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Technology-Raw Materials

PROGRESS REPORT ON RAW MATERIALS

FOR MARCH, 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 MARCH, 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.

ABSTRACT

Systematic Studies. In view of its recently indicated commercial availability at a feasible price, dihexyl hexylphosphonate (DHHP) was examined for use in Dapex synergistic extractant combinations. The synergistic enhancement of uranium extraction by D2EHPA was fourfold greater than that with tributylphosphate, and a little greater than that with dibutyl butylphosphonate (DBBP). Separation of sodium di(2-ethylhexyl)phosphate from kerosene solution was prevented by concentrations of DHHP similar to those required of TBP or DBBP, and a smaller amount was lost by distribution to the aqueous phase.

The rate of loss of three amines from kerosene solution to 0.5 M H_2SO_4 decreased as the percent of amine removed from the organic phase increased with increasing aqueous/organic phase ratio, giving a measure of the selective removal of the more water-soluble components. The loss rate of Amine S-24 became constant at about 9 mg amine per liter of aqueous phase after about 30% had been lost. Loss rates of tri-iso-octylamine and Amine 9D-178 decreased to about the same level after 40 and 50%, respectively, had been lost, but without indication of becoming constant.

Process Development Studies. Comparative uranium extraction isotherms are presented for a new tertiary amine, i.e., didodecenyl-n-butylamine, and for new samples of tri-iso-octylamine, Amine S-24, and Amine 9D-178. Isotherms are also presented for di(tridecyl P)amine with different amounts of alcohol added to the kerosene diluent. The addition of 5% tridecyl alcohol greatly improved the selectivity with respect to iron(III) without depressing the uranium extraction power.

In continued studies on Amex processing of monazite sulfate liquors, thorium was effectively extracted with di(tridecyl P)amine. Useful uranium extractions were obtained with tri-n-octylamine. The effectiveness of this reagent was improved by increasing the liquor pH. After thorium and uranium removal, rare earths were extracted and separated from phosphate with Primene JM-T. Chloride, nitrate, and possibly

carbonate solutions are effective stripping agents for rare earths.

Engineering Studies. Phase separation for the Dapex extraction process was evaluated in a large-scale mixer settler at flow rates up to 60 gpm. The nominal aqueous flow capacity (50% of flooding) was 1.1 gpm/sq ft for organic-continuous dispersions and ranged from 1.5 to 3.9 gpm/sq ft for aqueous-continuous dispersions, depending on the ratio of flow rates. The residual entrainment of organic in the aqueous phase immediately after primary separation was consistently less than 0.01 v % for organic-continuous dispersions compared to an average of 0.15 v % for aqueous-continuous dispersions.

Fundamental Studies. A method has been developed to estimate the bisulfate dissociation and the actual ionic concentrations of H^+, $SO_4^=$, HSO_4^- in a useful range of sulfuric acid--sodium sulfate solutions. The basis for the method and the range of applicability are discussed; results compared favorably with the experimental information now available. Numerical results in terms both of the dissociation quotient $Q = [H^+][SO_4^=]/[HSO_4^-]$ and of the fraction of total sulfate as bisulfate ion are tabulated in sets at constant total sulfate concentrations and at constant ionic strengths.

1.0 SYSTEMATIC STUDIES

In addition to the work described below, systematic studies during the month have included (1) testing of new organophosphorus compounds and amines as uranium extractants, (2) testing of new compounds for use in synergistic extractant combinations, (3) extraction of thorium with D2EHPA, (4) extraction and separation of other metals (rare earths; hafnium and zirconium) with organophosphorus compounds and amines, (5) preparation and purification of some long-chain monoalkylphosphoric acids for definitive measurement of uranium extraction power, solubility, etc., and (6) testing of the organic and aqueous solubility of some sodium monoalkylphosphates.

1.1 Dihexyl Hexylphosphonate (C. A. Blake, D. E. Horner, J. M. Schmitt)

Commercial availability of dihexyl hexylphosphonate (DHHP) has recently been announced at prices which appear feasible for process use.* The information already available from studies

*Gilbert P. Heathcote, Shea Chemical Corporation, 114 East 40th Street, New York 16, N. Y., in letter to C. A. Blake, March 25, 1957: "... we propose the following price schedule for Dihexylhexane Phosphonate:

100 lb lots	90¢ per pound	f.o.b. Adams, Mass.
Truckload quantities	80¢ per pound	f.o.b. Adams, Mass.

Should this product ever develop into a million-pound class, we would probably anticipate a selling price of 55-60¢ per pound."

of other neutral organophosphorus compounds indicates that DHHP can be a useful component in Dapex synergistic extractants. It may be expected to show some advantage over tributylphosphate (TBP) because of its chemical structure* and over both TBP and dibutyl butylphosphonate (DBBP) because of its higher molecular weight. Accordingly, the extraction behavior of a sample of DHHP from this source is being examined.

Synergistic Enhancement of Uranium Extraction. Comparison of extraction coefficient shows that the synergistic enhancement of uranium extraction by 0.1 M di(2-ethylhexyl)phosphoric acid (D2EHPA) is fourfold greater with DHHP than with TBP and a little greater than with DBBP:

Neutral Compounds	Batch No.	Uranium Extraction Coefficients, o/a From 0.5 M $SO_4^=$, pH 1	From 1.5 M H_2SO_4
None		110	3
TBP	op-338	470	13
DBBP	op-306	1700	30
DHHP	op-383	2200	45

Each reagent was used at 0.1 M concentration, in kerosene diluent. The initial aqueous uranium concentration was 0.004 M (~1 g/liter) and the phase ratio was 1/1. The extractions from the 0.5 M sulfate, pH 1, solution are of principal interest since this solution approximates many of the ore leach liquors. The enhanced extraction coefficients are important whenever the aqueous uranium concentration is low, as in extraction from dilute liquors or in the lower stages of a countercurrent system where a low-uranium raffinate is to be achieved, and they also permit reasonably good extraction from solutions otherwise difficult to extract. Extractions from 1.5 M H_2SO_4 were included in these tests to facilitate comparisons between reagents, by avoiding some of the analytical difficulty necessarily encountered in raffinate uranium determinations when the extraction coefficients are very high.

Diluent Modification for Miscibility. Another contribution of the neutral component in a Dapex synergistic combination, and in some circumstances the most important, is the maintaining of miscibility of the sodium dialkylphosphate formed in the kerosene diluent during alkaline stripping. The minimum concentration of modifier required for this (other conditions constant) is a linear function of the dialkylphosphoric acid concentration. With DHHP and D2EHPA, for contact with 10% sodium carbonate solution at 29.5°C, this linear function is w/v % DHHP = 1.6 + 3.7 M D2EHPA, or M DHHP = 0.048 + 0.11 M D2EHPA. Corresponding equations for other modifiers were listed in ORNL-2171, p. 9. For comparison, the requirements are

---

*Cf. Comparison of effectiveness, $PO(OR)_3 < RPO(OR)_2 < R_2PO(OR) < R_3PO$, in ORNL-2172, p. 10, and in references cited there.

**The abbreviation w/v % means grams per 100 ml.

	0.1 M D2EHPA	0.3 M D2EHPA
TBP:	2.2 w/v %	3.3 w/v %
DBBP:	1.3	2.4
DHHP:	2.0	2.7

Thus the concentration required of DHHP is approximately the same as that of TBP, and a little higher than that of DBBP, to an extent probably offset by the lower solubility loss rate of DHHP.

Loss to Aqueous Phases. On the basis of its higher molecular weight, the loss rate by distribution to aqueous solutions is expected to be lower for DHHP than for TBP or DBBP. The loss to 0.5 M sulfate solution at pH 1, measured by titration to the critical miscibility point (ORNL-2172 p. 17), was less than 5 mg/liter aq., as compared with about 25 mg/liter loss of either TBP or DBBP (ORNL-2172 p. 19). In extraction from a similar liquor containing, e.g., 1 g of U_3O_8 per liter, this would correspond to <0.005 lb/lb U_3O_8, and at the proposed 80-90¢ price cited above, to <0.5¢ per pound of U_3O_8 from solubility loss.

Losses through entrainment, spillage, etc. have been previously compared on the assumed basis of 0.5 ml loss per liter of raffinate (ORNL-2172 p. 31). On this basis, entrainment loss of extractant containing 3 w/v % DHHP would amount to 15 mg DHHP/liter aq., or about 1.3¢ per pound of U_3O_8 from a 1 g U_3O_8/liter liquor. The costs per pound of U_3O_8 due to both solubility and entrainment losses would, of course, be proportionately less in plants handling higher grade liquors.

Other Extraction Characteristics. The effects of DHHP on selectivity, efficiency of stripping, and phase separation have not yet been examined in detail. However, there is no apparent reason to expect DHHP to be out of line with the general behavior of TBP, DBBP, and phosphine oxides, since it may be considered an intermediate member of that group. No indication of impaired phase separation was seen in the tests reported above.

1.2 Rates of Loss of Amines to Aqueous Solutions (J. G. Moore)

The losses of Amine 9D-178, Amine S-24, and tri-iso-octylamine by distribution from kerosene solution to a 0.5 M H_2SO_4 solution were measured over a wide range of aqueous/organic phase ratios, to find whether the loss rates after selective removal of more soluble fractions in long recycling might become significantly lower than those predicted from measurements in which only a small fraction of the amine content is removed. Loss is usually measured (ORNL-1734 p. 45, -1922 p. 38, -2099 p. 41) by separate batch equilibrations at successively larger aqueous/organic phase ratios up to, e.g., 100/1 or 200/1, followed by determination of the amine concentration left in each organic solution. A plot of the equilibrium organic-phase amine concentrations against phase

ratio (a/o) is typically a straight line (sometimes after a rapid initial drop) whose slope gives the prevailing amine loss rate.

The same general procedure was used for the present tests, but extended until at least half the amine was removed. The results appeared close to linear for all three amines with phase ratios from about 50/1 to 200/1, but at much higher ratios some curvature became apparent with Amine S-24, and considerably more with both Amine 9D-178 and tri-iso-octylamine:

Amine and Diluent	Range of Phase Ratios, a/o	Cumulative Loss, % of Initial Amine	Average Loss Rate: meq Amine / liter Aq	Average Loss Rate: mg Amine* / liter Aq
Tri-iso-octyl	0- 50	4		
(batch 239C)	50- 400	22	0.0445	16
97% kerosene--	400- 800	36	0.0310	11
3% tridecanol	800-1400	50	0.0250	9
S-24	0- 50	2		
(batch 30B)	50- 250	11	0.0368	13
kerosene	250- 750	27	0.0304	11
	750-1000	33	0.0264	9
	1000-1800	53	0.0245	9
9D-178	0- 30	6		
(batch 193H)	30- 200	18	0.0625	23
kerosene	200- 500	33	0.0467	17
	500-1000	51	0.0375	14
	1000-1500	62	0.0210	8

*Conversion from meq/liter to mg/liter was made by using the theoretical equivalent weight 354 of Amine S-24 and tri-iso-octylamine and the initial average equivalent weight 370 of Amine 9D-178.

These phase ratio ranges were chosen from the plots so that the straight line segments lay within the experimental scatter of the points, which was within ±0.002 M. The cumulative percent losses listed correspond to the high-ratio ends of the ranges; the change of loss rate with cumulative loss is shown more clearly in Fig. 1.1.

The loss rate of Amine S-24 [nominally the single compound bis(1-isobutyl-3,5-dimethylhexyl)amine] reached a constant level of about 9 mg/liter. This rate alone would account for loss of 46% of the initial amine in contacting 1800 volumes of aqueous solutions. The difference between this and the 53% actually lost suggests (assuming negligible interaction between species) that the initial content of more water-soluble amines was about 8%. It can be estimated from the Amine S-24 curve in Fig. 1.1 that, if no other type of loss was involved in a recycling process, the partial replenishing of the more soluble fractions in the course of make-up would lead to leveling off at about

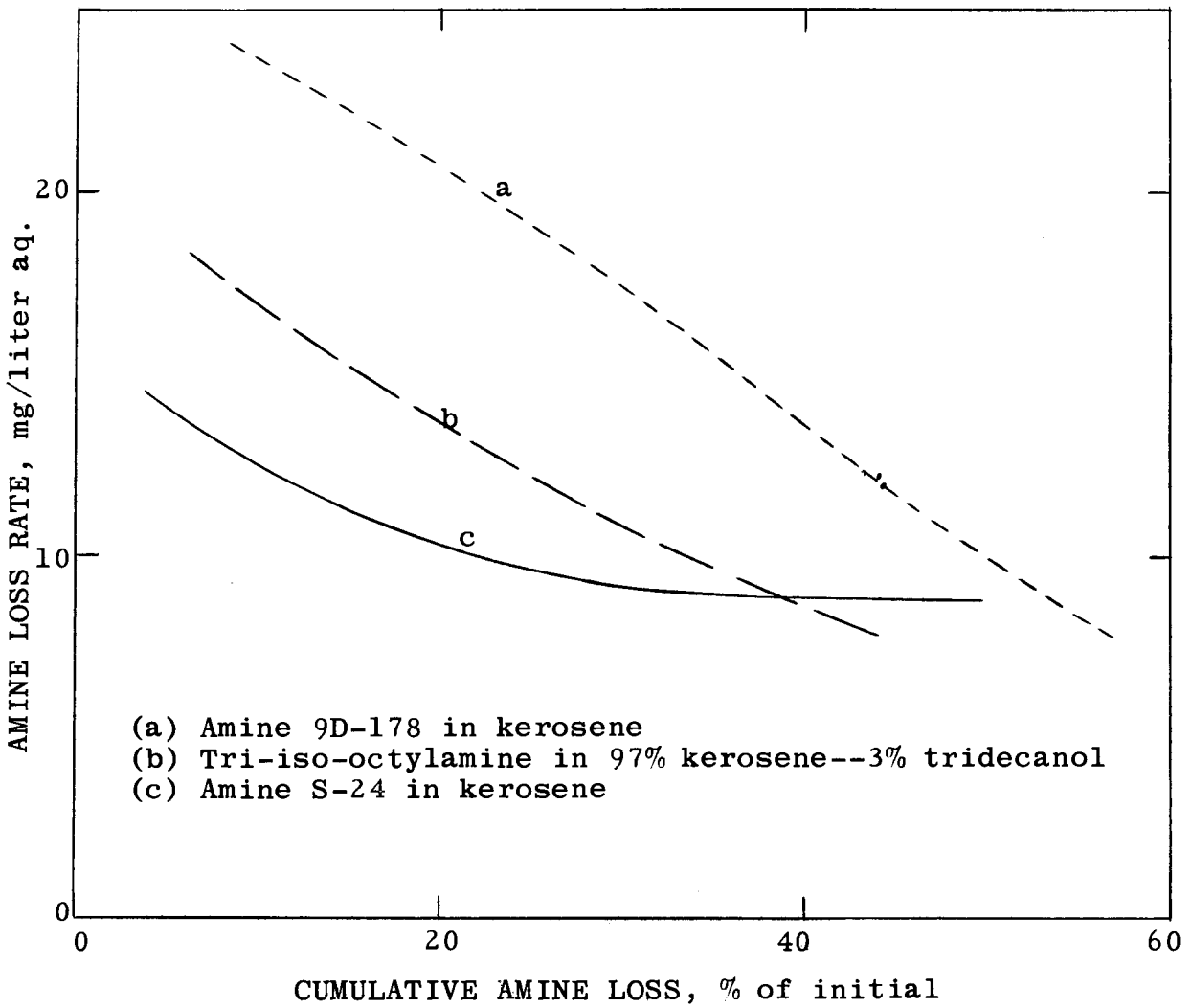

Fig. 1.1 Change of Solubility Loss Rate of Amines. Initial amine concentration, 0.1 M; aqueous solution, 0.5 M H_2SO_4.

10 instead of 9 mg/liter. If the amount of make-up required was increased significantly by other losses, the solubility loss rate would be still higher. For example, if 0.1 M amine solution was lost by entrainment, etc. to the extent of 0.5 ml per liter of raffinate, the loss of contained amine would be 18 mg/liter. In this case, the steady-state solubility loss rate would probably be not much below the 13 mg/liter observed at low phase ratios.

Both tri-iso-octylamine (nominally a mixture of isomers) and Amine 9D-178 (a mixture of homologous compounds) showed the presence of some components less water soluble than Amine S-24, as well as considerable fractions more water soluble. The shape of their curves does not permit the behavior on long recycling with make-up to be estimated in the same way as with

Amine S-24. However, they suggest that if 15-20 mg/liter was lost by entrainment, the steady-state solubility loss rate to this solution might be close to 10 mg/liter with tri-iso-octylamine and not a great deal higher with Amine 9D-178, or about 2/3 of the rates observed at low phase ratios. Thus, the make-up costs of these two reagents, and presumably of others which are similar mixtures, can be significantly lower than has been previously estimated in process evaluations.

2.0 PROCESS DEVELOPMENT

In addition to the studies described below, process development projects during the month have included (1) continued study of the compatibility of amines with liquors containing molybdenum, (2) further evaluation of the Amex process for vanadium recovery, (3) investigation of the effect of temperature on the rate of stripping of vanadium, iron, and aluminum with sulfuric acid in the Dapex vanadium system, (4) study of methods for avoiding phosphate contamination of vanadium products produced by the Dapex and Amex processes, (5) study of the rate of oxidation of Fe(II) in the Dapex extraction system, (6) evaluation of possibilities for limiting molybdenum contamination of Dapex uranium products by control of uranium precipitation conditions, and (7) continued study of uranium extraction from carbonate solutions with quaternary ammonium compounds.

2.1 Comparative Uranium Extraction Isotherms for Several New Amine Samples (W. D. Arnold)

Distribution isotherms for the extraction of uranium from synthetic Marysvale liquor with a number of different amines have been presented in previous reports (ORNL-1959, -2099). Additional comparative isotherm data have been obtained from the same liquor with the following amine samples at 0.10 M amine concentration: a new tertiary amine, i.e., didodecenyl-n-butylamine, submitted by Rohm and Haas, two new samples of tri-iso-octylamine, a new sample of Amine S-24, and a new sample of Amine 9D-178. One of the tri-iso-octylamine samples was submitted by the Gulf Refining Company. The other tri-iso-octylamine sample and the Amine S-24 sample are from pilot scale batches produced by Carbide. The Amine 9D-178 is a relatively recent shipment received from Rohm and Haas on January 21, 1957. Analyses of the purity of these samples and their solubility losses to aqueous liquors are given in Sec. 1.2 of ORNL-2269.

The extraction performances of the two tri-iso-octylamine samples and didodecenyl-n-butylamine were nearly the same (Table 2.1) and comparable to those reported previously for tri-n-octylamine and for a previous tri-iso-octylamine sample (laboratory batch) submitted by Carbide. As expected, all these tertiary amines showed high uranium extraction power, relatively high uranium loadings (~5 g/liter), and excellent selectivity for uranium in the presence of iron(III).

Table 2.1 Extraction Isotherm Data for Several Amines

Aqueous: synthetic Marysvale liquor [in g/liter, 0.15-3.0 U, 5.8 Fe(III), 3.3 Al, 50 SO_4, 2.0 PO_4, 1.7 F; pH 0.9
Organic: 0.10 M amine
Phase ratio, a/o: 2/1
Contact time: 5 min

Amine	Diluent	U (g/liter) Head Liquor	U (g/liter) Organic	U (g/liter) Aqueous	Fe in Organic (g/liter)	Uranium Extraction Coefficient, E_a^o
Tri-iso-octylamine from Gulf (Compound 239B)	97% kerosene--3% tridecanol	0.15	--	0.0009	0.011	~330
		0.3	0.61	0.0018	0.010	340
		0.6	1.2	0.0042	0.008	280
		1.0	2.1	0.0079	0.012	270
		1.25	2.6	0.012	0.006	220
		1.5	3.1	0.019	0.005	160
		2.0	4.1	0.042	0.004	98
		3.0	5.4	0.42	0.002	13
Tri-iso-octylamine from Carbide (pilot batch) (Compound 239C)	97% kerosene--3% tridecanol	0.15	0.25	0.0008	0.015	310
		0.3	0.60	0.0018	0.013	330
		0.6	1.2	0.0038	0.012	320
		1.0	2.0	0.008	--	250
		1.25	2.4	0.012	0.007	200
		1.5	2.8	0.020	0.006	140
		2.0	3.8	0.046	0.004	82
		3.0	5.0	0.41	0.003	12
Didodecenyl-n-butylamine (Compound 253A)	97% kerosene--3% tridecanol	0.15	0.29	0.0010	0.025	290
		0.30	0.62	0.0024	0.021	260
		0.60	1.2	0.0047	0.018	250
		1.0	2.0	0.013	0.012	150
		1.25	2.5	0.017	0.010	150
		1.5	3.0	0.024	0.008	120
		2.0	3.7	0.054	0.005	69
		3.0	5.1	0.38	<0.005	13

Table 2.1 (continued)

Amine	Diluent	U (g/liter) Head Liquor	U (g/liter) Organic	U (g/liter) Aqueous	Fe in Organic (g/liter)	Uranium Extraction Coefficient, E_a^o
Amine S-24 (pilot batch) (Compound 30D)	kerosene	0.15	0.30	0.0009	--	330
		0.30	0.61	0.0017	0.18	360
		0.60	--	0.0039	0.13	~300
		1.0	2.0	0.0088	0.10	230
		1.25	2.4	0.013	0.084	180
		1.5	2.9	0.021	0.068	140
		2.0	3.9	0.066	0.038	59
		3.0	4.3	0.79	0.010	5.5
Amine 9D-178 (Compound 193H)	kerosene	0.15	0.30	0.002	0.40	150
		0.30	0.60	0.003	0.33	200
		0.60	1.2	0.007	0.30	170
		1.0	2.0	0.016	0.14	120
		1.25	2.4	0.027	0.14	90
		1.5	2.8	0.048	0.08	58
		2.0	3.3	0.28	0.015	12
		3.0	3.5	1.2	0.005	2.9

The pilot scale Amine S-24 sample also gave good extraction results. Conformable with past experience, the uranium coefficients were equivalent to and the selectivity with respect to ferric iron only slightly poorer than that of the tertiaries. However, maximum uranium loading of this sample (~4.3 g/liter) was somewhat lower than that shown previously by the laboratory S-24 sample (~4.8 g/liter).

The extraction pattern for the Amine 9D-178 sample was essentially the same as that of the sample tested earlier. Maximum uranium loading was in the vicinity of 3.5 g/liter.

2.2 Effect of Alcohol on Extraction with Di(tridecyl P)amine in Kerosene (W. D. Arnold)

In earlier studies (ORNL-1959, -2099), the selective extraction of uranium in the presence of iron(III) by di(tridecyl P)amine in kerosene was shown to be poor. Addition of alcohol to the kerosene diluent decreased the amount of iron extracted but with 3 v % capryl alcohol added, the selectivity was still poor compared to the more selective secondary amines, e.g., Amine S-24 and Amine 9D-178. Recent tests with 5 v % tridecanol added to the diluent (Table 2.2) show that the addition of

Table 2.2 Effect of Alcohol Addition on Extractions with Di(tridecyl P)amine

Aqueous: synthetic Marysvale liquor [in g/liter, 0.15-3.0 U, 5.8 Fe(III), 3.3 Al, 50 SO_4, 2.0 PO_4, 1.7 F; pH 0.9]
Organic: di(tridecyl P)amine in indicated diluent
Phase ratio, a/o: 2/1
Contact time: 5 min

Diluent	Amine Conc. (M)	U (g/liter) Head Liquor	Org	Aq	Fe in Organic (g/liter)	Uranium Extrn. Coeff., E_a^o
Kerosene*	0.114	0.15	0.3	0.0027	1.3	110
		0.30	0.6	0.0047	1.2	130
		0.60	1.2	0.012	1.0	100
		1.0	1.9	0.024	0.80	80
		2.0	3.6	0.153	0.17	24
		3.0	4.2	0.681	0.048	6.2
95% kerosene-- 5% tridecanol	0.100	0.15	0.3	0.0024	0.40	120
		0.30	0.6	0.0052	0.33	110
		0.60	1.1	0.012	0.31	92
		1.0	1.8	0.026	0.27	70
		1.25	2.3	0.042	0.14	55
		1.5	2.7	0.067	0.090	40
		2.0	3.3	0.200	0.026	16
		3.0	3.9	0.900	0.008	4.3

*Same data as previously reported (ORNL-1959).

alcohol reduced iron extractions by di(tridecyl P)amine to a level comparable to that of Amine 9D-178 in kerosene (see Table 2.1).

Uranium extraction coefficients were not decreased appreciably by the presence of alcohol. This behavior is in marked contrast to that exhibited by certain other secondary amines, e.g., Amine S-24 and Amine 9D-178, where the addition of as little as 2 v % tridecanol severely depressed uranium extractions (ORNL-2269, Sec. 2.2).

2.3 Amex Process for Recovery of Thorium, Uranium and Rare Earths from Sulfuric Acid Digests of Monazite Sands (D. J. Crouse, W. D. Arnold)

Preliminary studies of the Amex process for recovery of thorium and uranium from monazite sulfate liquors were reported in ORNL-1859. It was shown that thorium could be separated from most of the uranium, rare earths, and phosphate by extraction with primary amines. Extractions of rare earths were minimized by loading the solvent to near saturation with thorium. The thorium product was a more suitable feed for subsequent TBP purification processes than the products obtained from the usual fractional precipitation methods.* Uranium was extracted from the thorium-barren liquor with tertiary or certain secondary amines. Uranium extraction coefficients were low but useful.

Since ORNL-1859 was issued, further studies have been made of the Amex process for thorium and uranium recovery from monazite liquors with different reagents or different process conditions. Recovery of rare earths by Amex has also been briefly examined. The composition of the liquors used in these tests, as shown by analysis, was:

	Amount (g/liter)	
	Liquor A	Liquor B
Th	6.9	7.7
U	0.17	0.21
Total rare earth oxides (including Ce_2O_3)	44.2	51.9
Ce_2O_3	21.9	--
SO_4	129	137
PO_4	28	33
pH	0.05	0.1

Extraction of Thorium with Di(tridecyl P)amine. The secondary amines previously tested were weak extractants for thorium from monazite liquors. Tests recently completed on thorium extraction from the same liquor with di(tridecyl P)-

*K. G. Shaw, M. Smutz, and G. L. Bridger, "A Process for Separating Thorium Compounds from Monazite Sands," Ames Laboratory, ISC-407, January, 1954.

amine in kerosene have shown more promise. (This particular amine has shown exceptionally high coefficients for extraction of thorium from sulfate liquors similar in composition to those obtained by processing ores from the Blind River district of Canada (ORNL-2173). The extraction coefficient at low thorium loading is about 5 with 0.1 M amine* in kerosene (Table 2.3). This coefficient, although much lower than obtained with

Table 2.3 Extraction of Thorium with Di(tridecyl P)amine

Organic: 0.10 or 0.20 M di(tridecyl P)amine in kerosene (converted to the amine salt with H_2SO_4 at equilibrium pH 1)
Aqueous: Monazite liquor A (analysis p. 13)
Contact time: 5 min

Amine Conc. (M)	Phase Ratio, o/a	Phase Sep'n Time (sec)	Final pH	Amount (g/liter) Organic Th	Organic Ce	Aqueous, Th	Thorium Extraction Coefficient, E_a^o
0.10	8	70	0.05	0.71	0.11	0.14	5.1
	5	*	0.05	1.15	0.085	0.25	4.6
	2	*	0.05	2.3	0.035	1.10	2.1
0.20	4	*	0.05	1.42	0.20	0.22	6.5
	2.5	*	0.05	2.1	0.16	0.46	4.6
	1	*	0.05	4.5	0.05	1.38	3.3

*Phase separation very slow, i.e., 5-15 min.

primary amines, is of usable magnitude. Since the amounts of cerium (and presumably other rare earths) extracted were small in all tests, control of rare earth contamination of the thorium should be easier with this amine than with primary amines. However, control of uranium contamination (not measured in these tests) may be more difficult because of the weaker competition from rare earths and thorium.

Extraction of Uranium with Tri-n-octylamine. Isotherms have been determined for uranium extraction with 0.05 M tri-n-octylamine in 97% kerosene--3% tridecanol from thorium-barren monazite liquors at two different pH levels (Fig. 2.1). As expected, uranium extractions were better at the higher pH level, e.g., uranium extraction coefficients at low loadings

*In all the extraction tests with monazite liquors subsequently described, the amine was converted to the salt form prior to extraction by contact with dilute sulfuric acid. It is not anticipated that this procedure would be required in process use, but was done only for convenience in experimental testing to avoid excessive pH changes when high organic/aqueous phase ratios were used.

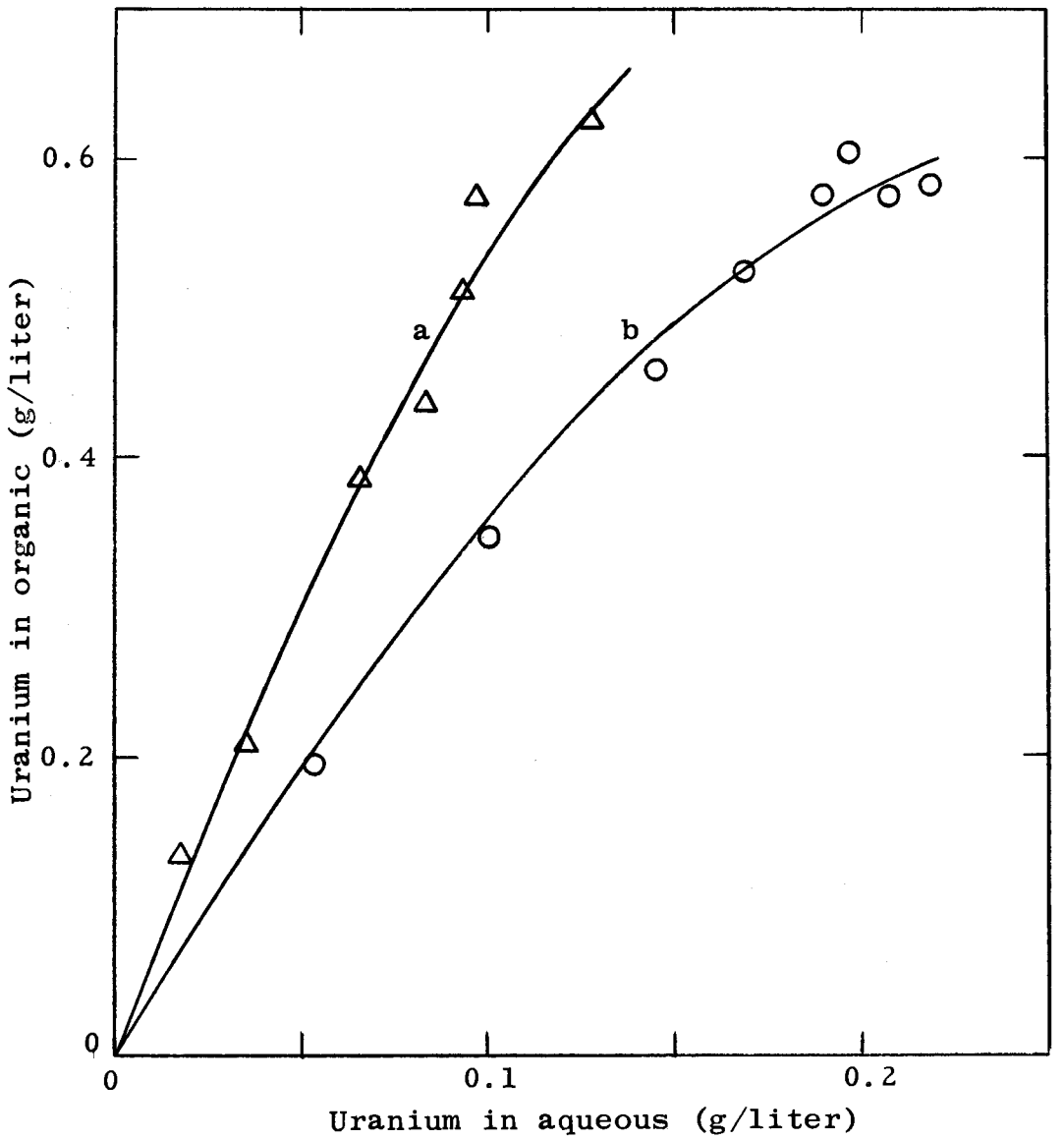

Fig. 2.1 Extraction of Uranium from Thorium-barren Monazite Liquors with 0.05 M Tri-n-octylamine in 97% kerosene--3% Tridecanol. Thorium removed from aqueous feeds with Primene JM-T; (a) (Liquor A p. 13) pH adjusted to 0.4 with NH_4OH (5% NH_3), head U = 0.14 g/liter; (b) (Liquor B) pH 0.1, head U = 0.21 g/liter. Procedure for uranium extraction: organic cascaded against fresh volumes of aqueous, 2 min contact per stage.

were approximately 3.5 at pH 0.1 and 6 at pH 0.4. The indicated maximum uranium loadings in these tests were about 0.6 g/liter at pH 0.1 and 0.7 g/liter at pH 0.4. Phase separation rates, reasonably rapid in all tests, were appreciably faster at pH 0.4 (0.5 - 1 min) than at pH 0.1 (1-2 min).

Rare Earth Extractions. Rare earths have been recovered from the monazite liquors and separated from phosphate by extracting with a primary amine. Prior to rare earth extraction, thorium was removed from the liquor with Primene JM-T. The liquor pH was then adjusted to 0.4 with ammonium hydroxide (5% NH_3) and the uranium extracted with tri-n-octylamine.

The rare earth extraction isotherm for 0.2 M Primene JM-T in kerosene (Fig. 2.2) shows a maximum loading of 7-8 g of rare earth oxide per liter. Extraction coefficients, although low, are adequate for process use. The phosphate content of the extract varied with the rare earth loading, decreasing from 0.47 g/liter at low loading to 0.055 g/liter at a loading of 7.0 g of rare earth oxide per liter. The latter figure corresponds to 0.8% PO_4 based on total rare earth oxide.

Rare Earth Stripping. The rare earths were stripped effectively from 0.2 M Primene JM-T with acidic nitrate and chloride solutions (Table 2.4). As with uranium, nitrate is the more effective stripping anion. Partial precipitation of rare earths occurred in some tests, particularly with chloride. The precipitates were readily redissolved by addition of acid and undoubtedly could have been avoided by using more acidic strip solutions.

Regeneration of the amine to the free base form by contact with a base would be necessary after either chloride or nitrate stripping to avoid interference from these anions in the extraction system. The nitrate or chloride salt formed could be recycled for further stripping.

Sodium carbonate solutions have also been briefly examined as a stripping agent. In this case, the rare earths are nearly completely precipitated in the stripping system. However, in initial tests with 0.2 M Primene JM-T in kerosene, emulsion difficulties were severe and separation of the three phases (aqueous, organic, precipitate) was difficult. Successful use of the carbonate stripping method would thus depend on solving this problem. On the other hand, it should be mentioned that conditions were not controlled in these tests to ensure organic-continuous mixing, a condition which usually is essential for successful operation in the presence of solids. Also, better separations were observed when the Primene JM-T concentration was reduced from 0.2 to 0.1 M.

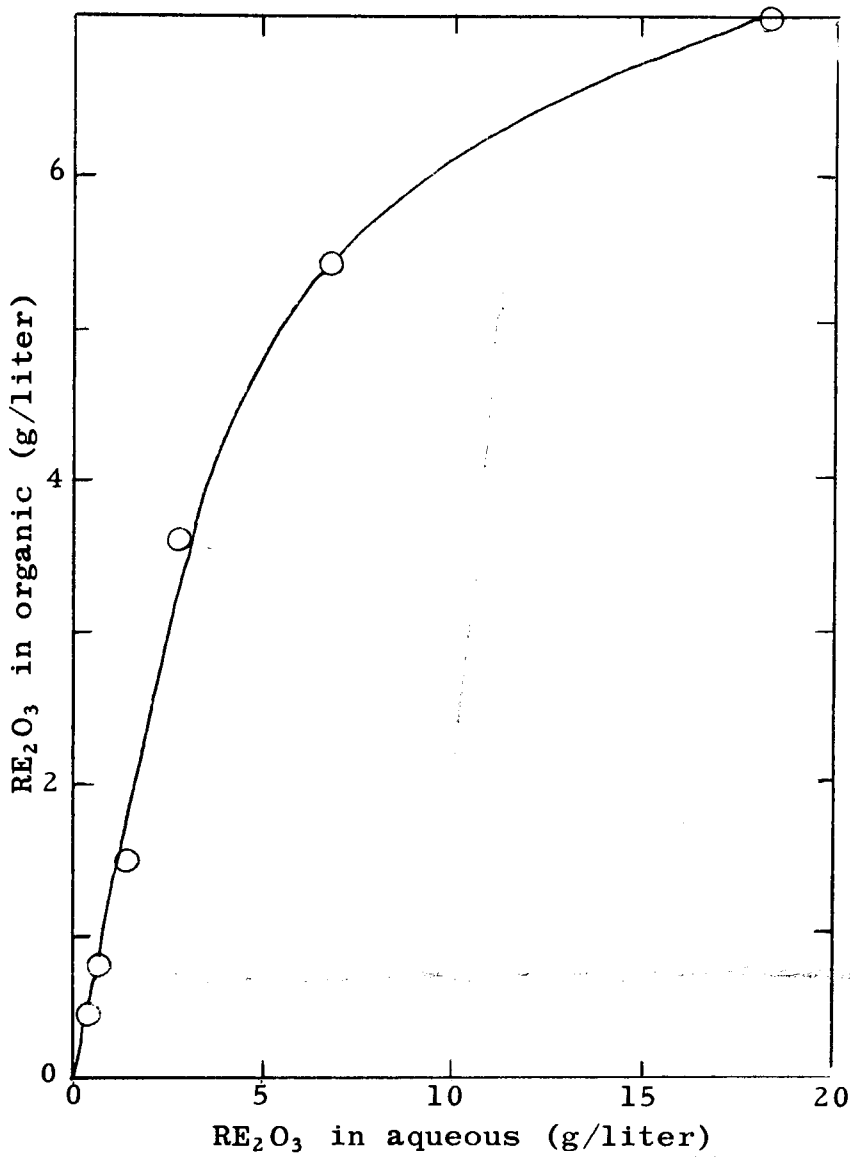

Fig. 2.2 Extraction of Rare Earths from a Thorium- and Uranium-barren Monazite Liquor at pH 0.4 with 0.2 M Primene JM-T in Kerosene. Aqueous phase: thorium extracted from Liquor A (p. 13) with Primene JM-T, liquor pH adjusted to 0.4 with NH_4OH (5% NH_3), and uranium extracted with tri-n-octylamine; head RE_2O_3 = 40 g/liter. Procedure: aqueous phase cascaded against fresh volumes of organic, 2 min contact per stage.

Table 2.4 Stripping of Rare Earths from Primene JM-T with Nitrate and Chloride Solutions

Organic: 0.2 M Primene JM-T in kerosene loaded with 6.7 g RE_2O_3 per liter from a thorium- and uranium-barren monazite liquor
Contact time: 5 min

Stripping Solution	Phase Ratio, o/a	Phase Sep'n Time (sec)	Final Aqueous pH	RE_2O_3 (g/liter) Aqueous	RE_2O_3 (g/liter) Organic	Amount Stripped (%)	Stripping Coefficient, S_o^a
0.1 M HNO_3--0.9 M NH_4NO_3	1	75	1.15	6.1	<0.125	>98	>50
	2	70	1.25	13.3	<0.125	>98	>100
	3	65	1.30	20.3*	<0.125	>98	>150
	4	65	1.35	25.5*	<0.125	>98	>200
	8	**	1.35	29.1*	3.0	55	10
0.1 M HCl--0.9 M NaCl	1	30	--	***	<0.125	>98	>50
	1.5	30	--	***	<0.125	>98	>70
	2	30	--	***	<0.125	>98	>90
	2.5	30	--	***	<0.125	>98	>120
	3	30	--	***	0.150	97.8	120

*Precipitate formed in aqueous after 15-20 min standing but redissolved readily on addition of nitric acid.

**Emulsion formed which was broken by centrifugation.

***Precipitation occurred during stripping. This precipitate settled predominantly in the aqueous phase.

3.0 ENGINEERING STUDIES

In addition to the studies described below, engineering projects during the month have included continuous flow mixer efficiency tests of (1) uranium extraction in the Dapex process and (2) uranium stripping from the Dapex-type solvent with sodium carbonate.

3.1 Continuous Flow Settler Tests of the Dapex Extraction Process (H. F. Bauman)

Engineering studies of the Dapex process are being made to obtain fundamental data on phase separation that can be used as a basis for design of large-scale mixer-settlers. Some of the important criteria for mixing have been previously established in small model equipment which can be scaled up by use of known mixing theory involving geometric similitude and fluid mechanics (ORNL-2213, -2214, -2269). The principles governing phase separation, however, are not so well developed as those for mixing and scale-up factors for settlers, as determined in small model equipment, could involve considerable error. Consequently, the phase separation studies reported here were made in equipment large enough to permit evaluation of variables at flow rates up to 60 gpm of aqueous liquor.

3.1.1 Equipment and Operation

The experimental equipment (Fig. 3.1) consisted of a single mixer-settler unit in which both the organic and aqueous phases of fixed compositions were recycled. The mixer was a baffled tank (12 by 12 in.) and the settler was a 4-ft-dia tank, 3 ft deep. The total liquid depth in the settler was 32 in. (240 gal), composed of equal volumes of each phase (17 in. depth of aqueous and 15 in. depth of organic). The aqueous phase was pumped directly from the bottom of the settler to the mixer, and the organic phase overflowed to a surge tank from which it was pumped to the mixer. Each phase was metered with a rotameter. The interface was observed through a movable periscope immersed in the settler. The temperature was controlled in the range 25 to 28°C.

The organic phase was 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene containing 30 g of TBP per liter. The aqueous phase was a uranium-barren sulfate solution containing sodium sulfate and sulfuric acid (SO_4, 70 g/liter; pH 0.5). In batch tests the settling rate with this solution was determined to be of the same magnitude as that of samples of actual plant liquors from the Colorado Plateau. Thus, in first approximation, the experimental results presented here can be considered as simulating those expected in the raffinate stage of an operating Dapex plant. The physical properties of the phases were:

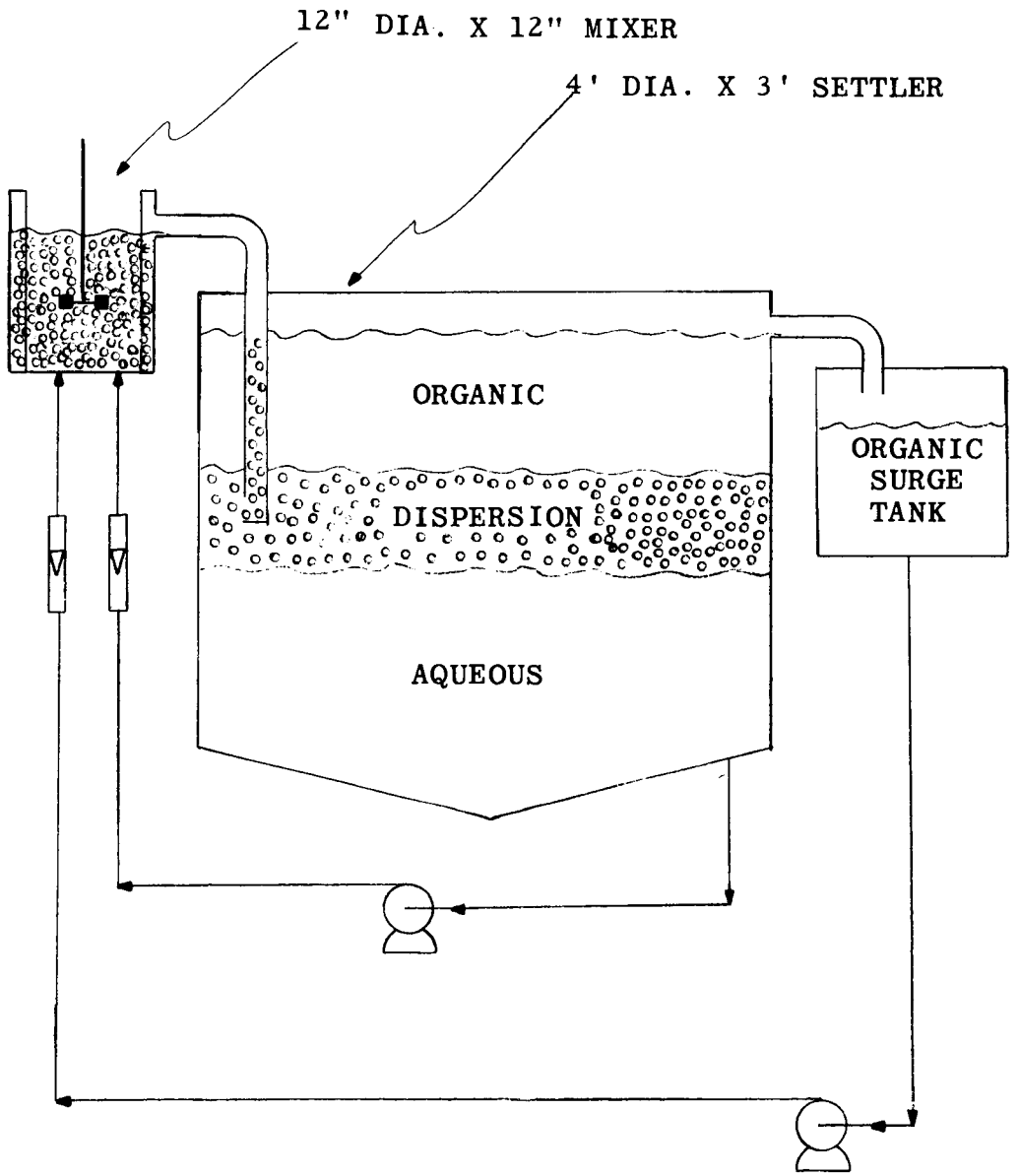

Fig. 3.1. Single Mixer-Settler Unit with Transverse Flow in Settler.

	Aqueous	Organic
Density (g/cc)	1.07	0.82
Viscosity (cp)	1.0	2.2
Interfacial tension (dynes/cm)	19	
Batch settling time in 12- by 12-in. tank (sec)		
Organic continuous dispersion	120	
Aqueous continuous dispersion	90	

Either oil-in-water or water-in-oil dispersions can be formed and maintained for stable operation in the mixer by controlling startup conditions and maintaining the flow ratio of continuous phase to dispersed phase at 1/3 or greater. For example, an oil-in-water dispersion is obtained by starting the aqueous flow first with the mixer agitator running and then starting the organic flow. Conversely, water-in-oil dispersions are obtained by starting the organic flow first. Either type of dispersion will invert when the ratio of continuous phase to dispersed phase is less than 1/10. However, water-in-oil dispersions have been maintained for long periods of operation when the organic/aqueous volume ratio* was 1/3. An electric resistance meter is used to determine the type of dispersion present. When the aqueous phase is continuous (oil-in-water) the resistance of the mixture is of the same order of magnitude as that of the aqueous phase (20-100 ohms); when the organic phase is continuous (water-in-oil) the resistance is much higher (>10,000 ohms).

3.1.2 Experimental Results and Discussion

At steady state a distinct band of dispersion existed at the interface which was of uniform thickness across the entire area of the settler. The thickness of the dispersion increased with increased flow rate until the settler was flooded with dispersion. By measuring the dispersion thickness as a function of flow rates, it was possible to define the relative effects of mixing power, flow patterns, and phase ratio on throughput capacity of the settler for either oil-in-water or water-in-oil dispersions. In general, the dispersion band was thicker for water-in-oil dispersions, confirming the slower settling rate observed in batch tests.

Variation of power input to the mixer over the range of 0.004 to 0.8 hp/gal caused no change in the dispersion band thickness; therefore, the mixing was standardized at 0.03 hp/gal, using a 3-in. flat-bladed turbine at a speed of 1340 rpm.

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*For standard plant practice, to ensure against phase inversion which may be caused by surging flow, it is advisable to maintain at least a 1/1 phase ratio. In the usual case, where aqueous flow into the extraction section is greater than the organic, proper proportions in the mixer are attained by recycling organic from each settler.

Two types of flow in the settler were investigated (Fig. 3.2). One consisted of introducing the mixed phases through a distributor box which was a 45° sector of the settler with the distributor outlet located 315° from the settler outlets, resulting in a circular flow pattern. An unbaffled distributor box was compared with boxes having either a perforated plate or a slot as the distributor outlet. The other flow arrangement consisted of feeding the mixed phases at the side opposite the outlets so that a transverse flow pattern was established. Comparison of the results (Table 3.1) showed no marked difference

Table 3.1 Comparison of Flow Patterns

Phase Ratio, a/o	Cont. Phase	Aq Flow (gpm)	Dispersion Thickness (in.)				
			Perforated[a]	Slot[b]	None[c]	Transverse[d]	Avg.
1/1	Aq	10	1.4	2.3	2.6	1.4	1.9
		22.5	7.9	15	9.1	8.5	10
2/1	Aq	13.3	1.0	.8	1	.75	0.9
		26.7	5.4	5.8	5.8	5.0	5.5
1/1	Org	10	1.3	3	2.4	2.3	2.3
		22.5	10	18	14	16	15
2/1	Org	13.3	2.5	3.4	3.6	3.0	3.1
		26.7	24	26	24	24	24

[a]Distributor box with perforated plate (1/2-in.-dia holes on 1-in. centers)

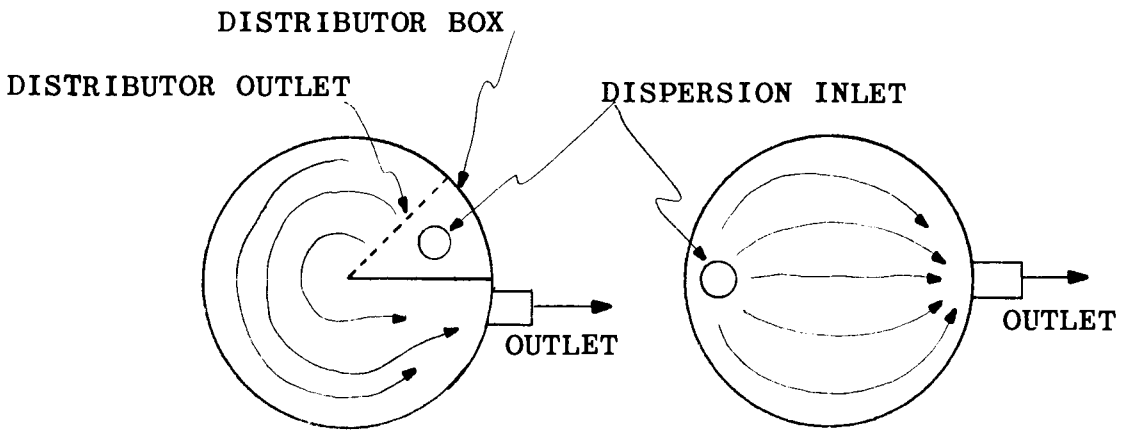
[b]Distributor box with slot (3 by 18 in.)

[c]Distributor box with opening (24 by 32 in.)

[d]Transverse flow, no distributor box

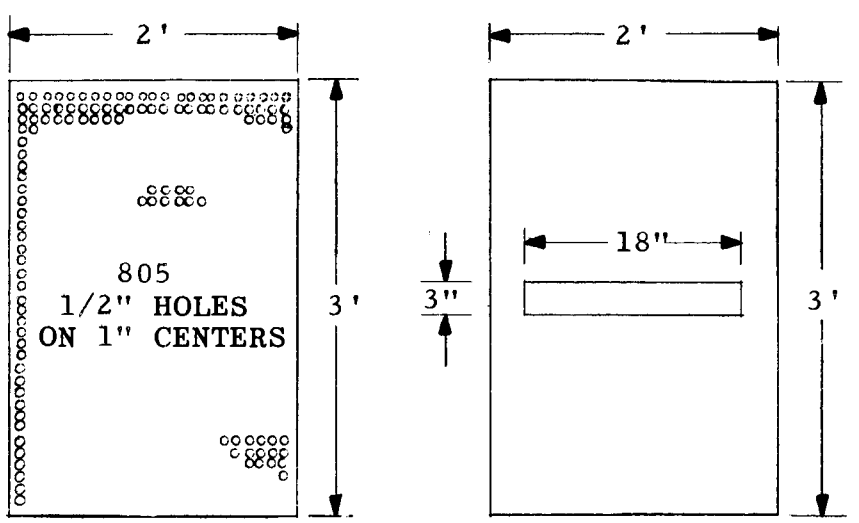
in dispersion thickness with any of the flow patterns tested. In all cases there was a distinct dispersion band in the distributor box which was only slightly thicker than that in the rest of the settler. In subsequent tests, only the transverse flow pattern was used.

Effect of Flow Rate and Phase Ratio. The dispersion thickness for transverse flow in the settler was measured for both oil-in-water and water-in-oil dispersion at aqueous flow rates from 5 to 60 gpm and aqueous/organic flow ratios of 1/2, 1/1, 2/1, 3/1, and 4/1. The data are summarized in Table 3.2 and in Fig. 3.3, where dispersion thickness is plotted against aqueous flow rate per square foot of settler area. The result is a family of nearly parallel lines for different phase ratios, showing that the dispersion thickness increased fivefold when the flow rate was doubled. With either type of dispersion, the band thickness in the settler at constant total flow increased with increased ratio of dispersed continuous phase. In Fig. 3.3,



CIRCULAR FLOW TRANSVERSE FLOW

FLOW PATTERNS (PLAN VIEW)



PERFORATED PLATE SLOTTED PLATE

DISTRIBUTOR OUTLETS

Fig. 3.2. Flow Patterns and Distributors

Table 3.2 Capacity of 4-ft-dia Settler

(Interface area = 12 sq ft)

Phase Ratio, a/o	Aqueous Flow Rate gpm	Aqueous Flow Rate gpm/sq ft	Dispersion Thickness (in.) Oil-in-water dispersion	Dispersion Thickness (in.) Water-in-oil dispersion
1/2	5	.42	--	.5
	10	.83	--	2.5
	15	1.25	--	9.3
1/1	10	.83	1.4	2.3
	15	1.25	2.9	5.5
	20	1.67	8.1	14
	25	2.08	12	26
	30	2.50	22	32
2/1	13	1.11	0.8	3.0
	20	1.67	3.6	9.3
	30	2.50	5.3	24
	40	3.33	12	32
	60	5.00	27	--
3/1	15	1.25	0.6	3.5
	30	2.50	4.6	--
	45	3.75	8.3	--
	60	5.00	20	--
4/1	20	1.67	0.5	--
	40	3.33	7.3	--
	60	5.00	9.9	--

where dispersion thickness is shown as a function of only the aqueous flow rate, the effect of phase ratio on organic-continuous dispersion is minimized, i.e., the results are nearly the same for aqueous/organic ratios of 1/2, 1/1, and 2/1. For aqueous-continuous dispersions, the band thickness increased with increased organic content. For example, at an aqueous flow rate of 2 gpm/sq ft the band thickness at phase ratio of 4/1 and 1/1 was 1 and 10 inches, respectively.

The flow capacity of the 4-ft settler can be summarized in terms of aqueous flow rate (gpm/sq ft) at constant dispersion thickness. Three band depths were chosen and the flow capacity as read from Fig. 3.3 are

Dispersion Thickness (in.)	a/o	Aqueous Flow Rate (gpm/sq ft) Org. Continuous, 1/1	Aq. Continuous 1/1	Aq. Continuous 2/1	Aq. Continuous 3/1	Aq. Continuous 4/1
1		0.6	0.8	1.1	1.4	2.0
5		1.1	1.5	2.2	2.8	3.9
25 (flooding)		2.2	2.7	4.6	5.8	7.2

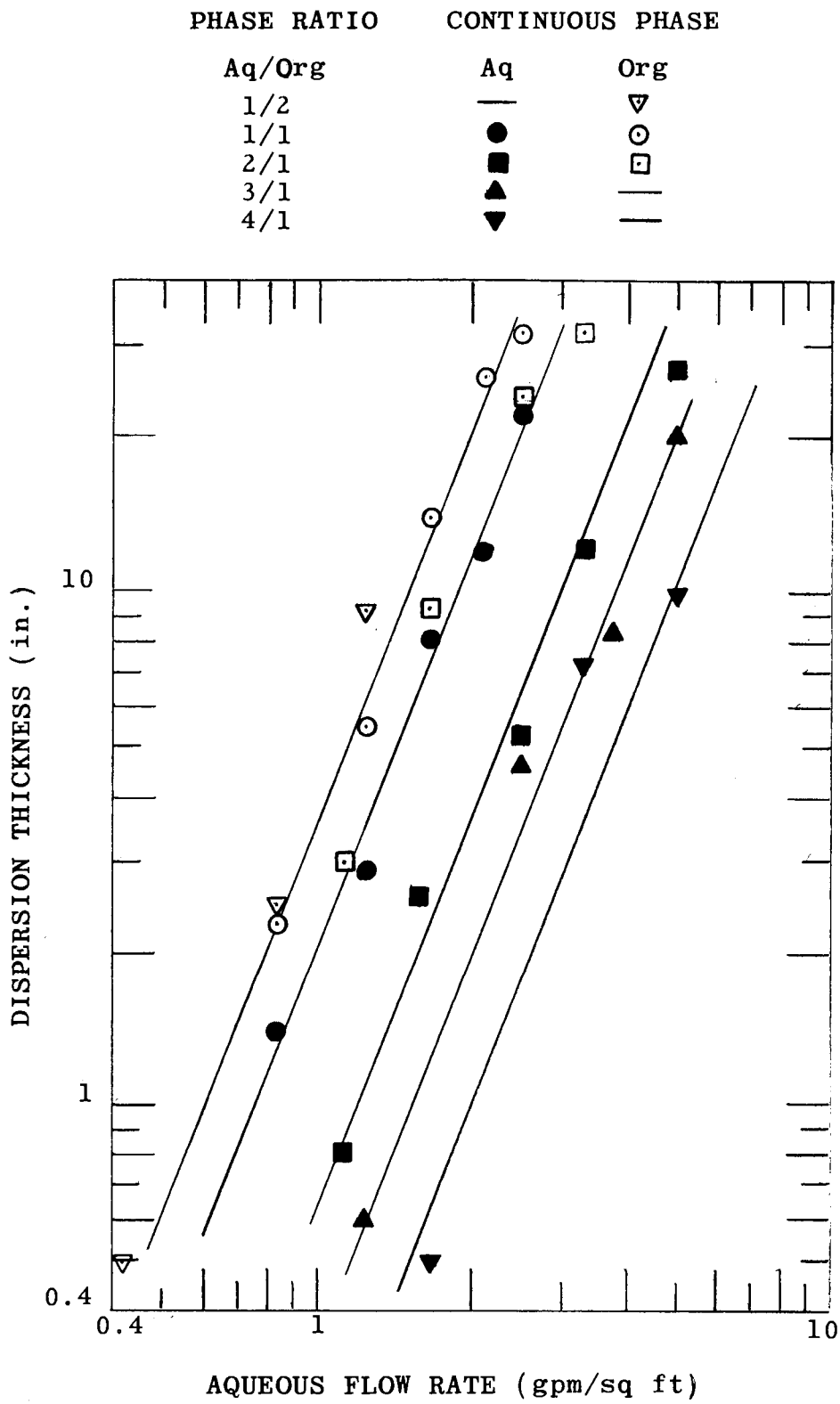


Fig. 3.3 Capacity of 4-ft-dia Settler.

The aqueous flow rate giving a 5-in. dispersion band may be considered the nominal flow capacity of the settler, being about half of the flow rate causing flooding with all types of dispersions tested. Use of this nominal capacity for design would allow a safety factor of 2 for variation in settling properties of the system and surges in flow. It would be advisable to design settlers with sufficient capacity to permit operation with the organic phase continuous in cases where there is a possibility of ore slimes entering the extraction plant or of encountering certain liquors that tend to form slow-breaking oil-in-water dispersions.

Entrainment. The amount of organic phase entrained in the aqueous phase leaving the settler was markedly affected by the type of dispersion formed in the mixer and was virtually independent of phase ratio, flow rate and flow pattern in the settler. For organic continuous dispersions, the organic entrainment, immediately after the primary phase break, was consistently less than 0.01 v % compared to an average of 0.15 v % for aqueous-continuous dispersions. This is consistent with the generality that the continuous phase usually contains a "haze" of the dispersed phase after primary phase separation.

Good process economy would require that a longer settling time be provided after aqueous-continuous mixing to permit recapture of the entrained organic. However, in most extraction plants it would probably be preferable to design for organic-continuous mixing, at least in the raffinate stage.

4.0 FUNDAMENTAL STUDIES

In addition to the work described below, fundamental projects studied during the month have included (1) uranium distribution between aqueous sulfate and organic amine solutions, (2) correlation of uranium extraction with aqueous uranium sulfate complex formation, (3) measurement of amine salt aggregation by light scattering, (4) determination of degree of uranium-organophosphate complex association by isopiestic vapor pressure measurements of the hydrocarbon diluent, and (5) preparation for a proposed study of species in organic amine solutions by means of dielectric measurements.

4.1 Estimation of Bisulfate Ion Dissociation in Sulfuric Acid--Sodium Sulfate Solutions (C. F. Baes)

In the course of recent solvent extraction and other chemical studies involving aqueous sulfuric acid--sodium sulfate solutions, estimation of the actual ionic concentrations of H^+, $SO_4^=$, HSO_4^- has been needed. The following method provides this by means of the relation of the bisulfate dissociation to the practical sulfuric acid activity coefficient and the ion activity coefficient product, together with a criterion for evaluation of the latter as a function of ionic strength and solution composition.

The practical activity coefficient $(\gamma\pm)_{H_2SO_4}$ and the ion activity coefficient product $g^2_{H^+}g_{SO_4^=}$ are defined by

$$a_{H_2SO_4} = C^2_{H^+}C_{SO_4^=} \; (\gamma\pm)^3_{H_2SO_4} \tag{1}$$

$$a_{H_2SO_4} = [H^+]^2[SO_4^=]g^2_{H^+}g_{SO_4^=} \tag{2}$$

where a designates activity, C designates nominal (stoichiometric) concentration, and quantities in brackets are the actual ionic concentrations. The practical activity coefficient of sulfuric acid is unusually low at ordinary solution concentrations. If sulfuric acid was completely dissociated, the ionic concentrations $[H^+]$ and $[SO_4^=]$ would equal the stoichiometric concentrations C_{H^+} (i.e., $2C_{\Sigma H_2SO_4}$) and $C_{SO_4^=}$ (i.e., $C_{\Sigma SO_4}$), and $g^2_{H^+}g_{SO_4^=}$ would equal $(\gamma\pm)^3_{H_2SO_4}$, in the same way that $g^2_{Na^+}g_{SO_4^=}$ equals $(\gamma\pm)^3_{Na_2SO_4}$, Na_2SO_4 being assumed completely dissociated. Since sulfuric acid is not completely dissociated, the product $C^2_{H^+}C_{SO_4^=}$ is greater than $[H^+]^2[SO_4^=]$, and $(\gamma\pm)^3_{H_2SO_4}$ is correspondingly less than $g^2_{H^+}g_{SO_4^=}$.

From the combination of Eqs. 1 and 2,

$$(\gamma\pm)^3_{H_2SO_4} = \frac{[H^+]^2[SO_4^=]}{C^2_{H^+}C_{SO_4^=}} \; (g^2_{H^+}g_{SO_4^=}) \tag{3}$$

it is clear that if the dissociation of bisulfate is known (i.e., if $[H^+]$ and $[SO_4^=]$ are known) it is possible to calculate the product $(g^2_{H^+}g_{SO_4^=})$ from $(\gamma\pm)_{H_2SO_4}$. Conversely, if $(g^2_{H^+}g_{SO_4^=})$ can be estimated for a given solution, then the dissociation can be determined from $(\gamma\pm)_{H_2SO_4}$.

The Raman measurements of Young et al.[1] provide the most extensive information on the variation of the bisulfate ion dissociation quotient

$$Q = [H^+][SO_4^=]/[HSO_4^-] \tag{4}$$

with ionic strength in pure sulfuric acid solution. Their results in the range 0.05-2 M H_2SO_4, along with results of

(1) T. F. Young, Rec. Chem. Progr., 12: 81 (1951); T. F. Young, L. F. Maranville, and H. M. Smith, U. of Chicago, private communication, March, 1956.

conductivity calculations by Sherrill and Noyes[2] at lower concentrations, are fitted adequately by the equation

$$\log Q = \log 0.0102 + \frac{2.036\ I^{1/2}}{1 + 0.4\ I^{1/2}} \qquad (5)$$

where I is the ionic strength.[3] Values of $(\gamma\pm)_{H_2SO_4}$ are available for pure sulfuric acid solutions[4] and can be obtained for sulfuric acid--sodium sulfate solutions.[5] First, $g^2_{H^+}g_{SO_4^=}$ was calculated as a function of ionic strength for pure sulfuric acid solutions, using the dissociation quotients given by Eq. 4. It was found that this ion product plotted against

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(2) M. S. Sherrill and A. A. Noyes, J. Am. Chem. Soc., 48: 1861 (1926).

(3) The ionic strength was determined from the calculated concentrations of H^+, HSO_4^-, $SO_4^=$, and Na^+, the only species assumed to be present in the solutions considered. It can then be shown that $I = 3C_{\Sigma SO_4} - 2[HSO_4^-]$, where $C_{\Sigma SO_4}$ denotes the total sulfate concentration.

(4) H. S. Harned and W. J. Hamer, J. Am. Chem. Soc., 57: 27 (1935); R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," Academic Press, Inc., New York, N. Y., 1955, p. 462.

(5) H. S. Harned and R. D. Sturges, J. Am. Chem. Soc., 47: 945 (1925); G. Åkerlöf, J. Am. Chem. Soc., 48: 1160 (1926); M. Randall and C. T. Langford, J. Am. Chem. Soc., 49: 1445 (1927). These are e.m.f. measurements involving the Hg_2SO_4 electrode. They were recalculated for the present purpose, using the subsequent determination of E^o for this electrode (0.61515 v) by Harned and Hamer.[4] The resulting $(\gamma\pm)_{H_2SO_4}$ values are described adequately by the empirical equation

$$\log (\gamma\pm)_{H_2SO_4(x)} = \log (\gamma\pm)_{H_2SO_4(c)} - [0.2305 - 0.3355(\tfrac{x}{c}) + 0.1050(\tfrac{x}{c})^3]c^{0.6233}$$

in the range c = 0.1-2 m. The subscripts (x) and (c) denote activity coefficients in x molal sulfuric acid - (c-x) molal sodium sulfate and in pure c molal sulfuric acid, respectively.

ionic strength nearly coincides with the corresponding curve for $(\gamma\pm)^3_{Na_2SO_4}$ in pure sodium sulfate solution,[6] in the range I = 0.16-1.8 m. Since at a given ionic strength in this range, $g^2_{H^+}g_{SO_4^=}$ nearly equals $g^2_{Na^+}g_{SO_4^=}$ [i.e., $(\gamma\pm)^3_{Na_2SO_4}$] for the separate electrolytes, the assumption was tried that for all mixtures of them at this ionic strength $g^2_{H^+}g_{SO_4^=}$ would retain the same value. This assumption is analogous to the expected behavior for mixtures of two completely dissociated 1-1 electrolytes if they exhibit the same activity coefficient behavior when in separate solutions.[7]

On this basis, values of $(\gamma\pm)_{Na_2SO_4}$ in pure sodium sulfate solution[6] and of $(\gamma\pm)_{H_2SO_4}$ in sulfuric acid--sodium sulfate solutions,[5] read from smoothed plots, were used in Eq. 3 to calculate the ion concentrations and hence the bisulfate dissociation quotient Q (Eq. 4). Values of the parameters were chosen to give sets of values of Q at constant ionic strength and sets at constant total sulfate (all concentrations in molality):

$\left(\frac{C_{H_2SO_4}}{C_{\Sigma SO_4}}\right)\backslash C_{\Sigma SO_4}$:	Q = $[H^+][SO_4^=]/[HSO_4^-]$			
	0.1	0.2	0.5	1
0	0.061	0.096	0.178	0.3
0.25	0.057	0.089	0.167	0.3
0.5	0.056	0.085	0.172	0.37
0.75	0.056	0.088	0.183	0.47
1	0.059	0.091	0.196	0.54

$\left(\frac{C_{H_2SO_4}}{C_{\Sigma SO_4}}\right)\backslash$ I:	0.4	0.7	1	1.5
0	0.072	0.102	0.131	0.178
0.25	0.079	0.117	0.150	0.207
0.5	0.086	0.136	0.182	0.281
0.75	0.103	0.162	0.229	0.39
1	0.116	0.185	0.283	0.50

(6) Values of $(\gamma\pm)_{Na_2SO_4}$ are listed by H. S. Harned and B. B. Owen ("The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 415), and by R. A. Robinson and R. H. Stokes (Ref. 4, p. 486).

(7) Cf. H. S. Harned and B. B. Owen, op. cit., pp. 461-466.

The same calculations provided values of the ratio of the actual ionic concentration of bisulfate to total sulfate:

$\left(\frac{C_{H_2SO_4}}{C_{\Sigma SO_4}}\right)$ \ $C_{\Sigma SO_4}$:	$[HSO_4^-]/C_{\Sigma SO_4}$ 0.1	0.2	0.5	1
0.25	0.28	0.30	0.33	0.3
0.5	0.48	0.53	0.56	0.55
0.75	0.61	0.66	0.69	0.65
1	0.69	0.74	0.76	0.70

$\left(\frac{C_{H_2SO_4}}{C_{\Sigma SO_4}}\right)$ \ $C_{\Sigma SO_4}$:	0.4	0.7	1	1.5
0.25	0.30	0.32	0.33	0.34
0.5	0.53	0.55	0.56	0.56
0.75	0.66	0.68	0.69	0.66
1	0.74	0.76	0.75	0.71

Besides providing the desired ready means of estimating the actual ionic concentrations through the range covered, these tabulations also show several interesting features: (1) At constant total sulfate concentrations of 0.1, 0.2, and 0.5 m, the dissociation quotient Q is nearly constant as the composition is changed, although the accompanying change in ionic strength is considerable; (2) Q varies with composition at constant ionic strength by as much as a factor of 3; (3) the ratio $[HSO_4^-]/C_{\Sigma SO_4}$ is roughly constant as the total sulfate concentration, $C_{\Sigma SO_4}$, is changed at a constant ratio of acid to total sulfate.

The foregoing values of Q compare favorably with the limited information available in the literature. The values of Q for pure sulfuric acid agree with the experimental values within about ±10%. Young et al.[1] have also measured bisulfate dissociation in ammonium bisulfate solutions. The present Q values at $C_{H_2SO_4}/C_{\Sigma SO_4} = 0.5$ (i.e., sodium bisulfate) agree with these results within experimental error. Eichler and Rabideau[8] found, by potentiometric measurements at 1 M ionic strength in acid perchlorate solutions containing a small amount of sodium sulfate, Q = 0.095 in 0.99 M $NaClO_4$--0.01 M $HClO_4$ and 0.30 in 1 M $HClO_4$. The present values at I = 1 m in sodium sulfate solution (Q = 0.13) and in sulfuric acid solution (Q = 0.27) show about the same variation with change in acidity.

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(8) E. Eichler and S. Rabideau, J. Am. Chem. Soc., 77: 5501 (1955).

Raman measurements on sulfuric acid--sodium sulfate solutions, which when completed will provide probably the best test of the present calculations, are underway in the laboratory of Prof. T. F. Young, University of Chicago. Preliminary results[9] obtained over most of the range corroborate the calculated $[HSO_4^-]/C_{\Sigma SO_4}$ ratios with a relative mean deviation of about 8%.

(9) At the invitation of Professor Young, Dr. Baes visited his laboratory to participate with him and his student, B. M. McCarroll, in these preliminary measurements.