH	Filtrate pH	Filtrate V(IV)/V(V)	Vanadium Ppt'd., %	Calcined Product, % V_2O_5	Calcined Product, % P
0.45	10	0.4	<0.0	<0.05	67	98	0.02
0.45	10	1.1	0.3	0.5	70	99	0.02
0.45	10	2.0	0.3	0.4	76	99	0.04
1.0	10	0.4	<0.0	<0.05	67	97	0.04
1.0	10	1.1	0.3	0.5	72	98	0.07
1.0	10	2.0	0.3	0.5	78	97	0.05
1.0	25	2.0	0.3	0.2	80	99	0.06
1.0	35	2.0	0.3	<0.05	83	99	0.06

Synthetic strip solutions: 55 g V_2O_5, 0.45 or 1.0 g PO_4, 0.5 g Fe(III), 0.5 g Al, and 98 g SO_4/liter at pH 0.4; pH adjustment to 1.1 or 2.0 made with ammonia gas.

Products obtained from the strip solution containing 0.45 g PO_4/liter (wt % P/V_2O_5 = 0.27) were 0.02-0.04% in phosphorus content, the highest being obtained when the solution pH was adjusted to 2.0 prior to precipitation. Products from the 1.0 g PO_4/liter solution (wt % P/V_2O_5 = 0.59) barely met or slightly exceeded phosphorus specifications. The lowest result (0.04% P) was obtained at the lowest pH.

Vanadium recoveries were 67-83%, increasing with increase in pH. The vanadium in the filtrate would, of course, be recycled to the leaching system or possibly, in part, to the stripping system. Adjustment of the strip solution pH with ammonia increased the sodium chlorate requirements. Whereas 110% of stoichiometric sodium chlorate completely oxidized the vanadium in unadjusted solutions, oxidation was far from complete with this amount when the solutions were adjusted with ammonia prior to oxidation. Vanadium recoveries in the latter tests were adversely affected by the failure to achieve complete oxidation. When the amount of sodium chlorate was increased to 135% of stoichiometric, a solution adjusted to pH 2 was completely oxidized and vanadium recovery was at the highest value obtained, i.e., 83%.

In confirmation of previous results, recovery of vanadium from the strip solution by precipitation of "red cake" thus appears to be one of the more effective methods of limiting the phosphate content of the product. The high recycle of vanadium is a disadvantage. The amount of recycle can be decreased at the expense of higher ammonia consumption by adjusting the pH to ~1 after vanadium oxidation. Preliminary results showed that vanadium recovery improves and that very little phosphate precipitates from solution until the pH reaches ~1.5.

3.0 ENGINEERING STUDIES

In addition to the studies described below, engineering projects during the month have included (1) Dapex uranium extraction in continuous flow mixer, (2) Dapex vanadium extraction kinetics, and (3) countercurrent tests of amines with feed liquors containing molybdenum.

3.1 Continuous Flow Settler Tests of the Dapex Extraction Process (R. S. Lowrie)

The investigation of phase separation for the Dapex uranium extraction process has been continued to determine scaleup factors for gravity settlers. Previously (ORNL-2306) the flow capacity of a 48-in.-dia settler was determined. This month the results of tests made in 6-in.-dia glass, both with and without a plastic liner, and 22-in.-dia stainless steel settlers are reported and correlated with

the 48-in.-dia stainless steel settler data. In addition, the effects of temperature and mechanical coalescers on settler capacity were measured.

The aqueous feed, organic solvent, settler geometry and operational details were essentially the same as those used previously for the transverse flow tests in the 48-in.-dia settler.

3.1.1 Correlation of Settler Capacity

At steady state a distinct band of dispersion existed at the interface which was of uniform thickness across the entire area of each settler. The thickness of the dispersion increased with increased flow rate until the settler was flooded. Measurement of the dispersion thickness as a function of flow rate made possible a comparison of the capacities of each settler for oil-in-water type dispersions at phase ratios (aq/org) of 4/1 and 1/1, and for water-in-oil type dispersions at phase ratios (aq/org) of 1/1 and 1/2. The results are summarized in Table 3.1 and in Fig. 3.1 where the dispersion thickness is plotted against aqueous flow rate per square foot of settler area. The result is a family of nearly parallel lines for the different dispersions and settler sizes.

The nominal aqueous flow capacity of the 48-in.-dia settler had been previously selected as the flow rate giving a 5-in. dispersion band, being about half the flow rate at flooding with all types of dispersions tested. For comparison the flow rates in the 6- and 22-in.-dia settlers equivalent to a 5-in. band were read from Fig. 3.1. Because the curves are nearly parallel, equally valid comparisons could be made at any band thickness within the experimental points.

Comparison of flow rates (Table 3.2) shows good agreement with the exception of some of the results in the 6-in.-dia glass settler, where water-in-oil type dispersions coalesced on the walls. In a few tests with a plastic liner coalescence occurred on the wall with an oil-in-water type dispersion but not with a water-in-oil type dispersion. The dispersion thickness at constant flow rate was consistently greater when the dispersed phase did not wet the settler wall (Table 3.1). Coalescence on the walls would be significant only in small-diameter settlers where the ratio of wall area to cross-sectional area is large. Consequently, the wall effect should be minimized for valid comparisons of small and large settlers.

Comparison of nominal flow capacity of the 6-, 22-, and 48-in.-dia settlers (Table 3.2) shows good agreement when the wall effect in the 6-in.-dia settler was minimized, demonstrating that settlers can be scaled up, based on constant flow per unit cross-sectional area. The nominal aqueous flow capacity for water-in-oil type dispersions was 1.1 gpm per square foot at phase ratios (aq/org) of 1/1 and 1/2. For oil-in-water type dispersions the flow capacity was 1.4 gpm per square foot at a phase ratio (aq/org) of 1/1 and was 4.5 gpm per square foot at a phase ratio (aq/org) of 4/1.

Table 3.1 Summary of Settler Data

Type of Dispersion	Phase Ratio (a/o)	Aqueous Flow Rate, gpm/ft²	Dispersion Thickness, in. 6" Plastic	6" Glass	22" S.S.	48" S.S.
Oil-in-water	4/1	1.35	-	0.25	-	-
		2.70	-	1.5	-	-
		4.35	-	4.5	-	-
		5.40	-	9.3	-	-
		3.65	-	-	2.1	-
		5.40	-	-	8.2	-
		1.67	-	-	-	0.5
		3.33	-	-	-	7.3
		5.40	-	-	-	9.9
	1/1	0.68	-	0.8	-	-
		1.35	2.4	6.1	-	-
		1.47	-	-	4.9	-
		2.32	-	-	14.9	-
		0.83	-	-	-	1.4
		1.25	-	-	-	2.9
		1.67	-	-	-	8.1
		2.08	-	-	-	12.0
		2.50	-	-	-	22.0
Water-in-oil	1/1	0.68	2.3	-	-	-
		1.35	7.0	2.8	-	-
		2.02	-	8.3	-	-
		1.14	-	-	2.1	-
		1.80	-	-	8.5	-
		0.83	-	-	-	2.3
		1.25	-	-	-	5.5
		1.67	-	-	-	14.0
		2.08	-	-	-	26.0
		2.50	-	-	-	32.0
	1/2	0.68	2.5	-	-	-
		1.35	10.5	2.8	-	-
		1.82	-	9.8	-	-
		1.03	-	-	2.4	-
		1.47	-	-	13.2	-
		0.42	-	-	-	0.5
		0.83	-	-	-	2.5
		1.25	-	-	-	9.3

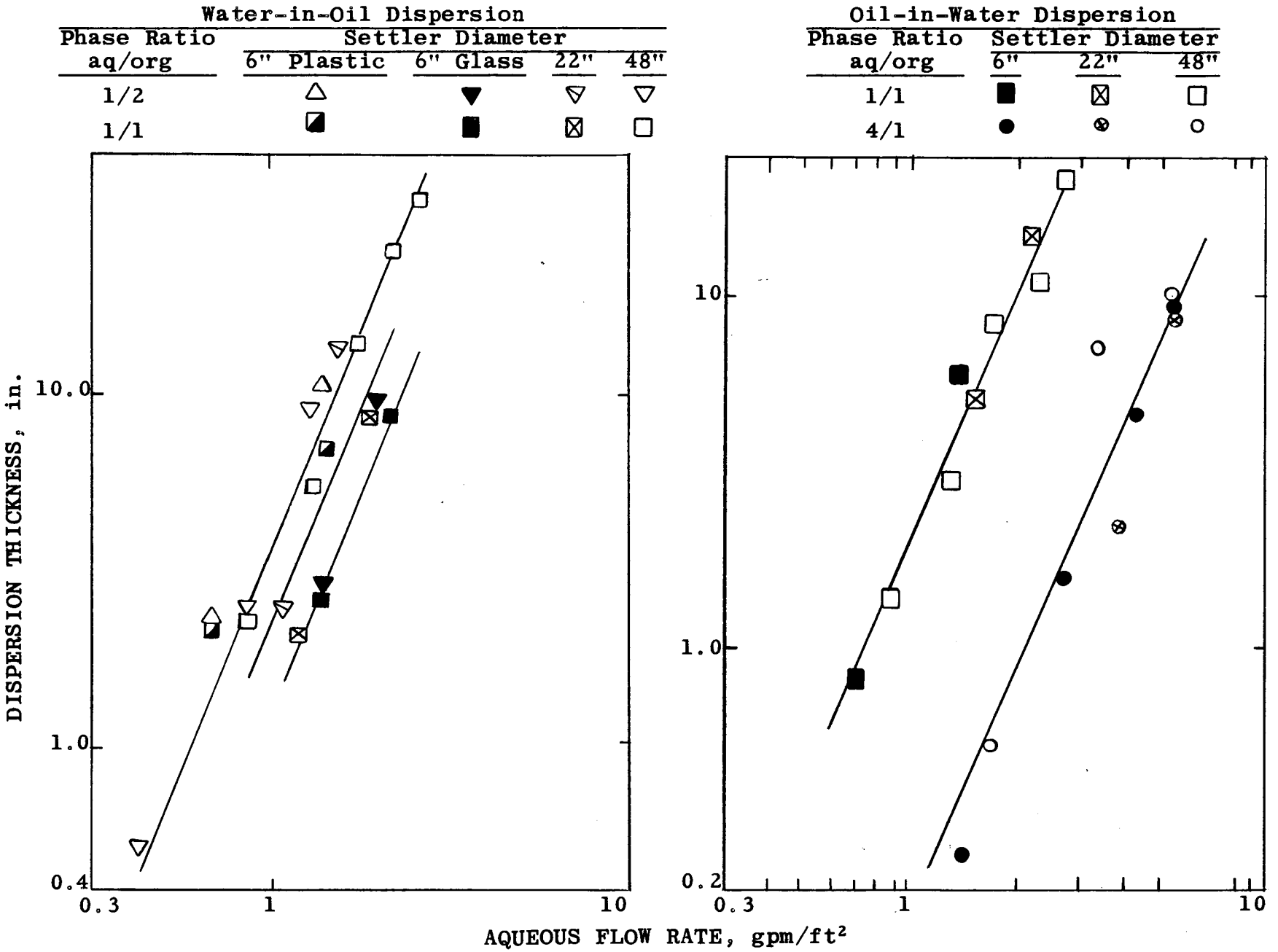

Fig. 3.1 Throughput Capacity of Settlers

Table 3.2 Nominal Flow Capacities for 6-, 22-, and 48-in.-dia Settlers

Type of Dispersion	Phase Ratio (a/o)	Aqueous Flow Rate, gpm/ft² 6" Plastic	6" Glass	22" S.S.	48" S.S.
Water-in-oil	1/2	1.1	1.6	1.4	1.1
	1/1	1.1	1.6	1.4	1.1
Oil-in-water	1/1	-	1.4	1.4	1.4
	4/1	-	4.5	4.5	4.5

3.1.2 Temperature Effect on Dispersion Band Thickness

In survey tests with oil-in-water dispersions at aqueous/organic phase ratios of 4/1 and 1/1 the dispersion band thickness decreased with increased temperature over the range 15 to 50°C (Fig. 3.2). Assuming that the correlation of dispersion band thickness and flow rate for 50°C is the same as for 25°C (Fig. 3.1), the nominal flow capacity of a settler operating at 50°C would be approximately 60% greater than at 25°C.

3.1.3 Effect of Wire Mesh Packing on Settler Capacity

Several tests of a wire mesh* packing, similar to that used in the Schiebel column, were made to determine the effect on flow capacity of the 6-in.-dia settler. The results (Table 3.3) showed virtually no effect with oil-in-water type dispersions, probably because the stainless steel was not wetted by the organic droplets. However, with water-in-oil type dispersions the flow capacity was approximately fourfold greater than that with no packing.

Before these data can be used for design of large packed settlers, the scaleup factors should be determined and the problem of possible plugging of the packing with accumulated solids or gruel should be investigated. Packing would probably be more useful as a method of increasing the capacity or decreasing the dispersion band in an existing mixer-settler extraction plant where large throughputs were desired.

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* Yorkmesh mist eliminator, a woven, stainless steel packing having 97% void volume and approximately 125 sq. ft. surface area per cu. ft. Manufactured by Otto H. York Co., East Orange, N. J.

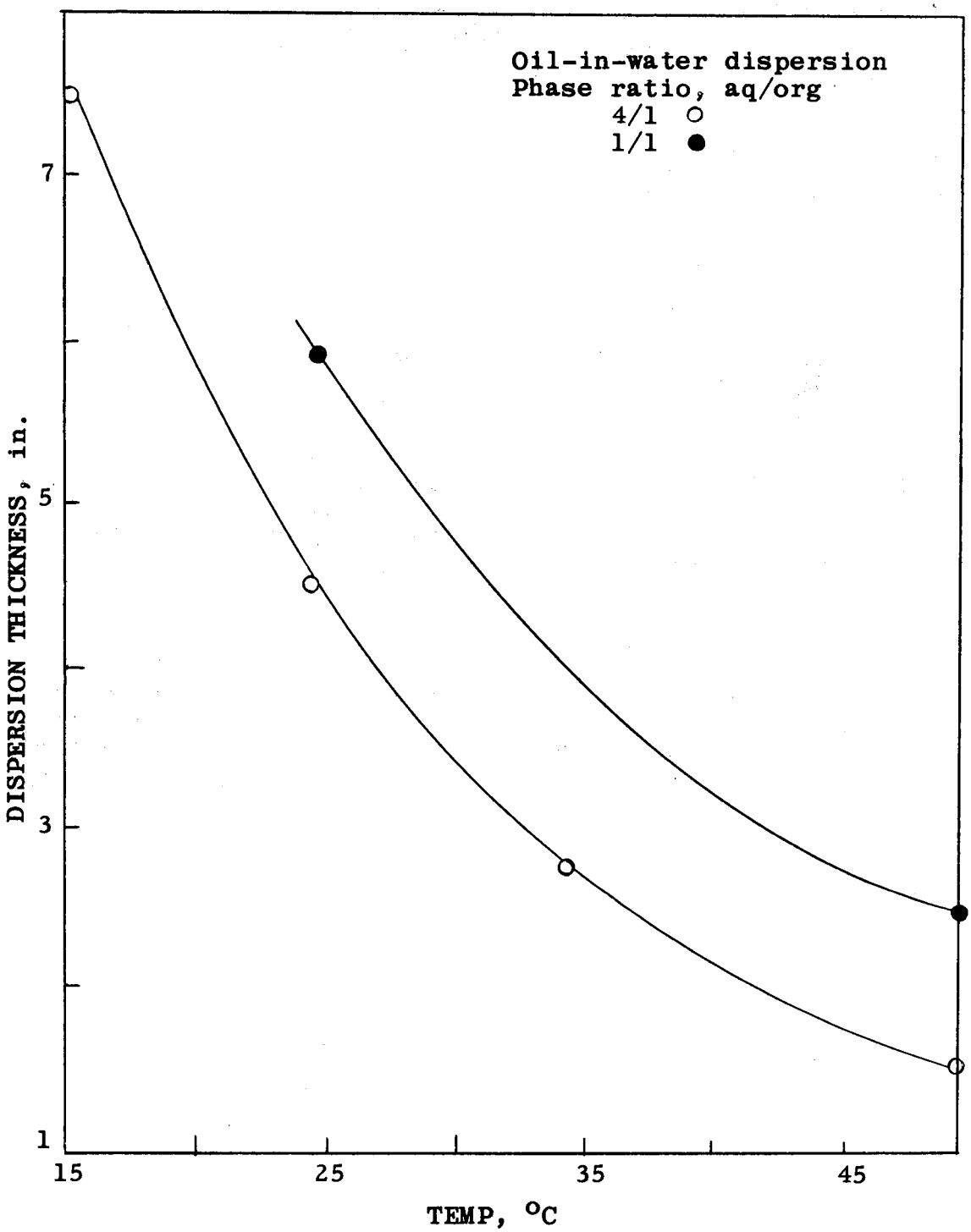

Fig. 3.2 Effect of Temperature on Dispersion Thickness

Table 3.3 Effect of Yorkmesh Demistor and 6-in.-dia Settler Capacity

Dispersion Type	Phase Ratio (a/o)	System	Max. Aq. Flow Rate, gpm/ft^2
Oil-in-water	4/1	A	5.5
		B	6.4
		C	5.8
	1/1	A	2.0
		B	2.0
		C	1.8
Water-in-oil	1/1	A	2.3
		B	9.5
		C	9.5
	1/2	A	2.3
		B	7.5
		C	10.0

System A: No packing

System B: Two 3-in. sections of wire mesh positioned 4 in. apart, with the dispersion entering the space between the sections

System C: A 6-in. section of wire mesh, with the dispersion entering in the center

4.0 FUNDAMENTAL STUDIES

In addition to the work described below, fundamental projects studied during the month have included (1) measurement 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 and by infrared spectrophotometry.

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

Previously reported results with tri-n-octylamine sulfate in benzene (ORNL-2380) indicated a molecular weight of ~800, corresponding to monomeric amine sulfate (mol wt 806), up to concentrations of at least 0.025 M in benzene solution. Experimental difficulties had prevented interpretation of the results at higher concentrations. In continuation of these tests, the difficulty

was found to arise from separation of some water on dilution of the more concentrated solutions, and had been avoided by partial dehydration* of the head solutions before preparation of each series by dilution. The relative scattering ratios were then found to be consistent up to 0.1 M amine sulfate (Fig. 4.1). The weight-average molecular weight calculated as previously described from the slope and intercept of this line indicates approximately the monomeric molecular weight over the entire concentration range.

The principal source of uncertainty in these measurements appeared to arise from the depolarization correction (described in ORNL-2380), which was much larger with tri-n-octylamine sulfate than with the other amine species so far examined and hence is relatively more important in the calculation. However, even the largest uncertainty estimated in the depolarization correction does not suggest that the molecular weight might be as high as that for even a dimer of tri-n-octylamine sulfate.

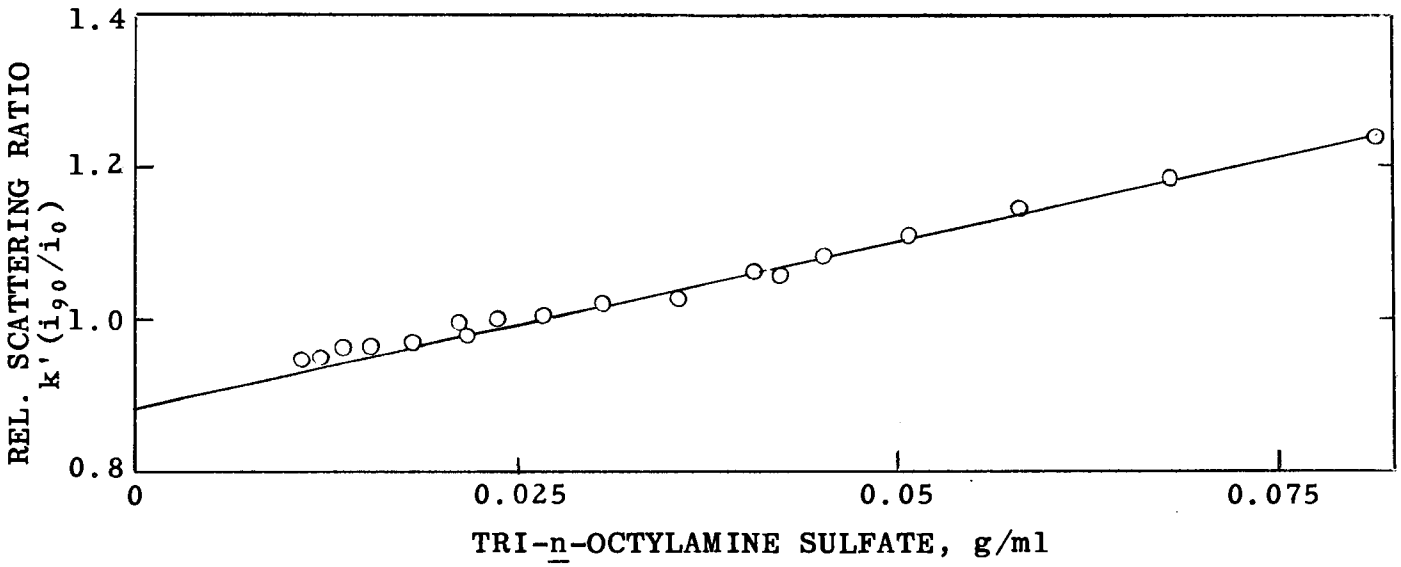

Fig. 4.1 Change of Relative Light Scattering Ratio with Change of Solute Concentration.

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*Some water separates from the benzene solutions on gentle heating, and is removed by centrifugation.

One of the higher concentration solutions was checked by isopiestic balancing of the benzene vapor pressure against a solution of a standard reference solute. The average molecular weight thus determined was 840, within a few percent of the monomeric molecular weight, at an equilibrium concentration of ~ 0.12 M, with good agreement between duplicates.

These results disagree with the previous interpretation of acid extraction equilibria,* which was that tri-n-octylamine sulfate in benzene is monomeric up to ~ 0.02 M and aggregated at higher concentrations. Those equilibria and corresponding uranium extraction equilibria will be re-examined to see if the disagreement can be resolved.

4.2 Extractions by Tri-n-octylamine Sulfate in Chloroform (K. A. Allen)

Uranium Extraction. In extraction of uranyl sulfate with solutions of tri-n-octylamine in benzene** and other hydrocarbon diluents (ORNL-1734, p. 112), the uranium extraction coefficient was found to vary linearly with the concentration of uncomplexed amine sulfate. In contrast, in extractions with chloroform as the diluent, the extraction coefficient varied as the square of the amine sulfate concentration (Fig. 4.2). In each set of extractions, the aqueous sulfuric acid activity was held constant, and the amine/uranium ratio was held constant at 50/1 so that most of the amine sulfate remained uncomplexed, while the concentration in the organic phase was varied by dilution with chloroform. For the upper curve the amine salt was essentially all normal sulfate, and for the lower curve ~ 60% of the amine was present as bisulfate.

Further extraction tests with higher ratios of uranium/amine indicated 5 or 6 amines complexed with each uranium. The saturation organic uranium concentration in 0.05 M tri-n-octylamine normal sulfate in chloroform appeared to be reached at an amine/uranium mole ratio close to 6/1, while the extraction coefficients matched the upper line of Fig. 4.2 well when free amine sulfate was calculated on the basis of 5/1, but not 4/1 or 6/1, amine/uranium.

Sulfuric Acid Extraction. Two-phase titration curves were previously reported (ORNL-2084, repeated in Fig. 4.3) showing much stronger extraction of sulfuric acid by di-n-decylamine than by tri-n-octylamine, each in benzene solution. Acid extraction by the latter was enhanced in the region below the normal sulfate equivalence point, and a sharp inflection appeared at the equivalence

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* K. A. Allen, "The Equilibria Between Tri-n-octylamine and Sulfuric Acid", J. Phys. Chem. 60, 239 (1956); ORNL-1977.

** K. A. Allen, "Uranium Extraction by Tri-n-octylamine Sulfate", to be presented at ACS Meeting, New York, Sept. 13, 1957.

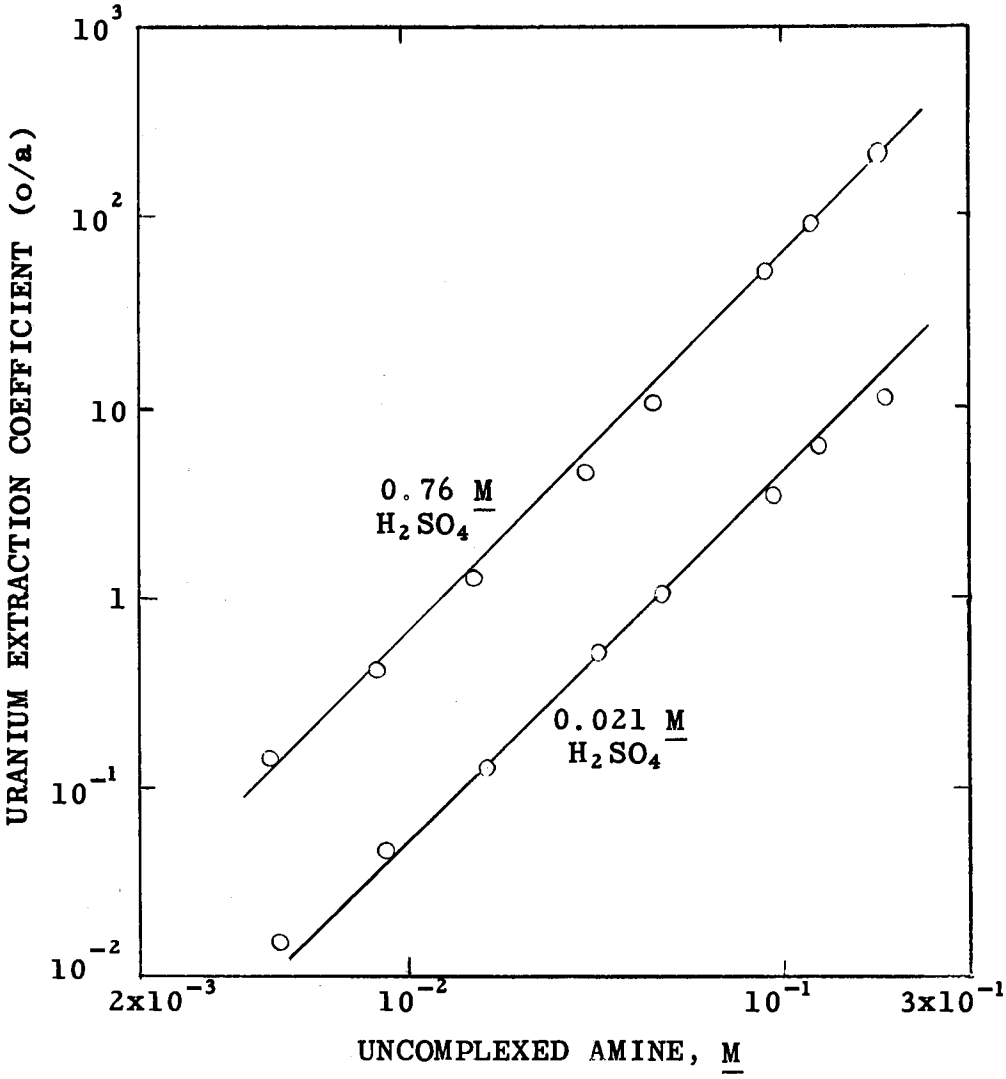

Fig. 4.2 Extraction of Uranium from Acidic Sulfate Solutions by Tri-n-octylamine Sulfate in Chloroform; lines drawn with slope $\cong$ 2.

point, when chloroform replaced benzene as the diluent. The chloroform-diluent curve crossed over and rose considerably above the benzene-diluent curve in the bisulfate region, i.e., additional sulfuric acid was extracted less strongly by the tri-n-octylamine normal sulfate in chloroform than in the benzene solution. Thus the change in acid extraction with change to chloroform diluent appears to involve a stabilization of the normal sulfate salt rather than merely increased relative basicity of the amine.

A curve with n-nonane as the diluent is also shown in Fig. 4.3. Acid extraction was considerably weaker with this diluent than with benzene in the normal sulfate region, but the curve was generally similar to the benzene-diluent curve and approached it in the bisulfate region.

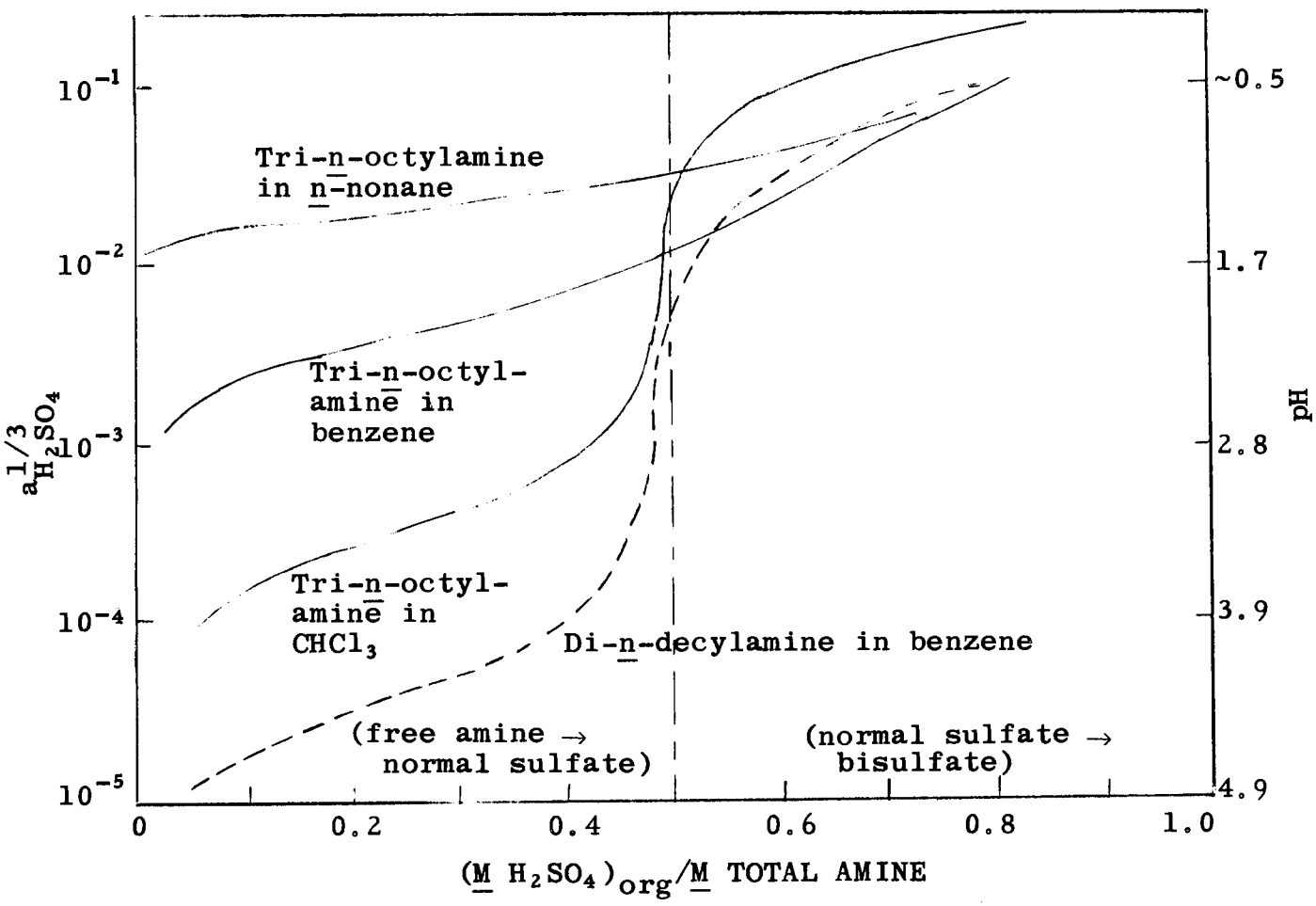

Fig. 4.3 Amine Titration Curves. Aqueous pH and Cube Root of Aqueous Sulfuric Acid Activity vs. Mole Ratio of Extracted Sulfuric Acid to Amine.