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ORNL-2380
Technology-Raw Materials

PROGRESS REPORT ON RAW MATERIALS

FOR JUNE, 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 JUNE, 1957

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

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

OTHER REPORTS IN THIS SERIES

Preliminary,	ORNL-2268	(20¢)
February,	ORNL-2269	(25¢)
March,	ORNL-2306	(25¢)
April,	ORNL-2346	(25¢)
May,	ORNL-2366	(25¢)

ABSTRACT

Systematic Studies. Some new organonitrogen compounds are described, and uranium extraction power in standard tests and reagent loss by distribution to an aqueous solution are reported. A sample representative of the Rohm and Haas Amine 9D-178 now commercially available in pilot plant quantities was similar in assay, uranium extraction power, and loss rate to samples examined previously. A sample of trilaurylamine, which may become commercially available, showed good extraction power, comparable to other long straight chain tertiary amines, and low loss rate.

The uranium extraction power of N-benzyl-1-isobutyl-3,5-dimethylhexylamine was much higher than that of most other types of amines, but not so high as that of N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine. A series of N-cyclohexylmethyl secondary amines containing the same branched alkyls showed only the usual order of uranium extraction power, confirming the importance of the benzene ring in the N-benzyl amines.

Acetylation of the sterically hindered Amine 9D-178 (a step in the differential determination of primary, secondary, and tertiary amines) gave constant results over a range of reagent quantities and reaction times, indicating complete reaction of secondary amine without significant degradation of tertiary amine present in the sample.

Mono-n-alkylphosphoric acids prepared from 2,6,8-trimethylnonanol-4 (DDPA), 2-methyl-7-ethyl-undecanol-4 (TDPA), and 3,9-diethyltridecanol-6 (HDPA) were removed almost completely

from kerosene solution (0.1 M) by formation of the sodium salts. The HDPA salt was nearly insoluble in 10% aqueous sodium carbonate or sodium hydroxide solution, while the other two were highly soluble. Precipitation of the HDPA salt was prevented by modification of the kerosene, but high modifier concentrations were required, i.e., 25% TBP or 15% decanol. The uranium extraction power from sulfate solution was severely depressed by such modifier concentrations.

Loss of monoalkylphosphoric acids by distribution from 0.1 M kerosene solution to 0.5 M sulfate solution, pH 1, was 0.10 g of DDPA, 0.03 g of TDPA, and 0.005 g of HDPA per liter of aqueous solution. Loss of DDPA from 0.5 M kerosene solution was 0.26 g/liter.

Process Development Studies. Preliminary attempts to adapt the Amex process to treatment of ore leach slurries resulted in excessive volume losses of the organic phase and preferential loss of amine from the diluent, apparently through chemi-sorption on the solid surfaces. Loss of amine by the latter mechanism varied with change in amine type and structure but was excessive for all compounds tested.

Uranium extraction isotherms determined for two new tertiary amine samples, i.e., a mixed tertiary amine (General Mills) and trilaurylamine (Archer-Daniels-Midland), were essentially identical to those determined previously for other tertiary amines. Both amines showed high uranium extraction power, relatively high uranium loadings, and excellent selectivity with respect to ferric iron.

Engineering Studies. The stage efficiency of a baffled tank mixer for extraction of uranium by D2EHPA in 97% kerosene-3% TBP from a solution of typical composition increased with increased impeller speed at fixed residence time, ranging from 14% at 150 rpm to 92% at 1170 rpm in 4.8 min. At constant turbine speed the efficiency increased with increased holdup time; for example, at 400 rpm the efficiency ranged from 35% in 0.17 min to 81% in 4.8 min residence time. These efficiencies are lower than those previously obtained with a relatively high grade uranium liquor under somewhat different operating conditions.

Fundamental Studies. Measurement of light scattering by amine species in benzene solution indicated the weight-average molecular weight of di-n-decylamine sulfate to be 24,000-30,000, corresponding to association into aggregates averaging ~40 amine sulfate units per aggregate, over the concentration range from 0.0024 to 0.05 M. Less complete data indicated that tri-n-octylamine sulfate is monomeric at concentration up to 0.025 M.

1.0 SYSTEMATIC STUDIES

In addition to the studies described below, systematic studies during the month have included (1) preliminary study of the applicability of amine and organophosphorus extractants to separations in fuel reprocessing and waste disposal, (2) screening new organophosphorus compounds as uranium extractants, (3) testing new phosphonate esters as solvent modifiers for Dapex extraction, (4) comparison of base strengths of amine diluent combinations, (5) extraction of thorium from sulfate liquor with di- and monoalkylphosphoric acids, and (6) extraction of rare earths with di- and monoalkylphosphoric acids.

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

The uranium extraction power of several new compounds was determined by extraction tests previously described (ORNL-1734, p. 6; cf. ORNL-2269). These compounds included simple amines and some other types of basic compounds submitted by vendors for evaluation and a series of amines specially prepared for correlation of extraction power with variation in structure. In addition to the new compounds, new batches of Amine 9D-178, N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine, and trilaurylamine were tested for comparison with previous batches (Table 1.1). The purity of most of these amines was examined by direct potentiometric titration in nonaqueous medium to determine the apparent equivalent weights, and by differential titration as a measure of primary, secondary, and tertiary amine contents (Table 1.2). The loss rates to a sulfate liquor were measured for some of the amines (Table 1.3).

The new batch of Amine 9D-178 was supplied by Rohm and Haas Co. as representative of the product now commercially available in pilot-plant quantities, and the trilaurylamine by Archer-Daniels-Midland as a product which may become commercially available. Both gave good uranium extraction and good phase separation. The extraction coefficients with Amine 9D-178 were nearly the same as had been obtained with previous batches. The mean equivalent weight, 370, is about the same as of previous batches (mostly 370-380), indicating that the range of homologous components is similar. (Amine 9D-178 is nominally a mixture of 24- to 27-carbon amines, individual equivalent weights 350-400.) The loss rates to a sulfate liquor were in the same range as with previous batches, and the decrease in loss rate (20 to 15 mg per liter of aqueous) after extended scrubbing of a sample with dilute sulfuric acid is consistent with the previously reported decrease of loss rate at very high aqueous/organic phase ratios (ORNL-2306).

The extraction coefficients with the trilaurylamine were similar to those with a previous batch, prepared in this laboratory (ORNL-1734), and also to those with the mixed n-octyl-n-decyl tertiary amine (reported last month) and with dilaurylbutylamine. The extraction in kerosene diluent was a little better with trilaurylamine than with the mixed octyl-decyl amine or with tri-n-octylamine, but (as also with those) it was improved by addition of tridecanol, showing that there is still

Table 1.1 Preliminary Tests of Uranium Extractions from Sulfate Solutions

Compound	Batch No.	Concn., M	% U Extracted and Extraction Coeff. (o/a) Kerosene %	Kerosene E	Chloroform %	Chloroform E	Benzene %	Benzene E	Benzene Prewashed %	Benzene Prewashed E	Phase Separation
Primary Amines											
Armeen O	275A	0.1	32	0.5	62	2	20	0.2	1	0.1	Cloudy phases
Armeen OD	276A	0.1	16	0.2	52	1	20	0.2	1.2	0.1	Poor
Secondary Amines											
Amine 9D-178	193H	0.01	35	-	-	-	35	-	36	-	
		0.1	99	70	-	-	98	60	97	35	Good
N-Benzyl-1-isobutyl-3,5-dimethylhexyl	244B	0.01	31	-	25	-	34	-	34	-	
		0.1	>99	1400	99	150	>99	3000	>99	1000	Good
N-Benzyl-1-(3-ethylpentyl)-4-ethyloctyl	228B	0.01	42	-	22	-	39	-	41	-	
		0.1	>99	8000	99	70	>99	2000	>99	1500	Good
4-RKB-21 N-(cyclohexylmethyl)-1-isobutyl-3, 5-dimethylhexyl	297A	0.01	37	-	2	-	36	-	33	-	
		0.1	99	85	84	5	99	90	98	50	Good
4-RKB-20 N-(1-methylcyclohexylmethyl)-1-isobutyl-3,5-dimethylhexyl	296A	0.01	34	-	4	-	42	-	26		
		0.1	96	20	64	2	96	25	94	15	Good
4-RKB-16 N-(2,4,6-trimethylcyclohexylmethyl)-1-isobutyl-3,5-dimethylhexyl	293A	0.01	38	-	4	-	29	-	28	-	
		0.1	99	70	59	1.5	96	25	95	20	Good

Table 1.1 (Cont'd)

Compound	Batch No.	Concn., M	% U Extracted and Extraction Coeff. (o/a) Kerosene %	Kerosene E	Chloroform %	Chloroform E	Benzene %	Benzene E	Benzene Prewashed %	Benzene Prewashed E	Phase Separation
Secondary Amines											
4-RKB-19	295A	0.01	41	-	5	-	42	-	39	-	
N-(cyclohexylmethyl)-1-(3-ethylpentyl)-4-ethyloctyl		0.1	96	25	75	3	99	95	98	50	Good
4-RKB-18	294A	0.01	38	-	2	-	31	-	32	-	
N-(1-methylcyclohexylmethyl)-1-(3-ethylpentyl)-4-ethyloctyl		0.1	99	120	54	1	97	35	96	25	Good
4-RKB-15	292A	0.01	36	-	2	-	27	-	27		
N-(2,4,6-trimethylcyclohexylmethyl)-1-(3-ethylpentyl)-4-ethyloctyl		0.1	99	130	44	0.8	96	25	95	20	Good
Tertiary Amines											
Butyldilauryl	101A	0.1	Insoluble		88	7	99	140	99	100	Good
Trilauryl	86B	0.01	41	-	7	-	51	-	52	-	
		0.1	99[a]	80[a]	83	5	99	150	99	100	Good
Other Compounds											
Aminopolybutene	285A	10 v %[b]	0.5	-	nil	-	0.4	-	0.5	-	Good
Arneel S	269A	10 v %[b]	1	-	2	-	1	-	0.5	-	Good
"Duomeen T" salt of poly-dodecylbenzenesulfonic acid	284A	10 v %[b]	0.3	-	1.6	-	0.8	-	0.2	-	Poor in Kerosene

Table 1.1 (Cont'd)

Compound	Batch No.	Concn., M	% U Extracted and Extraction Coeff. (o/a) Kerosene %	Kerosene E	Chloroform %	Chloroform E	Benzene %	Benzene E	Benzene Prewashed %	Benzene Prewashed E	Phase Separation
Other Compounds											
Emery 578-42-R	288A	0.1	Emulsion		Emulsion		Emulsion		Emulsion		
Imidazoline from fatty acid mixture and triethylenetetramine	286A	0.1 M	nil	-	-	-	ppt.		ppt.		Poor
Polyrod 0100	282A	0.1	ppt.		ppt.		42	0.7	41	0.7	Poor
Polyrod 0200	283A	0.1	Emulsion		51	1	3rd phase		0.3	-	Poor

[a] In 97% kerosene-3% tridecanol: 99% extraction, $E_a^o = 80$
In 95% kerosene-5% tridecanol: 99% extraction, $E_a^o = 95$

[b] Arbitrary concentration of 10 v % was used because the equivalent weight could not be determined for the sample as received.

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

Compound	Batch No.	Source[a]	% by Differential Titration			Equiv. Wt.	
			Prim.	Secon.	Tert.	Theo.	Found
Primary Amines							
Armeen O (derived from red oil -- primarily Oleic acid)	275A	A	-	-	-	287	288
Armeen OD (distilled red oil Amine)	276A	A	-	-	-	265	266
Secondary Amines							
Amine 9D-178	193H	R	7	83	10	-	370
N-Benzyl-1-isobutyl-3, 5-dimethylhexyl	244B	CU	5	92	3	275	277
N-Benzyl-1-(3-ethylpentyl)-4-ethyloctyl	228B	C	4	95	<1	347	357
4-RKB-21 N-(cyclohexylmethyl)-1-isobutyl-3, 5-dimethylhexyl	297A	C	2+	96	1+	282	281
4-RKB-20 N-(1-methylcyclohexylmethyl)-1-isobutyl-3, 5-dimethylhexyl	296A	C	2	97	<1	296	295
4-RKB-16 N-(2,4,6-trimethylcyclohexylmethyl)-1-isobutyl-3, 5-dimethylhexyl	293A	C	4+	94	1	324	326

Table 1.2 (Cont'd)

Compound	Batch No.	Source[a]	% by Differential Titration			Equiv. Wt.	
			Prim.	Secon.	Tert.	Theo.	Found
Secondary Amines							
4-RKB-19 N-(cyclohexylmethyl)-1-(3-ethylpentyl)-4-ethyloctyl	295A	C	6	93	1	352	349
4-RKB-18 N-(1-methylcyclohexylmethyl)-1-3-ethylpentyl)-4-ethyloctyl	294A	C	2	97	1	366	363
4-RKB-15 N-(2,4,6-trimethylcyclohexylmethyl)-1-(3-ethylpentyl)-4-ethyloctyl	292A	C	4	95	<1	408	392
Tertiary Amines							
Butyldilauryl	101A	ORNL	1	5+	93+	410	418
Trilauryl	86B	ADM	2	9	89	522	542
Other Compounds							
Deriphat No. 157 Sodium tallow-β-aminopropionate	279A	G	-	-	-	-	176
Deriphat No. 160 "Solubilized" derivative of sodium lauryl-β-aminopropionate	280A	G	-	-	-	-	132
Emery 578-41-R	287A	E	-	-	-	-	287
Emery 578-42-R	288A	E	-	-	-	-	429

Table 1.2 (Cont'd)

Compound	Batch No.	Source[a]	% by Differential Titration			Equiv. Wt.	
			Prim.	Secon.	Tert.	Theo.	Found
Other Compounds							
Emery 578-49-R	259A	E	-	-	-	-	420
Suconox 12 N-Lauroyl-p-aminophenol	262A	S	-	-	-	291[b]	-
Suconox 18 N-Stearoyl-p-aminophenol	263A	S	-	-	-	375[b]	-
Polyrod 0100	282A	H	-	-	-	360[b]	363
Polyrod 0200	283A	H	-	-	-	402[b]	419
"Imidazoline from fatty acid mixture and triethylene-tetramine" Alkyl side chain, 16-18 C	286A	L	-	-	-	-	624

[a]
A = Armour Chemical Division, Chicago
ADM = Archer-Daniels-Midland Co., Minneapolis, Minn.
C = Carbide and Carbon Chemicals Co., New York
CU = Columbia University, New York
E = Emery Industries, Inc., Cincinnati
G = General Mills, Inc., Kankakee, Ill.
H = Hercules Power Co., Wilmington, Del.
L = The Lubrizol Corp., Cleveland
R = Rohm and Haas Co., Philadelphia
S = Sumner Chemical Co., Inc., New York

[b]Equivalent weight furnished by vendor.

Table 1.3 Losses of Amine to Aqueous Solution

Organic = 0.1 M Amine in kerosene

Aqueous = synthetic sulfate liquor containing (g/liter): 5.8 Fe(III), 3.3 Al, 50 SO_4, 2 PO_4, and 1.7 F; pH 0.8

Amine	Batch No.	Loss of Amine: Fraction Readily Lost, % of Initial	Loss of Amine: Steady-State Loss, mg/liter Aqueous	Maximum A/O Ratio Examined
Amine 9D-178	193H	6	20	125/1
Amine 9D-178, scrubbed[b]		-	15	200/1
N-Benzyl-1-(3-ethylpentyl)-4-ethyloctyl	228B	0	<5	500/1
4-RKB-21 N-(cyclohexylmethyl)-1-isobutyl-3,5-dimethylhexyl)	297A	-	≥500	50/1[a]
4-RKB-20 N-(1-methylcyclohexylmethyl)-1-isobutyl-3,5-dimethylhexyl	296A	-	≥500	50/1[a]
4-RKB-16 N-(2,4,6-trimethylcyclohexylmethyl)-1-isobutyl-3,5-dimethylhexyl	293A	~15	~100	200/1
4-RKB-19 N-(cyclohexylmethyl)-1-(3-ethylpentyl)-4-ethyloctyl	295A	<1	5	250/1
4-RKB-18 N-(1-methylcyclohexylmethyl)-1-(3-ethylpentyl)-4-ethyloctyl	294A	<1	<5	500/1
4-RKB-15 N-(2,4,6-trimethylcyclohexylmethyl)-1-(3-ethylpentyl)-4-ethyloctyl	292A	<1	<5	200/1
Didodecenyl-n-butyl[c]	253B	4	5	100/1
Trilauryl	86B	<1	5	200/1

Table 1.3 (Cont'd)

[a] All of the amine transferred to the aqueous phase at a/o = 50, the lowest phase ratio tested.

[b] 0.1 M Amine 9D-178 solution in kerosene scrubbed with 500 volumes of 0.5 M H_2SO_4, removing 30% of the initial amine content, before the loss-rate measurements were started.

[c] Titrations and extraction tests with didodecenyl-n-butylamine were reported in ORNL-2269.

some limitation of compatibility of the straight chain alkyl amine with unmodified kerosene. The loss rate to sulfate liquor from unmodified kerosene was low, 5 mg/liter, and would be expected to be even lower from alcohol-modified kerosene or from aromatic diluent.

Uranium extraction was poor by Armeen O and OD and by the compounds other than simple amines. Several other compounds similarly submitted for evaluation, Suconex 12 and 18, Deriphat 157 and 160, and Emery 578-41R and 478-49R, were insufficiently soluble in kerosene, chloroform, and benzene for testing.

The new batch of N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine was similar in purity and extraction behavior to that previously examined; the uranium extraction power of both batches was so high that intercomparison of the actual extraction coefficients is not significant. N-benzyl-1-isobutyl-3,5-dimethylhexylamine, similar in structure but with a smaller alkyl group, gave extraction coefficients that were much lower but still an order of magnitude higher than those obtainable with most other types of amine. The N-cyclohexylmethyl secondary amines in Table 1.1 have the same two alkyl groups as these N-benzyl amines. None of them gave unusually high extraction coefficients, confirming that the benzene ring in the N-benzyl amines is an important contributor to the high extraction power. The N-cyclohexylmethyl amines gave fair to good extraction in benzene and kerosene, but poor extraction in chloroform diluent, which has been typical of highly branched secondary amines. The extraction power decreased with increased branching (methyl groups substituted on the cyclohexyl ring) when the diluent was benzene, but, except with the lowest molecular weight amine, it increased when the diluent was kerosene.

Differential Titration to Determine Primary, Secondary, Tertiary Amines. In the differential method (described in ORNL-1922, p. 84) the tertiary amine content is titrated after primary and secondary amines have been converted to non-titratable acetamides. Acetylation under the conditions specified (5 ml of 0.1 M amine in benzene refluxed for 1 hr with 15 ml of acetic anhydride and 1 ml of acetic acid) proceeds smoothly with unbranched and slightly branched amines. However, early results obtained with Amine 9D-178 (R_3CNHR), which has a tertiary alkyl bonded to the nitrogen, suggested that the acetylation of this compound might be incomplete. Any unreacted secondary amine would, of course, be titrated and erroneously reported as tertiary amine. A series of tests with increasing quantity of acetic anhydride and increasing reflux time showed about 10% unreacted amine in 9D-178, Batch 193H, after 30 min refluxing of 5 ml with 30 ml of acetic anhydride, and little further change on doubling the acetic anhydride or extending the time to 3 hr (Table 1.4). It appears that acetylation of the secondary amine was complete and that no appreciable degradation of actual tertiary amine to secondary, which might occur under too drastic conditions, had been produced. Thus the 10%

Table 1.4 Acetylation of Branched Secondary Amine

5 ml 0.1 M Amine 9D-178 (193H) in benzene, refluxed with 1 ml of glacial acetic acid and volumes of acetic anhydride as noted

Acetic Anhydride, ml	Reflux Time, min	Titratable Amine, % of initial
15	0	98
	30	30
30	0	97
	30	11
	180	10
60	30	10

correctly represents the tertiary amine content of the original mixture, provided, of course, that no bases other than simple amines were present. On basis of these results, future testing is planned to use 1 hr reflux at an acetic anhydride/0.1 M amine ratio of 6/1, with a check at a ratio of 12/1 when hindered reaction appears possible.

1.2 Monoalkylphosphoric Acids in Alkaline Systems (C. A. Blake, J. M. Schmitt, D. E. Horner)

The distribution of three purified monoalkylphosphoric acids* between kerosene and alkaline aqueous solutions was measured to determine the feasibility of stripping these extractants with such solutions. Pure reagents were required for these tests, since there have been discrepancies in the behavior of different batches of monoalkylphosphoric acids which may have been due to specific effects of contaminants, e.g., reaction by-products or unreacted starting materials.

Preparation of Reagents. The TDPA and HDPA were prepared by alcoholysis of P_2O_5 in kerosene. Each reaction mixture was hydrolyzed by refluxing for 2 hr with 6 M HCl. The monoalkylphosphoric acid was extracted into propyleneglycol and fractionated between propyleneglycol and petroleum ether. The DDPA was prepared from an existing supply of fairly pure reagent. It was scrubbed with hydrochloric and phosphoric acids, extracted into sodium carbonate solution, and then reacidified and fractionated by partitioning between propyleneglycol and petroleum ether. In each case the final product was recovered from petroleum ether solution by evaporation.

Titration of the final products (OP-394, -395, -393, Table 1.5) showed close agreement between the assays of stronger and

*Mono(2,6,8-trimethylnonyl-4)phosphoric acid, DDPA, mol. wt. 266; mono(2-methyl-7-ethylundecyl-4)phosphoric acid, TDPA, mol. wt. 294; mono(3,9-diethyltridecyl-6)phosphoric acid, HDPA, mol. wt. 337.

Table 1.5 Titration Assay of Reagent Batches

Reagent	Batch No.	"pK_1"[a]	"pK_2"[a]	Acid Assay, meq/g Theo.[b]	"Strong"	"Weak"	Inert,[c] w %
DDPA	OP-394	4.1	9.8	3.76	3.65	3.66	2.6
TDPA	OP-395	3.9	9.4	3.40	3.25	3.23	4.5
HDPA	OP-393	4.1	9.7	2.97	2.92	2.92	1.5
HDPA	OP-382	4.0	9.5	2.97	2.76	2.76	7

[a]"pK" = apparent pH at half neutralization in the 70% ethanol titration medium.

[b]Theoretical assay both for the stronger and the weaker ionizable hydrogens.

[c]From difference between theoretical and found equivalent weights.

weaker hydrogens, indicating good separation from monobasic acids. The assay of each was a little lower than theoretical, indicating contamination with some inert material, probably the corresponding alcohol.

A separate batch of HDPA (OP-382) was prepared by alcoholysis of P_2O_5 in hexane and was hydrolyzed by refluxing with both hydrochloric acid and sodium hydroxide solutions. The resulting HDPA sodium salt was extracted into water, reacidified and partitioned between propyleneglycol and petroleum ether, and recovered by evaporation. Titration showed equivalence of the stronger and weaker hydrogens (Table 1.5), but also showed more inert contaminant (7%) than in the other reagent batches.

The uranium extraction power of these four reagent batches was similar, i.e., $E_a^o \approx 500$ from 0.5 M sulfate solution at pH 1 and 7-8 from 1.5 M H_2SO_4, by 0.1 M reagent in kerosene.

Phase Distribution of the Sodium Salts. All three reagents (originally 0.1 M) were removed nearly completely from kerosene solution by contact with sodium carbonate and sodium hydroxide solutions (Table 1.6). The solubility of the resulting sodium salts in the aqueous solutions varied with the molecular weights: the DDPA salt was highly soluble in 10% Na_2CO_3 and 10% NaOH solutions, while the HDPA salt was scarcely soluble and most of it precipitated. The TDPA salt dissolved nearly completely in the 10 and 15% Na_2CO_3 and 10% NaOH solutions at the volume ratios used, although most of it precipitated when the NaOH concentration was 15%. Thus, reasonably dilute alkaline solutions dissolved too much of either DDPA or TDPA to be attractive for stripping.

The differing solubility of the TDPA salt in the different aqueous solutions probably reflects a difference in solubility

Table 1.6 Phase Distribution of Sodium Monoalkylphosphates

Organic phase initially 0.1 M reagent in kerosene
Agitated for 1 hr at 26°C

Initial Kerosene Soln.		Initial Aq. Soln.		Phase Ratio	Distribution, g/liter[b]		% in
Reagent[a]	Decanol, %	Base	Concn., g/liter	(o/a)	Kerosene	Aqueous	Ppt.[c]
DDPA	-	Na_2CO_3	100	1/1	<1[d]	25	none
	2			1/1	<1[d]	25	none
	4			1/1	<2[d]	25	none
	-			5/1	0.3	120	none
	-	NaOH	100	5/1	0.1	100	none
TDPA	-	Na_2CO_3	100	1/1	(<4)[d]	25	(<10)[e]
	4			1/1	(<4)[d]	25	(gel)
	-			5/1	0.7	120	15[e]
	-		150	1/1	1.3	25	10[e]
	-			2/1	0.2	55	10[e]
	-	NaOH	100	5/1	0.6	120	20[e]
			150	1/1	0.3	≲0.3	98
				2/1	1.3	≲0.3	95
HDPA	-	Na_2CO_3	100	5/1	0.2	≲0.4	99
	-			1/10	-	0.05	-[f]
	-	NaOH	100	5/1	0.3	≲0.2	98
	-			1/10	-	0.009	-[f]

[a]DDPA = Mono(2,6,8-trimethylnonyl-4)phosphoric acid; TDPA = Mono(2-methyl-7-ethylundecyl-4)phosphoric acid; HDPA = Mono(3,9-diethyltridecyl-6)phosphoric acid.

[b]Weight calculated on basis of acid form of reagent.

[c]Percent of total reagent in precipitate, by difference.

[d]Concentration in organic phase by difference.

[e]Precipitation was slow, occurring after 0.5 hr or longer.

[f]Precipitate present, but the quantity cannot be estimated since the organic phase concentration was not measured.

between the mono- and disodium salts, on the assumption that the monosodium salt was formed in equilibrium with the carbonate solutions and the disodium salt in equilibrium with at least the more concentrated sodium hydroxide solution. A decrease of organic salt solubility with increase of ionic concentration might also be involved.

The tests with HDPA at high organic/aqueous phase ratios were repeated at high aqueous/organic ratios to obtain a more sensitive measure of the aqueous solubility, showing 50 mg/liter in 10% Na_2CO_3 and 9 mg/liter in 10% NaOH.

Diluent Modification to Maintain Organic Solubility. Since the aqueous HDPA solubility was low, alkaline stripping of this reagent might be attractive if precipitation of the sodium salt from the organic phase could be readily prevented. Modification of the kerosene diluent with long-chain alcohols or with tributylphosphate has been tried previously, in analogy to their successful use with sodium di(2-ethylhexyl)phosphate. Workers at Dow Chemical Company have reported that the precipitation of the HDPA salt from 0.1 M solution in kerosene was prevented by addition of 6% n-decanol (DOW-149) or 2.4% TBP (DOW-152). Much higher concentrations had been required in tests in this laboratory, e.g., 20% TBP for Batch OP-279 HDPA. That reagent batch was prepared by alcoholysis of P_2O_5 followed by acid hydrolysis but without any fractionation. The purified HDPA (Batch OP-393) required even more modifier, 25% TBP or 15% mixed primary decanols, to maintain solubility of 0.08 M* HDPA salt on contact with 10% solutions of either sodium carbonate or sodium hydroxide.

The possibility is obviously suggested that other components of the P_2O_5-alcoholysis reaction mix, incompletely removed, might contribute toward solubilizing the HDPA sodium salt in kerosene. A partial confirmation of this possibility was obtained with the residual HDPA in the acid-treated reaction mix from which Batch OP-393 had been extracted. This solution was diluted with kerosene to bring the dibasic acid content (presumed to be mainly HDPA) to 0.1 M. Addition of 10% TBP or decanol was then sufficient to prevent precipitation on contact with 10% Na_2CO_3 or 10% NaOH solution.

Effect of Modifiers on Uranium Extraction Power. As was reported previously, addition of alcohol (ORNL-2173, p. 83) or TBP (ORNL-2346) markedly decreased the uranium extraction power of all the monoalkylphosphoric acids tested. Relatively small concentrations of the modifiers had been used in those tests, e.g., 0.1 M (~3% TBP), similar to the concentrations used in the Dapex process. On the possibility that the antagonism might level off or even be reversed, uranium extraction by Batch OP-393 HDPA was measured with addition of modifiers at the concentration levels required to maintain solubility of 0.1 M HDPA salt. The extraction coefficients were depressed considerably more with higher modifier concentrations:

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*The organic solution, initially 0.1 M HDPA, was diluted to about 0.08 M by the addition of the TBP or the alcohol.

Modifier added to 0.1 M HDPA/kerosene	U E_a^o 0.5 M SO_4, pH 1	1.5 M H_2SO_4
None	500	7
~3% TBP (0.1 M)	60	1
30% TBP	2	0.1
15% Decanol	2	0.05

The aqueous phase contained initially 1 g of uranium per liter; the phase ratio was 1/1 and the contact time 10 min at room temperature.

These results are in disagreement with those reported tests (DOW-152) that showed no decrease of uranium extraction power on addition of 2.4% TBP to 0.1 M HDPA in kerosene. This difference, as well as the difference in reported TBP concentration required to prevent precipitation, might be due to the presence of other components in the reagent solution.

1.3 Solvent Extraction Reagent Losses Through Distribution to the Aqueous Liquor (C. A. Blake, D. E. Horner)

Consideration is being given to the use of mono- and dialkylphosphoric acid extractants in treating liquors containing lower concentrations of metal values (uranium, thorium, vanadium, etc.) than those normally handled. Since losses of extractants through solubility are of increased economic importance when treating lower grade liquors, a more intensive study is being made of the losses of various alkylphosphoric acids under a variety of process conditions.

Distributions from kerosene to sodium sulfate--sulfuric acid solutions are reported here for several monoalkylphosphoric acids (DDPA, TDPA, and HDPA) and di(2-ethylhexyl)phosphoric acid (D2EHPA). The results supplement those reported previously in ORNL-1903 and -2172. The distributions were measured by a method previously described (ORNL-1903, p. 57), in which a volume of accurately titrated reagent in kerosene was contacted with a large volume of aqueous solution, after which the organic phase was retitrated for reagent content.

D2EHPA Losses from 0.4 M Reagent in Kerosene. Kerosene solutions of 0.25-0.4 M D2EHPA are used for recovery of vanadium from ore leach liquors which contain, in some cases, as little as 1 g of V_2O_5 per liter. Preliminary measurements of losses from the 0.4 M reagent level to pure sulfate solution were made and should approximate those that might be obtained in actual processing of leach liquors.

As shown in Table 1.7, the amount of D2EHPA reporting to the sulfate solutions (pH 1) was about 0.01 g/liter at a sulfate level of either 0.2 or 0.5 M. Losses of this order are tolerable in processing even the dilute vanadium liquors. A more important source of reagent loss would arise through physical entrainment of the total solvent in the liquor raffinate.

Table 1.7 Solubility Distribution Losses of Alkylphosphoric Acids

Reagent	Final Organic Conc., M	Phase Ratio at Contact (a/o)	Amount, g/liter Organic Phase	Amount, g/liter Aqueous Phase
		0.5 M sulfate, pH 1		
DDPA[a]	0.025	400	6.7	0.057
	0.075	75	20.0	0.090
	0.451	50	120	0.261
TDPA[b]	0.09	100	26.5	0.029
HDPA[c]	0.10	400	33.6	<0.005
D2EHPA	0.38	400	122	0.010
		0.2 M sulfate, pH 1		
DDPA[a]	0.45	50	120	0.245
HDPA[c]	0.10	400	33.6	<0.005
D2EHPA	0.38	400	122	0.009

[a]Prepared from 2,6,8-trimethylnonanol-4

[b]Prepared from 1-isobutyl-4-ethyloctanol

[c]Prepared from 3,9-diethyltridecanol-6

Uranium recovery circuits ordinarily use D2EHPA at a concentration of 0.1 M in kerosene. Losses of reagent from this solvent to sulfate liquors have been measured previously in both batch and continuous tests. In batch tests with various liquors, the indicated losses varied from 0.0003 to 0.009 g of D2EHPA per liter of aqueous. In a single continuous test the indicated loss was about 0.01 g per liter of aqueous or possibly somewhat higher, depending on assumptions of the amount of solvent evaporated during the run. All these losses are low from the standpoint of process economy. However, since the results from the various tests were not in complete agreement, further countercurrent tests are planned with P^{32}-labeled D2EHPA as the extractant. This technique will permit direct determination of the amount of D2EHPA that reports to the raffinate under conditions nearly identical to those in plant practice. The uncertainties involved in the previous indirect measurements should be eliminated.

Preparation of the labeled D2EHPA has been started and will be used in tests at both the 0.1 and 0.4 M reagent levels.

Monoalkylphosphoric Acid Losses from Kerosene Solutions. Losses of the monoalkylphosphoric acids to the pure sulfate solutions (Table 1.7) decreased with increasing molecular weight. Thus from 0.1 M reagent in kerosene, distribution losses to 0.5 M sulfate, pH 1, solution were 0.10, 0.03, and 0.005 g/liter for DDPA, TDPA, and HDPA, respectively. With DDPA, the only reagent for which increasing concentrations were studied, the losses increased when the reagent concentration in the kerosene was increased. Variation in the composition of the aqueous phase from 0.5 to 0.2 M sulfate showed little effect on the losses of DDPA or HDPA.

The correlation of distribution losses with molecular weight is in general agreement with previous data (DOW-97). However, the specific losses with DDPA are in poor agreement with other data. For example, losses of 0.1 g per liter of aqueous have been reported for batch contacts of 0.35 M sulfate, pH 1.2, solutions with a kerosene solution containing 0.34 M DDPA and 0.21 M of the corresponding dialkylphosphoric acid (DOW-97). From interpolation of the data in Table 1.7, a loss of about twice this amount is indicated.

Losses from 0.1 M DDPA in kerosene to an ore leach liquor have been reported as 0.03 g/liter on the basis of results from an 80-cycle continuous test. The indicated losses for this reagent level to pure sulfate liquor (Table 1.7) is again higher, in this case by a factor of 3 or 4.

In view of the apparent disagreement in data, and since the magnitude of the DDPA losses are in a region of economic importance, further studies are being made with this reagent. As suggested earlier for D2EHPA, the use of P^{32}-labeled DDPA should provide a more direct means for determining losses under simulated process conditions.

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) stripping vanadium from amines with ammonium hydroxide, (3) control of phosphate contamination of Amex vanadium products, and (4) study of the effect of several variables in stripping uranium from amines with magnesium oxide.

2.1 Extractions from Western Ore Leach Slurries with Amines (W. D. Arnold, D. J. Crouse)

Preliminary studies on adaptation of the Amex process to treatment of ore leach slurries showed excessive volume losses of the organic phase and preferential loss of amine from the diluent, apparently through chemi-sorption on the ore slime solids. These earlier tests were limited, however, to study of only two amines. Consequently further tests have been made to

determine whether the tendency of the amine to adsorb on the slurry solids might vary with change in amine type and structure.

Although some variation in performance was noted, none of the compounds were practicable for process use. Charcoal was added to the organic phase and Jaguar gum to the slurry phase in an attempt to reduce the amine loss to the ore solids but without success.

Batch Tests. In a series of batch tests, solutions of 10 different amines (0.08-0.10 M in kerosene or kerosene plus alcohol) were contacted with an ore leach slurry (8.5% solids, pH 1.2) by vigorous stirring for 15 min in a baffled mixer. The slurry was a sample of feed from the National Lead Company's resin-in-pulp pilot plant at Grand Junction, and had been prepared by leaching Lukachukai ore with sulfuric acid and subsequent sand-slime separation to remove ore solids above 325 mesh.

Prior to use, each organic solution was thoroughly scrubbed with dilute sulfuric acid in order to eliminate lower molecular amines present as impurities, which would distribute readily to the slurry phase and lead to spurious conclusions. A high organic/slurry ratio (3/1) was used in each contact to prevent excessive formation of emulsions, which frequently occur in the presence of slime solids. Samples of the organic phase were withdrawn after 2, 5, and 15 min and titrated for amine content.

As shown in Table 2.1, the losses in these single-stage contacts of di(tridecyl P)- and bis(1-methyl-4-ethyloctyl)amine were within the accuracy of experimental method. All the other amines showed appreciable concentration losses, which in most instances increased with increased contact time. The magnitude of these losses varied markedly with different amines. For example, the loss after 15 min contact was 12.5% for benzyldodecylamine, 5.0-7.7% for Amine 9D-178, 5.5% for Amine S-24, and 3.8% for tri-n-octylamine.

The above results express only the loss due to change in amine concentration, this loss being attributed primarily to preferential sorption of the amine salt on the slurry solids. In a slurry extraction operation, minimizing losses of total solvent to the slurry is also an important consideration. In the tests described, the amounts of total solvent reporting to the slurry phase were not measured. The bulk of the phases separated rapidly, but the presence of some interfacial emulsion and appreciable amounts of slurry solids floating at the interface indicated that solvent recovery would be a difficult problem in this system. There were no observable differences in the rate or cleanness of phase separation with the various amine solutions tested.

Cascade Tests. Since appreciable losses of di(tridecyl P)- and bis(1-methyl-4-ethyloctyl)amine were not detected after single-stage contacts, these compounds were further examined in cascade tests where any losses occurring would accumulate to give larger changes from the initial amine concentration. In

Table 2.1 Loss of Amines to an Ore Slurry

Organic: 0.08-0.10 M amine
Slurry: Lukachukai ore slime slurry (8.5% solids, ph 1.2)
Phase ratio: organic/slurry = 3/1
Procedure: Organic and slurry contacted in a baffled mixer at a stirrer speed of 400 rpm; organic samples removed and titrated for amine content after 2,5, and 15 min agitation

Amine	Diluent	% Loss in Amine Concentration after a Contact time of		
		2 min	5 min	15 min
Di(tridecyl P)	Kerosene	<2	< 2	< 2
	97% kerosene-3% C. A.*	<2	< 2	< 2
Bis(1-methyl-4-ethyloctyl)	98% kerosene-2% C. A.	<2	< 2	< 2
N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl	Kerosene	4	5	5
R&H 9D-178	Kerosene	5	6	8
	98% kerosene-2% C. A.	5	5	5
Amine S-24	Kerosene	3	4	6
Di(oxodecyl)	98% kerosene-2% C. A.	4	6	7
Benzyldodecyl	97% kerosene-3% C. A.	10	11	12
Armeen 212	97% kerosene-3% C. A.	<2	3	4
Tri-n-octyl	97% kerosene-3% C. A.	<2	3	4
Benzyldidodecyl	97% kerosene-3% C. A.	<2	3	4

* C. A. = capryl alcohol

the test procedure aliquots of the prewashed solvents used in the previous studies were stirred with the Lukachukai slurry for 2 min. After allowing the phases to separate, the solvent was removed and recontacted with a fresh volume of slurry. This procedure was followed through a total of six contacts with the organic/slurry ratio in each contact maintained at 3/1. After the first and sixth contacts, the amine concentration was determined for comparison with the head concentration.

	% Loss in Amine Concentration after	
	1 contact	6 contacts
Di(tridecyl P)amine in kerosene	<2	10
Bis(1-methyl-4-ethyloctyl)amine in 98% kerosene--2% capryl alcohol	<2	20

Losses after a single contact were again below the limit of detection by the experimental method used. However, after six contacts the losses were appreciable and too large to be tolerated in process practice. Unexplainably, the loss of bis(1-methyl-4-ethyloctyl)amine after six contacts was greater than could have been predicted from single-contact results. As in prior tests, phase separation was difficult with both amines, and volume losses of the total solvent were probably excessive.

Effect of Additives. Cursory tests have been made wherein surface active materials were added to either the organic or aqueous phase in an attempt to reduce the loss of amine to the ore solids.

In cascade tests similar to those described above, 20 g/liter of activated carbon was added to the 0.1 M di(tridecyl P)-amine solvent with the thought that the amine might be preferentially held on the carbon surfaces. The phase separation in this experiment was improved, and over-all solvent losses appeared to be considerably lower. However, the amine loss as measured by amine concentration change was no less than before.

In further cascade tests with di(tridecyl P)amine and R and H 9D-178 amine, the slurry solids were coagulated with Jaguar gum (4 lb per ton of slime solids) prior to extraction. It was thought that the ore solid surfaces, already coated with a surfactant, might have less tendency to sorb amines. Better phase separation and lower losses of total solvent were noted in the tests. However, the preferential losses of amine reagent were still excessive.

Amine	Diluent	% Loss in Amine Concentration after 6 contacts
Di(tridecyl P)	97% kerosene--3% capryl alcohol	8
R and H 9D-178	kerosene	23
R and H 9D-178	98% kerosene--2% capryl alcohol	14

2.2 Comparison of Uranium Extraction Isotherms (W. D. Arnold)

Isotherms were determined for extraction of uranium from synthetic Marysvale liquor with two new amine samples in 97% kerosene--3% tridecanol diluent (0.10 M amine concentration). The first sample, a mixed tertiary amine (55% n-decyl, 45% n-octyl), was submitted by General Mills and the second sample, trilaurylamine, by Archer-Daniels-Midland. Data on the purity of these compounds and their distribution losses to acid liquors are presented in a previous progress report (ORNL-2366) and in Sec. 1.1 of this report. The steady-state distribution loss of each sample was very low, i.e., 5 ppm or less.

Both amines showed high uranium extraction power, relatively high uranium loadings (~5 g/liter), and excellent selectivity with respect to ferric iron (Table 2.2). As expected, their performance in these respects was nearly identical to that shown previously by other tertiary amines, including tri-n-octyl, tri-isooctyl, and didodecenyl-n-butyl (ORNL-1959, -2099, and -2346).

Phase separation was rapid (<1 min) for the General Mills sample but relatively slow for the Archer-Daniels-Midland sample. In the latter case, the bulk of the phases separated in approximately 2 min, but a small band of emulsion remained at the interface for approximately 30 min.

3.0 ENGINEERING STUDIES

In addition to the studies described below, engineering studies during the month have included: (1) kinetics of uranium extraction in the Dapex process in 12- and 20-in.-dia mixers, (2) kinetics of vanadium extraction in the Dapex process, (3) phase separation and entrainment of Dapex organic in mixer-settler equipment, and (4) continuous countercurrent tests of Amex with liquors containing molybdenum.

3.1 Stage Efficiency of a Baffled Tank Mixer for Uranium Extraction by Dapex Organic (F. L. Daley)

Studies of the rate of uranium extraction from a relatively high-grade uranium liquor (5 g U/liter) in a 6-in. baffled tank mixer under continuous flow conditions were reported previously (ORNL-2214). A kerosene solution of 0.16 M D2EHPA was used in these tests at an aqueous/organic phase ratio of 1/1. At this ratio complete uranium extraction would give a solvent loaded to 80% of the maximum equilibrium loading from the aqueous feed.

Further studies of this type, under somewhat different conditions, have recently been made with a liquor more typical in uranium concentration (1.2 g/liter). In these recent tests the extracting solvent was 0.1 M D2EHPA in kerosene and the aqueous/organic phase ratio was 4/1. Again, complete transfer of uranium would give a solvent loaded to 80% of the maximum equilibrium loading from the aqueous feed. Test results are summarized in Table 3.1. The compositions of the aqueous feed was

Table 2.2 Extraction Isotherm Data for Two New Amines

Aqueous: 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; pH 0.9)

Organic: 0.10 M amine in 97% kerosene-3% tridecanol

Phase ratio, a/o: 2/1

Contact time: 2 min

Temperature: 25°C

Amine	U, g/liter			Fe in Organic g/liter	Uranium Extraction Coefficient, E_a^o
	Head Liquor	Organic	Aqueous		
Mixed Tertiary from General Mills (Compound 299)	0.15	0.3	0.001	0.020	300
	0.30	0.6	0.002	0.019	300
	0.60	1.2	0.005	0.018	240
	1.0	1.9	0.011	0.016	170
	1.25	2.4	0.018	0.013	130
	1.5	2.8	0.025	0.011	110
	2.0	3.8	0.062	0.008	60
	3.0	4.8	0.495	0.003	10
Trilauryl from Archer-Daniels-Midland (Compound 86B)	0.15	0.3	0.001	0.028	300
	0.30	0.6	0.002	0.026	300
	0.60	1.2	0.005	0.023	240
	1.0	2.0	0.007	0.021	290[a]
	1.25	2.5	0.014	0.017	180
	1.5	3.1	0.019	0.015	160
	2.0	4.0	0.042	0.011	95
	3.0	5.1	0.400	0.006	13

[a] Questionable analysis.

Table 3.1 Summary of Results

Continuous phase: aqueous
Temperature: 23-24°C

6 in mixer tank
3 in 6-bladed turbine

Run No.	Total Flow Rate gpm	Flow Ratio (a/o)	U conc., g/liter Aq in	U conc., g/liter Aq Out	Impeller Speed rpm	Power Per Mixer Volume, hp/1000 gal	Nominal Holdup Time min	Specific Energy, ft-lb/ft³	Extraction Efficiency, % E_m
658	0.153	4.20	1.26	1.08	150	0.46	4.8	546	14.3
659	0.153	4.20	1.26	0.410	262	2.5	4.8	2,970	70.7
660	0.153	4.20	1.26	0.330	350	5.9	4.8	7,010	79.4
661	0.153	4.20	1.26	0.305	524	20.0	4.8	23,800	82.3
662	0.153	4.20	1.26	0.270	787	67.0	4.8	79,600	86.1
663	0.153	4.20	1.26	0.230	1170	220.0	4.8	261,400	92.0
640	0.295	4.10	1.16	1.07	0	0	2.49	0	7.8
641	0.295	4.10	1.16	0.415	262	2.5	2.49	1,540	66.0
642	0.295	4.10	1.16	0.320	350	5.9	2.49	3,640	75.7
643	0.295	4.10	1.16	0.305	524	20.0	2.49	12,300	77.4
644	0.295	4.10	1.16	0.275	787	67.0	2.49	41,300	80.7
645	0.295	4.10	1.16	0.230	1170	220.0	2.49	135,600	86.1
633[a]	0.507	4.20	1.16	1.10	0	0	1.45	0	3.3
628[a]	0.507	4.20	1.16	0.547	262	2.5	1.45	897	53.7
629[a]	0.507	4.20	1.16	0.429	350	5.9	1.45	2,120	64.7
630[a]	0.507	4.20	1.16	0.400	524	20.0	1.45	7,180	67.5
631[a]	0.507	4.20	1.16	0.348	787	67.0	1.45	24,100	72.9
632[a]	0.507	4.20	1.16	0.296	1170	220.0	1.45	79,000	78.7
634	1.98	4.08	1.16	1.06	0	0	.371	0	4.75
635	1.98	4.08	1.16	0.785	262	2.5	.371	229	32.4
636	1.98	4.08	1.16	0.625	350	5.9	.371	542	46.5
637	1.98	4.08	1.16	0.545	524	20.0	.371	1,840	53.7
638	1.98	4.08	1.16	0.500	787	67.0	.371	6,150	57.7
639	1.98	4.08	1.16	0.435	1170	220.0	.371	20,200	63.8
646	5.1	4.15	1.16	1.10	0	0	.172	0	3.5
647	5.1	4.15	1.16	0.960	262	2.5	.172	106	17.2
648	5.1	4.15	1.16	0.805	350	59	.172	251	30.7
649	5.1	4.15	1.16	0.680	524	20.0	.172	851	41.6
650	5.1	4.15	1.16	0.590	787	67.0	.172	2,850	49.7
651	5.1	4.15	1.16	0.550	1170	220.0	.172	9,360	53.3

[a] Average of duplicate runs (Maximum deviation from average was 6%).

U	1.2	g/liter	SO_4	51	g/liter
Fe(III)	0.33		PO_4	1.9	
Al	2.8				
V	0.94		pH	1.1	
V(V)	0.05		Density (25°C)	1.06 g/ml	

and of the organic feed was

Di(2-ethylhexyl)phosphoric acid	0.097 M
Tributylphosphate	30 g/liter
Diluent	kerosene
Density (25°C)	0.813 g/ml

The Murphree stage efficiency* of the mixer in each test was calculated from measurements of the uranium concentration in the aqueous effluent and the equilibrium curve (Fig. 3.1) for the particular aqueous and organic solutions studied. The dependence of efficiency on turbine speed and calculated power input can be represented by a family of curves for different holdup times in the mixer (Fig. 3.2). At constant residence time, the efficiency increased rapidly as the turbine speed was increased from 150 to 400 rpm and then increased gradually up to the maximum speed tested (1170 rpm). For example, at the highest holdup time (4.8 min), the efficiency was 14% at 150 rpm (0.46 hp/1000 gal), 81% at 400 rpm (10 hp/1000 gal), and 92% at 1170 rpm (220 hp/1000 gal). At a constant turbine speed the efficiency increased with increased holdup time. Thus at 400 rpm the efficiency was 35% at 0.17 min, 50% at 0.37 min, 66% at 1.5 min, 76% at 2.5 min, and 81% at 4.8 min residence time.

The same data are also correlated by a method used by Flynn and Treybal[1] in Fig. 3.3. Here the stage efficiency is plotted as a function of the specific energy expended per unit volume of aqueous and organic processed. These data are fairly well grouped about a single curve, although there is a general increase in efficiency with increased holdup time at a constant specific energy level.

A comparison of these results with those previously obtained with the higher grade uranium liquor (ORNL-2214) shows that considerably longer residence time and greater power input were required in the recent tests to obtain comparable stage efficien-

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$$*E_m = \frac{C_1 - C_2}{C_1 - C^*} \times 100$$

C_1 = conc. of uranium in aqueous feed

C_2 = conc. of uranium in aqueous effluent

C^* = conc. of uranium in aqueous phase that would be in equilibrium with the organic effluent

[1] A. W. Flynn and R. E. Treybal, "Liquid-Liquid Extraction in Continuous-flow Agitated Extractors," AIChE J. 1: 324-28 (1955).

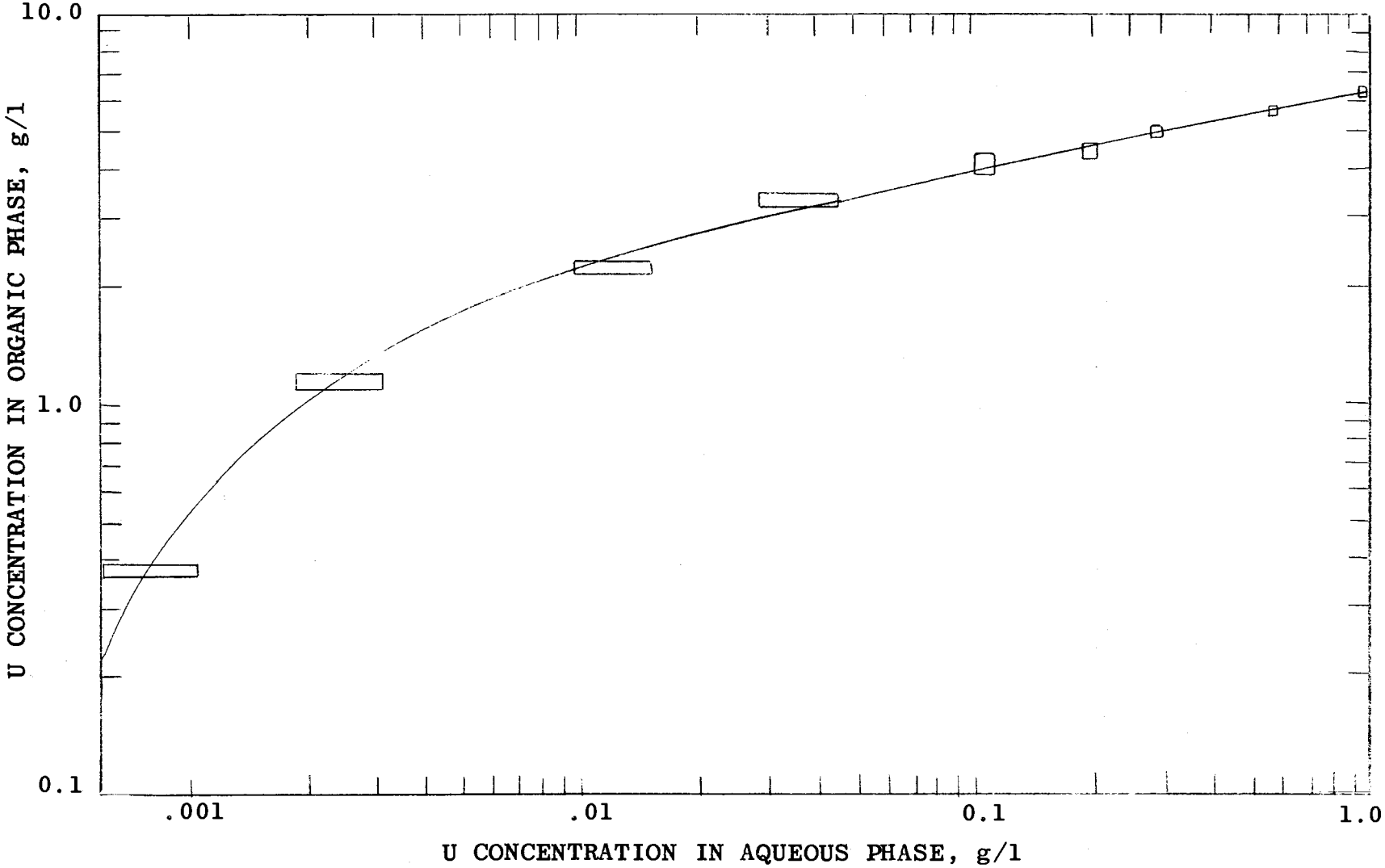

Fig. 3.1 Equilibrium Distribution of Uranium at 24°C

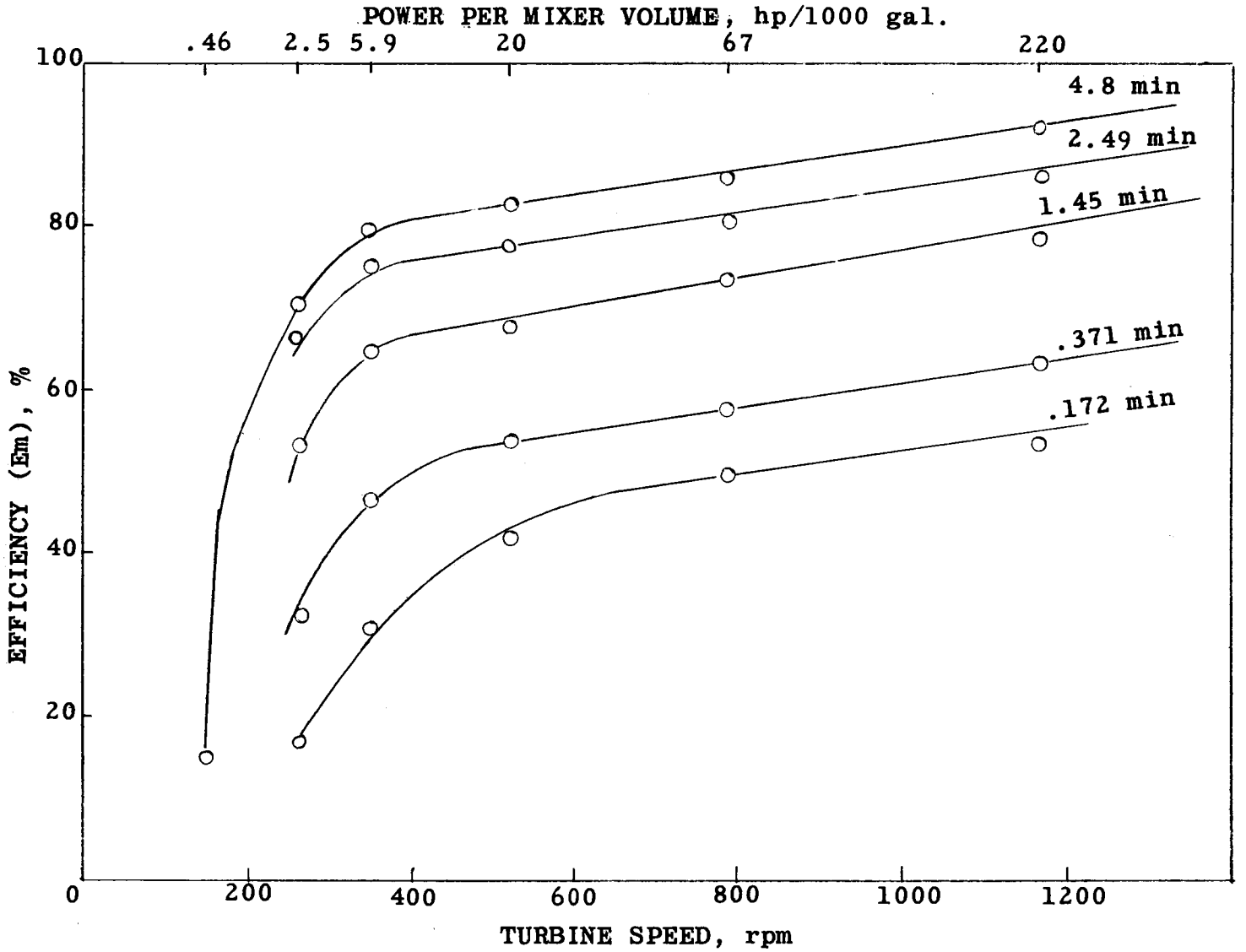

Fig. 3.2 Effect of Turbine Speed and Holdup Time on Mixer Efficiency

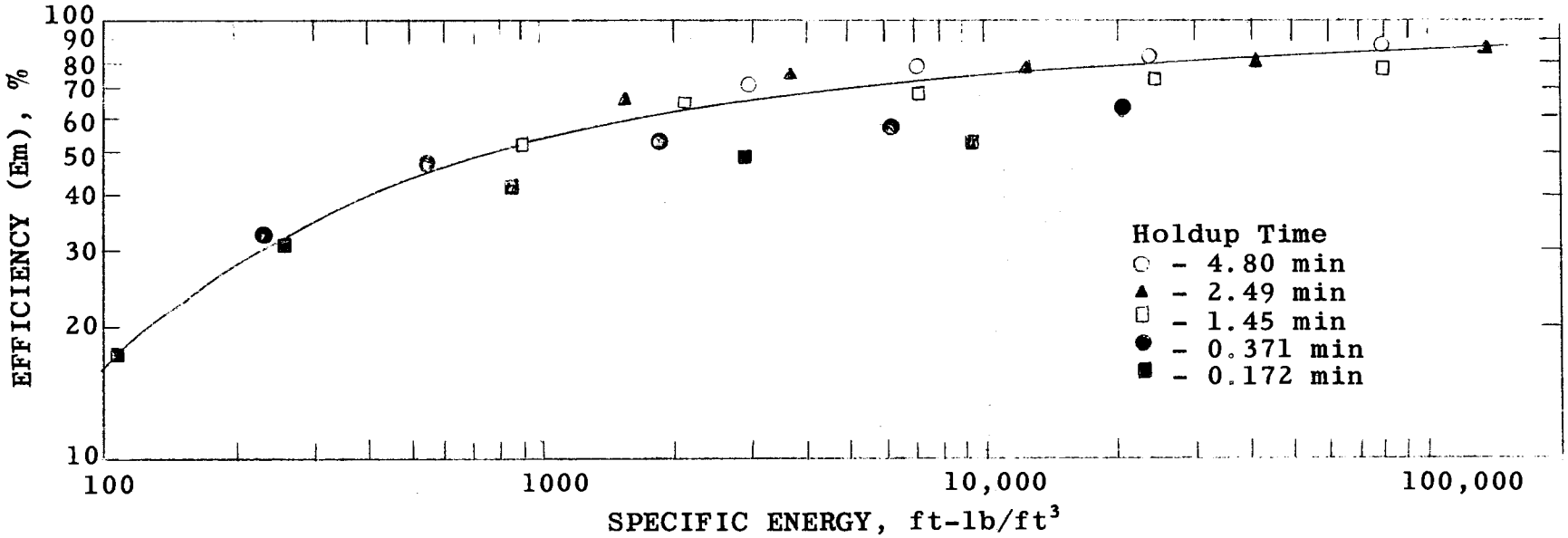

Fig. 3.3 Correlation of Mixer Efficiency with Specific Energy Input

cies. Based on results from the earlier studies, the minimum mixing requirements for 90% efficiency was reported* as 30 hp per 1000 gal of mixer volume and a total liquid residence time of 2 min for the case in which sufficient organic phase was recycled to maintain a 1/1 phase ratio in the mixer. With the same power input and mixer size, the stage efficiency for the low uranium liquor at a phase ratio of 4/1 would be closer to 80%. When loading to 5.0 g U/liter in the organic, four countercurrent mixer settlers would be required to produce a raffinate containing 0.003 g U/liter.

Differences in results between the two test series must be accounted for by differences in operating conditions, which include phase ratio, extractant concentration, and uranium concentration in the feed. Systematic studies of the effects of each of these variables are being made.

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) uranium and water distribution between aqueous sulfate and organic di(2-ethylhexyl)-phosphoric acid - tributylphosphate solutions, (4) examination of di(2-ethylhexyl)phosphoric acid - tributylphosphate - water association by isopiestic vapor pressure measurements of the hydrocarbon diluent and by infrared spectrophotometry, and (5) testing of equipment for use in measuring dielectric constants of organic solutions.

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

In previous studies, various phase equilibria involving amine salts have indicated that they exist as species of approximately constant activity in hydrocarbon solutions. This has been assumed to result from association of the amine salts into colloidal aggregates, perhaps micelles analogous to the micelles of soap or detergents in water. Information about the average size, size range, and structure of these aggregates is desired, e.g., to aid in establishing an appropriate measure of the organic phase activities of extracted acids and metals. One means of determining the size of such dispersed particles is by their effectiveness in scattering light, and measurements are in progress of light scattering by amines and amine salts in organic solutions.

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*K. B. Brown, D. J. Crouse, C. F. Coleman, "Some New Solvent Extraction Processes for Use in the Hydrometallurgical Treatment of Uranium, Thorium and Vanadium Ores," presented at the AIME meeting, New Orleans, La., Feb. 25-28, 1957.

Di-n-decylamine Sulfate (DDAS). Results obtained with the normal amine sulfate in benzene solution indicated a weight-average molecular weight of between 24,000 and 30,000, corresponding to an aggregation number of ~40 amine sulfate units per aggregate, over the concentration range from 0.0024 to 0.05 M. (The molarity is calculated on the basis of monomeric amine sulfate.) This corroborates the qualitative conclusions from the corresponding acid extraction equilibria (ORNL-1930 and -2084), which had indicated DDAS to be aggregated in benzene solution at all concentrations down to as low as ~0.001 M. The light-scattering data also suggest that the DDAS aggregates may be all of nearly the same size in this concentration range, as would be expected if they are indeed micelles.

Tri-n-octylamine Sulfate (TOAS). Less complete data obtained with TOAS in benzene indicated a monomer (molecular weight ~800) over the concentration range from 0.006 to at least 0.025 M. Experimental difficulties encountered in handling more concentrated TOAS solutions prevented definitive conclusions at concentrations above this level. Existence of TOAS as a monomer up to 0.025 M is in fairly close agreement with conclusions from the corresponding acid extraction equilibria (ORNL-1977), which had indicated it to be monomeric in benzene solution up to ~0.02 M and aggregated at higher concentrations.

Free Base Amines. Other observations have indicated that the free base amines are in true solution and probably monomeric in benzene. Preliminary light-scattering measurements at concentrations from about 0.05 to 0.1 M were consistent with the monomeric molecular weights, 300-450 for tri-n-octylamine (354) and 200-1000 for di-n-decylamine (298). The wider uncertainty for the latter is due to an apparent curvature of the plotted data in the short concentration range covered, and should be improved by extension of the concentration range.

The optical data and the calculation of the foregoing molecular weights are summarized in Table 4.1. The relative ratio of 90°-scattered to incident light, the difference in refractive index of solvent and solute, and the depolarization ratio of horizontally to vertically polarized light in the 90°-scattered beam were measured as a function of concentration of each solute. The molecular weight was then calculated from the relation*

$$M = \left(\frac{k}{H}\right)\left(\frac{a}{b}\right)\left(\frac{6-7\rho}{6+6\rho}\right)$$

Here a and b are the slope and intercept from a plot of the relative scattering ratio vs. solute concentration (Fig. 4.1). ρ is the depolarization ratio, k is a constant available from

*P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N. Y., 1953, Ch. VII, pp. 283-299.

Table 4.1 Molecular Weights of Amine Species in Benzene Solution

From light scattering at 546 mμ

$$M = \left(\frac{2.68\times10^{-4}}{H}\right)\left(\frac{a}{b}\right)\left(\frac{6 - 7\rho}{6 + 6\rho}\right)$$

Solute[a]	DDAS	TOAS	DDA	TOA
Formula Weight	694	806	298	354
Refr. Index Incr. ($\partial n/\partial c$)	-0.0477	-0.0650	-0.0735	-0.0790
Optical Constant[b] (H)	0.317×10^{-6}	0.586×10^{-6}	0.750×10^{-6}	0.866×10^{-6}
Slope[c] (a)	30	3	~1	1
Intercept[c] (b)	0.83	0.86	~0.9	0.9
Depol. Ratio[d] (ρ)	0.068	~0.2	negl.	negl.
Mol. Wt. (M)	24000-30000	600-800	200-1000	300-450
Aggregation[e] number (n)	~40	1	~1	1

[a]DDAS = $[(C_{10}H_{21})_2NH_2]_2SO_4$, TOAS = $[(C_8H_{17})_3NH]_2SO_4$, DDA = $(C_{12}H_{21})_2NH$, TDA = $(C_8H_{17})_3N$

[b]$H = (5.49\times10^{-22}/\lambda^4)n^2_{solv.}(\partial n/\partial c)^2$

[c]Slope a and intercept b from plots of relative scattering ratio vs. concentration, Fig. 4.1.

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

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

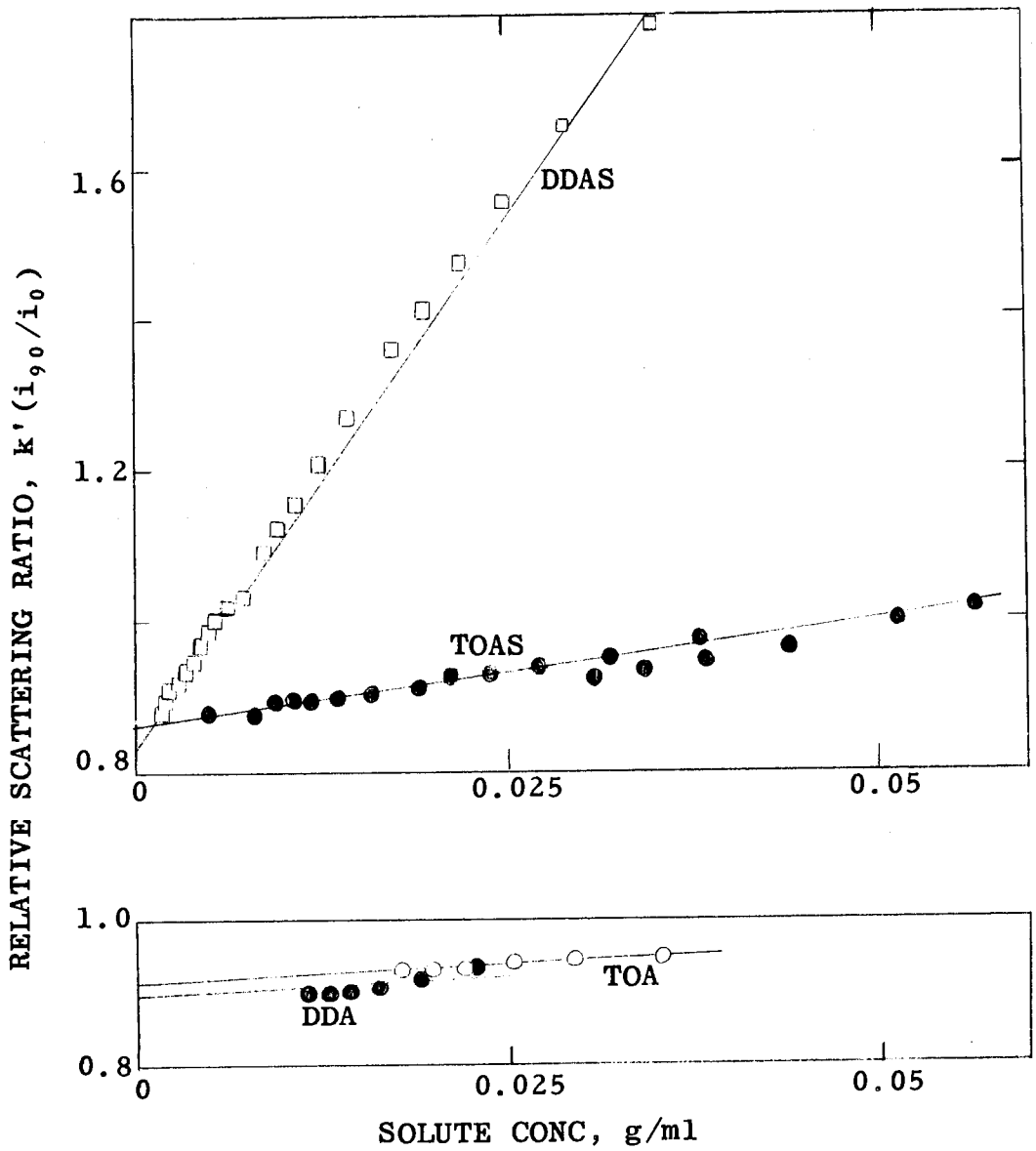

Fig. 4.1 Change of relative light scattering ratio with change of solute concentration. Slope a and intercept b of each line are used directly in calculation of the molecular weight, Table 4.1

the literature for the solute and wave length used ($k_{benzene}$ at 546 mμ is 2.68×10^{-4}), and H is an optical constant obtained from the refractive index increment by

$$H = (32\pi^3/3N)(n^2_{solv}/\lambda^4)(\partial n/\partial c)^2$$

where N is the Avagadro number, n is the refractive index, λ is wavelength in centimeter, and c is the concentration in grams per milliliter. The precision of the refractive index measurements was good, so that the uncertainty range in the calculated molecular weights corresponds to the uncertainty (scatter or curvature, Fig. 4.1) in the relative scattering ratios vs. concentration. While in some circumstances corrections are required for absorption or fluorescence by the solute or for dissymmetry of scattering, these have been found to be negligible at 546 mμ with the solutes so far studied. At 436 mμ the amine salts fluoresced to an extent which would have required correction; otherwise 436 mμ would have been preferred for the greater scattering and higher sensitivity characteristic of shorter wave length light.

The molecular weight determinations are being extended to solutions of mixed normal sulfate and bisulfate amine salts and to solutions containing extracted uranium.