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SOLVENT EXTRACTION OF URANIUM (AND VANADIUM) FROM ACID LIQUORS WITH TRIALKYLPHOSPHINE OXIDES

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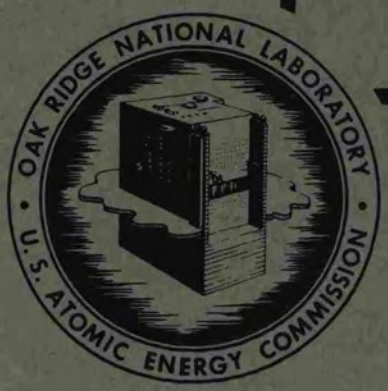

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SOLVENT EXTRACTION OF URANIUM (AND VANADIUM) FROM ACID LIQUORS WITH TRIALKYLPHOSPHINE OXIDES

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ABSTRACT

A number of symmetrical phosphine oxides have been prepared and examined systematically for their ability to extract uranium from acidic nitrate, chloride, sulfate, and phosphate solutions, and mixtures thereof. Most of the compounds tested showed high affinity for uranium, excellent extractions being obtained from nitrate and chloride solutions, and under the proper conditions from sulfate solutions, including a wide variety of solutions in which the structurally similar trialkylphosphates are ineffective. Extractions from sulfate or phosphate solutions were remarkably increased by the addition of very small amounts of nitrate and to a lesser degree by the addition of chloride. Uranium was effectively stripped from the organic solution with sodium carbonate. Brief tests with process-type liquors showed useful and selective uranium extraction from nitric acid leach liquors of Florida Leached Zone ore, from chloride-sulfate and "green-sludge" liquors as produced in a salt-roast, acid-leach process for Western ores, and, when the reagent concentration was sufficiently high, from sulfate liquors as produced in direct treatment of Western ores.

INTRODUCTION

A systematic study of organic complexing agents for uranium, particularly those reagents which might permit the solvent extraction of uranium from a wide variety of aqueous liquors, was initiated at this laboratory in December of 1950. The studies began with the consideration of long chain polyamines as possible organic complexing agents. Since that time, several hundred compounds of various types have been examined for ability to extract uranium. Meanwhile, detailed studies are being made of extractions with some of the more promising compounds found, emphasis being placed on two classes - the organonitrogen[1] and the organophosphorus compounds.

The work with the organophosphorus reagents has included numerous types of compounds such as mono-, di-, trialkylphosphates, alkylphosphonic and phosphinic acids and their esters, alkylphosphites, phosphine oxides, phosphoramides, bifunctional compounds such as alkyldiphosphates and -diphosphonates, and others. Data obtained from this work have been included in a series of progress reports[2-6]. A topical report has been issued describing the extraction and recovery of uranium and vanadium from acid liquors with di(2-ethylhexyl)phosphoric acid and some other alkylphosphoric acids[7]. It will be the purpose of the present report to give a detailed account of the studies of a second particular type of organophosphorus compound, the phosphine oxides. Additional reports on studies with other of the compound types will be issued later.

Prior to the work with the phosphine oxides reported here, K. Pickard (in 1906) reported the formation of solid compounds in reactions between phosphine oxides and certain metal salts and acids[8]. Hydrochloric acid formed a complex containing equal moles of acid and phosphine oxide, while for acids such as ferrocyanic, cobalticyanic, dichromic, chloroauric and camphoric and for salts such as zinc and cadmium chlorides the combining ratio was one mole for each two moles of phosphine oxide.

Considerably later (1951), workers at Hanford[9] reported correlation of the uranium extracting ability with the degree of ionic character of the phosphoryl bond (as inferred from spectroscopic data) in a homologous series of organophosphorus compounds prepared by systematic replacement of the ester groups in a trialkylphosphate with alkyl groups bonded directly to the phosphorus atom, i.e., trialkylphosphate,

dialkyl(alkylphosphonate), alkyl(dialkylphosphinate), trialkylphosphine oxide. In that investigation the trialkylphosphine oxide was reported to be the strongest uranium extractant in the series. At the same time, the same conclusion was reported by Baldwin at ORNL, who also extended the extractions with tributylphosphine oxide from nitrate solutions to chloride and sulfate solutions.[10,11] A memorandum[12] was later written describing the effectiveness of some organic reagents, including a phosphine oxide, in extracting uranium from liquors prepared from the Florida Leached Zone by the TVA process.[13]

The results obtained in the foregoing studies were of sufficient interest to encourage a much more detailed examination of the phosphine oxides as extractants for uranium from aqueous liquors widely varied in composition. In this study, particular emphasis has been placed upon uranium extraction coefficients and their dependence on the choice of phosphine oxide and diluent and on such variables as reagent concentration, uranium level, acidity, concentration of anions, and temperature. The uranium coefficients have been compared with those of other metal ions obtained under similar conditions, and the extraction of vanadium and its separation from uranium have been briefly considered. Associated problems of reagent loss during extraction and stripping, reagent preparation, purification and physical properties are also discussed.

The first part of the extraction tests comprises extractions with several phosphine oxides from solutions containing but one metal ion. The second part deals with extractions from solutions of uranium which are complicated by the presence of those contaminants typically dissolved from uranium ores during leaching, e.g., iron, aluminum, phosphate, etc. The selective extraction and subsequent stripping in the presence of other metals, and the successful competition for uranium between the extracting reagent and the other uranium complexing agents are considered in this section, the purpose being to obtain preliminary information as to the possible application of these reagents in the treatment of various types of process liquors.

DESCRIPTION OF COMPOUNDS

Most of the phosphine oxides discussed in this report were prepared (some of them for the first time) at Oak Ridge National Laboratory, using established procedures as described in Appendix A. The methods used to purify the products are also described there, and analytical data and physical constants are tabulated in Appendices A and B.

With the few exceptions which are specifically noted, the phosphine oxide batches used in this work are believed to be at a high level of purity, essentially free of contaminants which could affect the extraction results to an important degree. This confidence has of necessity been derived from the combination of a variety of observations. Lacking any direct and unequivocal method of assessing the absolute purity of these compounds, it has been necessary to rely on the indirect evidence of elemental analysis, physical constants, microscopic examination of crystals, and tests for certain likely impurities, together with judgements based on the behavior of the compounds in the extraction tests. Four classes of possible impurities may be considered: (a) impurities essentially inert with respect to extraction, (b) homologous compounds (i.e., some molecules of phosphine oxides containing other than the intended organic radicals), (c) impurities which impair the extraction power of the phosphine oxide, and (d) impurities which themselves have strong extraction power, either alone or in combination with the phosphine oxide. It appears that important effects from the first three can be discounted. Inert impurities would be important only if present in sufficient quantity to cause a significant error in calculated concentrations of the reagent, and such quantities can be ruled out on basis of the behavior in distillation and the analytical phosphorus contents. Homologous purity depended on the homologous purity of the starting materials, which were of reagent grade and generally redistilled, and although differences in extraction power were found with phosphine oxides prepared from different members of a homologous series of alkyls, the differences were not so great as to indicate that important differences in apparent extraction power should result from small amounts of homologous impurity. Even the possibility of extraction impairment by contaminants can be discounted, since it seems unlikely that any strong impairment affecting all of the reagent molecules could be produced by any much smaller number of contaminant molecules.

On the other hand, the possible presence of a contaminant which itself has high extraction power cannot be discounted,

as a very small amount of a strong extractant can increase the apparent extraction power of the nominal reagent to a marked extent whenever the quantity of material being extracted is small. At least one such contaminant has been found in some phosphine oxide preparations - a neutral compound which can be oxidized to a phosphinic acid and which is thought to be a dialkylphosphine oxide (or dialkylphosphinous acid), R_2HPO, formed as a by-product of the phosphine oxide. After the nature of this contaminant was recognized, it was removed from the reagents by oxidizing treatment followed by alkaline washing.

Assurance that there are not further contaminants of strong extraction power, stable to the treatments so far tried and therefore undetected, can be obtained only by examination of the extraction behavior at high loadings. That is to say, when so much uranium has been extracted that a large fraction of the phosphine oxide is tied up in the resulting complex, this loading and the corresponding extraction coefficient cannot be attributed to strong extraction resulting only from the presence of a minor component. Although most of the extraction tests were made at relatively low loadings, such assurance was clearly furnished for tridecylphosphine oxide (Batch 292), trioctylphosphine oxide (Batch 289), tridodecylphosphine oxide (Batch 288), and tri(3,5,5-trimethylhexyl)phosphine oxide (Batch 287) by extractions from pure uranyl sulfate-sulfuric acid solutions in which consistent extraction coefficients were obtained at uranium loadings up to more than half of the theoretical maximum. The general conformity of behavior between these and the other batches of reagents provides a reasonable basis for confidence that few if any of the results reported here could have been due to undetected contaminants.

EXTRACTION OF URANIUM FROM PURE SOLUTIONS

The effects of several variables were studied in the extraction of uranium with phosphine oxides (chiefly tri-n-octyl- and tri-n-decylphosphine oxide) from aqueous solutions containing only a single anion, i.e., chloride, sulfate, or phosphate, or a mixture of sulfate or phosphate with nitrate. The principal variables examined in each system were the pH and the concentrations of anion and of uranium in the aqueous phase, and the concentration of phosphine oxide in the organic phase. These variables are discussed individually for each system in the sections which follow.

More limited study was made of the choice of organic diluent, the reagent solubility, and the effect of temperature on uranium extraction. The last was found to be significant over the possible extremes of ambient room temperatures under which the tests were conducted (p. 39). Although it was of a secondary order of importance with respect to most of the variables studied, care has been taken in the treatment of the following data to compare results only where it has been established that the prevailing temperatures were similar.

Comparison of Several Phosphine Oxides

Single-stage uranium extractions have been made from several aqueous solutions with a series of symmetrical phosphine oxides including straight-chain alkyl compounds, compounds with branching in the alkyl chains, compounds with aryl substituents on the alkyl chains, and an aryl compound (phosphorus bonded directly to the benzene ring). The complete testing procedure and description of solutions used appear in Tables 1 and 2. Some of these tests constituted a part of the more general screening program which has been reported previously, in which carbon tetrachloride was used as the organic diluent because of its general applicability to a wide variety of types of organic compounds. (Most of the subsequent tests described in this report employed kerosene as the diluent, both because the extraction coefficients with the phosphine oxides are higher in the latter and because it is more suitable for process application.) It is apparent from Table 1 that most of the phosphine oxides have strong complexing action in the dilute nitrate system. For comparison, the extraction coefficient obtained under similar conditions with tributylphosphate in carbon tetrachloride is less than 0.05[14]. Extractions were also high from the sulfate-nitrate solution (Table 2) but were

Table 1

COMPARISON OF PHOSPHINE OXIDES - URANIUM EXTRACTION ABILITY FROM NITRATE AND SULFURIC ACID SOLUTIONS

Initial concentration of uranium(VI) in aqueous phase = 0.004 M
Concentration of phosphine oxide in organic diluent = as indicated

Phase Ratio, aqueous/organic = as indicated
Agitation Time = 10 minutes (wrist-action shaker)
Temperature = 27°C

Trialkylphosphine Oxide	Batch No.	Uranium Extraction Coefficient, E_a^o			
		0.1 M NO_3, pH = 1.0, a/o = 2		0.5 M H_2SO_4, pH = 0.32, a/o = 1	
		0.1 M Oxide in CCl_4	0.1 M Oxide in Kerosene	0.1 M Oxide in CCl_4	0.3 M Oxide in Kerosene
n-Butyl	300C	80	a	---	---
n-Octyl	289	310	1250	0.005	5.9
n-Decyl	292	280	1430	0.005	3.8
n-Dodecyl	288	240	1050	0.007	4.5
2-Ethylhexyl	299	8	50	---	0.1
3,5,5-Trimethylhexyl	287	330	1330	0.004	3.2
Phenyl	A	2[b]	----	---	---
β-Phenylethyl	A	10[c]	----	---	---
γ-Phenylpropyl	A	85	----	---	---

a) Third phase formation: total uranium extraction, 98%; 75% reported to major organic phase.

b) Precipitation. Figure based upon the amount of uranium removed from aqueous solution.

c) 0.05 M Reagent (upper limit of solubility in CCl_4 at room temperature). Extraction coefficient compares with value of 15 obtained with γ-phenylpropylphosphine oxide at same concentration level.

Table 2

COMPARISON OF PHOSPHINE OXIDES - URANIUM EXTRACTION ABILITY FROM SULFATE-NITRATE AND PHOSPHATE-NITRATE SOLUTIONS

Initial concentration of uranium(VI) in aqueous phase = 0.004 M
" " " sulfate or phosphate " " " = 0.5 M
" " " nitrate " " " = 0.3 M
Concentration of phosphine oxide in organic diluent = 0.1 M

Phase Ratio, aqueous/organic = 1
Agitation Time = 10 minutes (wrist-action shaker)

Trialkylphosphine Oxide	Batch No.	Uranium Extraction Coefficient, E_a^o		
		Sulfate-Nitrate Solution, pH 1.1		Phosphate-Nitrate Solution, pH 1.2
		CCl_4 Diluent 28°C	Kerosene Diluent 25°C	CCl_4 Diluent 28°C
n-Butyl	300C	13	a	1.6
n-Octyl	289	20	110	2.4
n-Decyl	292	(15)[b]	(110)[c]	(1.9)[b]
n-Dodecyl	288	15	---	1.6
2-Ethylhexyl	D	0.3	---	0.1
3,5,5-Trimethylhexyl	287	18	>100	2.7
γ-Phenylpropyl	A	8	---	3

a) Third phase formation: total uranium extraction, 98%; 27% reported to major organic phase.

b) Interpolated from data obtained at 32°C (cf. page 44).

c) " " " " " 27°C (cf. page 44).

appreciably lower from the phosphate-nitrate solution (Table 2) and also from the sulfuric acid solution (Table 1) in spite of the indicated increase in reagent concentration.

The extraction coefficients obtained with the tri-n-octyl-, tri-n-decyl-, and tri-n-dodecylphosphine oxides were of similar magnitude under each set of extraction conditions. The coefficient obtained with the tributylphosphine oxide in carbon tetrachloride from the 0.1 M nitrate solution (Table 1) was markedly lower than the corresponding value obtained with the other straight-chain compounds although this difference was not observed in similar tests from the phosphate-nitrate and sulfate-nitrate solutions (Table 2). It is possible that a higher degree of distribution of the tributylphosphine oxide complex to the more dilute nitrate solution could account for its poorer showing in this solution. Third-phase formation was observed when kerosene was used as the diluent for this reagent.

The extractions obtained with the tri(3,5,5-trimethylhexyl)phosphine oxide were similar to those with the three longer straight-chain compounds, while extraction with the tri(2-ethylhexyl)phosphine oxide was very much lower. Since the most obvious difference between these two compounds is the distance of the branching from the center of the molecule (the phosphorus atom), it seems reasonable to assume that extraction by the 2-ethylhexyl compound is impaired by strain or steric effects.

When comparisons were possible the extractions were significantly higher with kerosene than with carbon tetrachloride as the diluent (cf. "Choice of Diluent," below).

Precipitation rather than extraction of uranium was obtained with the triphenylphosphine oxide, which is in agreement with published results.[15] The uranium precipitate was nearly insoluble in all of the common solvents. Precipitation did not occur with either of the arylalkyl compounds tested, and the coefficients obtained with tri(γ-phenylpropyl)phosphine oxide were similar to those with tributylphosphine oxide. (Difficulty was encountered in an attempt to synthesize tribenzylphosphine oxide, which would have provided an interesting comparison point between the phenyl and β-phenylethyl compounds.)

On the basis of these extraction results, together with consideration of physical properties and availability, the n-octyl and n-decyl compounds were chosen for use in most of the subsequent tests. A more specific study of compound differences should be made at a later date, especially if phosphine oxides undergo extensive study for process application.

Extraction from Chloride Solutions

A series of solutions (1 g U/l) with chloride concentrations of 0.5 to 6.0 molar and at pH levels ranging from 1.6 to the natural pH of the acid solutions have been extracted with tridecylphosphine oxide in kerosene. The results are shown in Table 3.

Effect of Chloride

The data of Table 3 as plotted on Figure 1 show the effect of chloride at a phosphine oxide concentration of 0.05 M and at several pH levels. Hydrochloric acid and chloride salts enhanced the extraction, increasing the coefficient by a factor of at least 100 in changing from 0.5 to 5.0 molar chloride at a given pH in the range <0 to 1.6.

Effect of pH

Variations in the extraction coefficients over the pH range studied (< 0 to 1.6, Table 3) are small and random.

In a few experiments run with 0.2 M trioctylphosphine oxide (Batch A-2) in kerosene, a third phase was formed when the hydrochloric acid concentration was very high, i.e., 6 M. The uranium which was extracted reported to the third phase, and the percent extraction from the aqueous was less than that from 4.0 M HCl solutions. Similar behavior has been noted with tributylphosphate[16].

Effect of Phosphine Oxide Concentration

Data from Table 3 (corrected to 25°C according to Figure 18) plotted on Figure 2 show that the uranium extraction coefficients increased approximately as the square of the phosphine oxide concentration. A more complete discussion of the effects of chloride and phosphine oxide concentrations in relation to the extraction mechanism is included in a later section of this report (cf. p. 84).

The Effect of Uranium Concentration

Table 4 and Figure 3 show extractions with 0.05 M tridecylphosphine oxide from aqueous solutions containing from 0.0045 to $\sim$0.1 M uranium in 0.5 M chloride solution at pH $\sim$0.6. Extraction isotherms of this type served to verify that the extraction power shown by the reagent is truly a

Table 3

EXTRACTION FROM CHLORIDE SOLUTIONS

0.004 M U(VI)

Tridecylphosphine Oxide, No. 292, in kerosene

Phase Ratio, aqueous/organic = 1

Agitation, 10 minutes (wrist-action shaker)

Chloride (M)	Reagent (M)	Temp., °C	Initial pH	E_a^o
0.5	0.05	28	0.32	12
	"	"	0.70	11
	"	"	1.62	18
	0.2	25	0.70	280
1.5	0.05	28	< 0	150
	"	"	0.57	100
	"	"	1.30	120
4.0	0.05	28	< 0	3300
	"	"	0.63	4300
	"	"	1.63	4000
6	0.05	28	< 0	3600

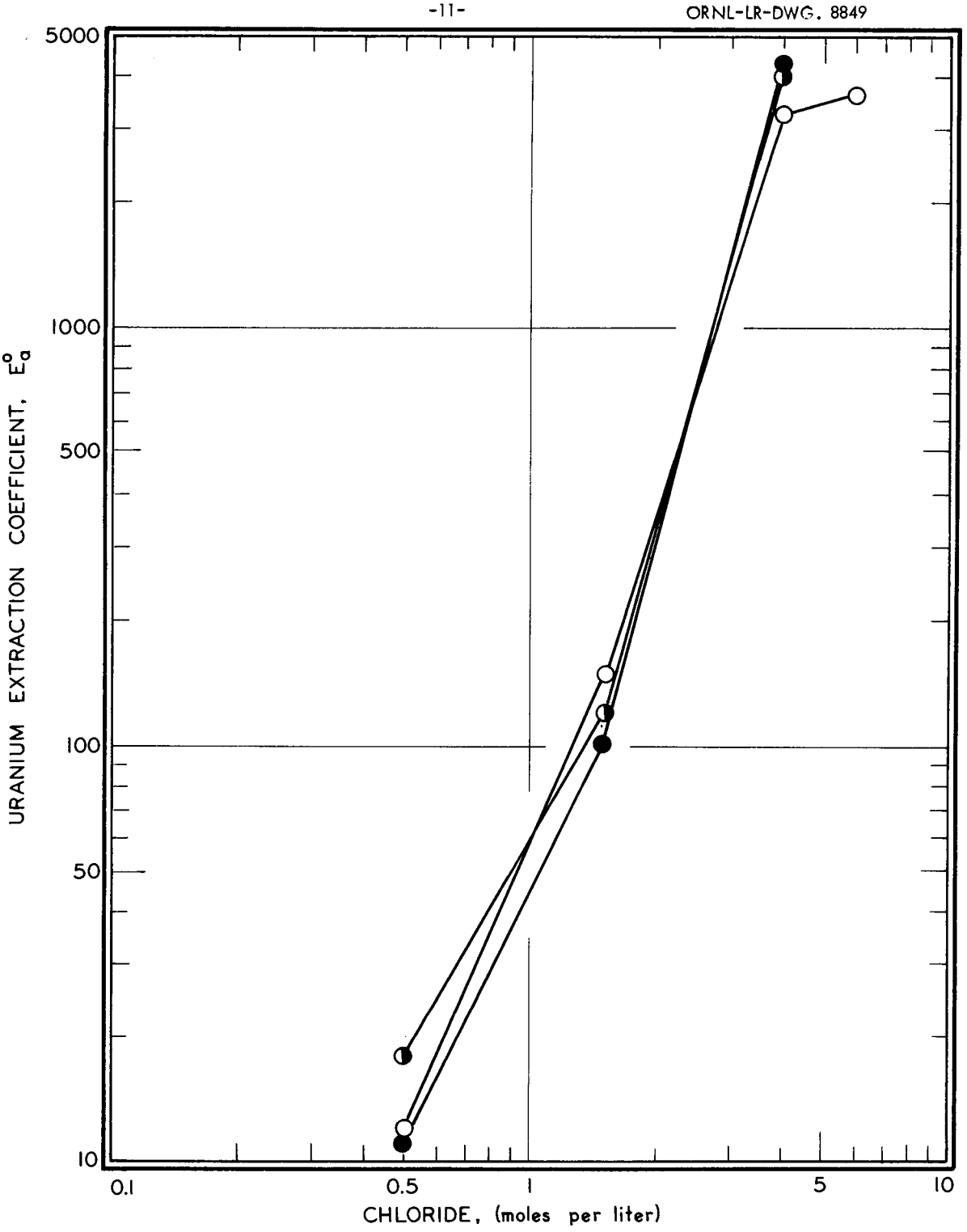

Figure 1

URANIUM EXTRACTION FROM CHLORIDE SOLUTION

EFFECT OF CHLORIDE CONCENTRATION

0.05 M Tridecylphosphine Oxide (Batch 292) in Kerosene
0.004 M U(VI), Phase Ratio 1, 28°C

○ pH of unbuffered HCl
● pH 0.7
◑ pH 1.3

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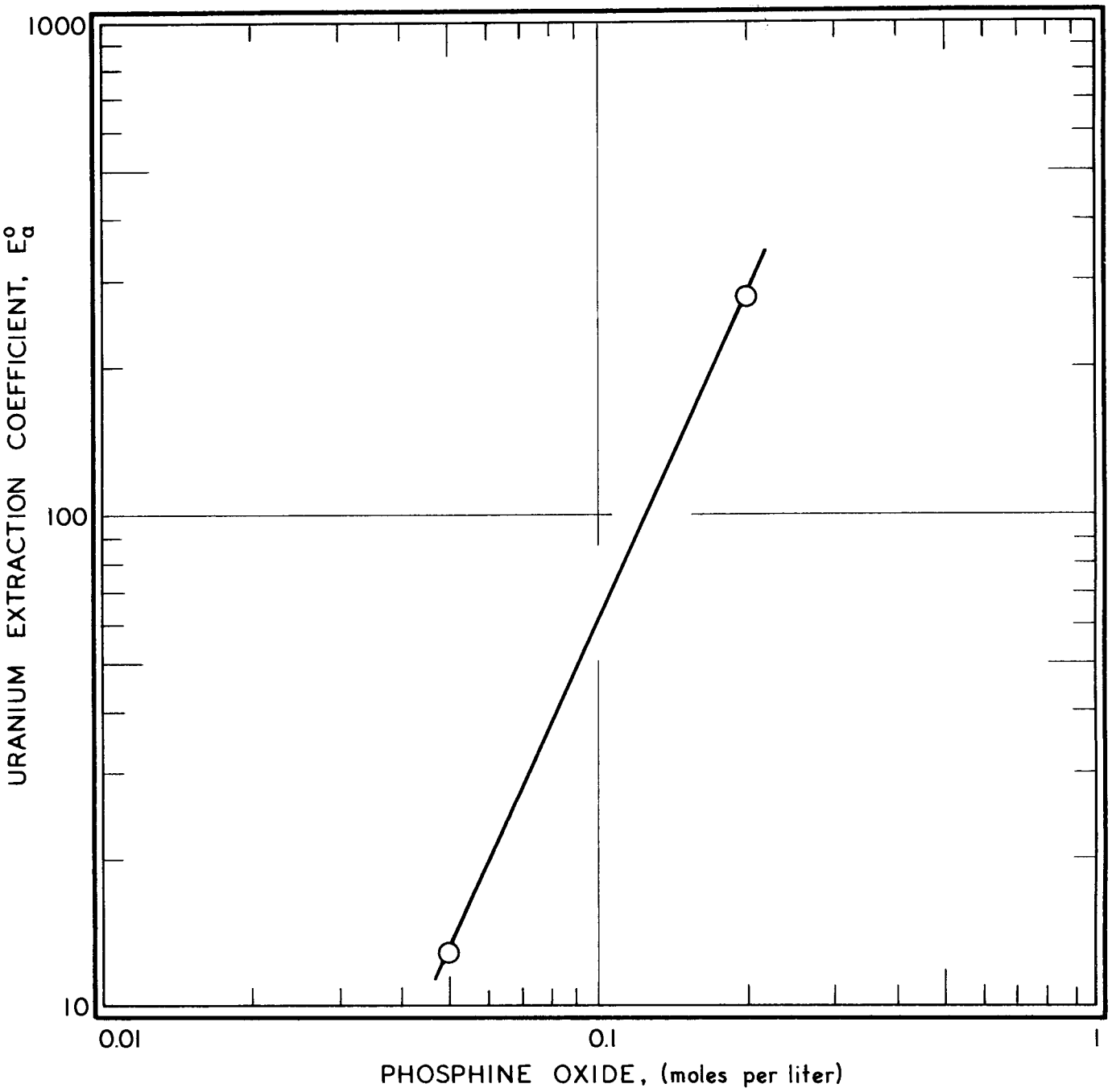

Figure 2

URANIUM EXTRACTION FROM CHLORIDE SOLUTION

EFFECT OF REAGENT CONCENTRATION

Tridecylphosphine Oxide (Batch 292) in Kerosene
0.004 M U(VI), 0.5 M Cl, Phase Ratio 1, pH 0.7, 25°C

Table 4

EFFECT OF URANIUM CONCENTRATION ON EXTRACTION FROM CHLORIDE SOLUTIONS

0.5 M Cl

0.05 M Tridecylphosphine Oxide, No. 292, in kerosene

Agitation 10 minutes (wrist-action shaker)

Initial (U) Aq M	Phase Ratio a/o	Initial pH	Temp. °C	Uranium Distribution, g/l		Extraction Coefficient[a] E_a^o	Est'd. Free Reagent[b] M	Calcd. E_a^o for 0.05 M Free Reagent, 0.5 M Cl, 28°C[b,c]
				Aq	Org			
0.005	0.1	0.7	28	0.006	0.106	17.7	0.0492	18
0.005	1	0.7	28	0.092	1.01	11.0	0.0416	16
0.1	0.1	0.5	25	0.735	1.94	2.9	0.0336	12[d]
0.005	10	0.7	28	0.750	3.2	4.3	0.0232	20
0.1	1	0.5	25	18.2	5.1	0.28	0.0072	14[e]

a) Extraction coefficient affected by high loading.

b) Calculated on the basis of a combining ratio of 2 molecules of reagent per uranium.

c) E_a^o for 0.05 M free reagent $= \dfrac{(E_a^o \text{ found})}{\left(\dfrac{\text{M free reagent}}{0.05}\right)^2}$

d) Calculated $E_a^o = 6.4$ at 0.34 M chloride (final) and 25°C. Corrected to 0.5 M chloride and 28° by means of Figures 1 and 18. Variation with pH negligible.

e) Calculated $E_a^o = 14$ at 0.46 M chloride (final) and 25°C. Corrected as in (d).

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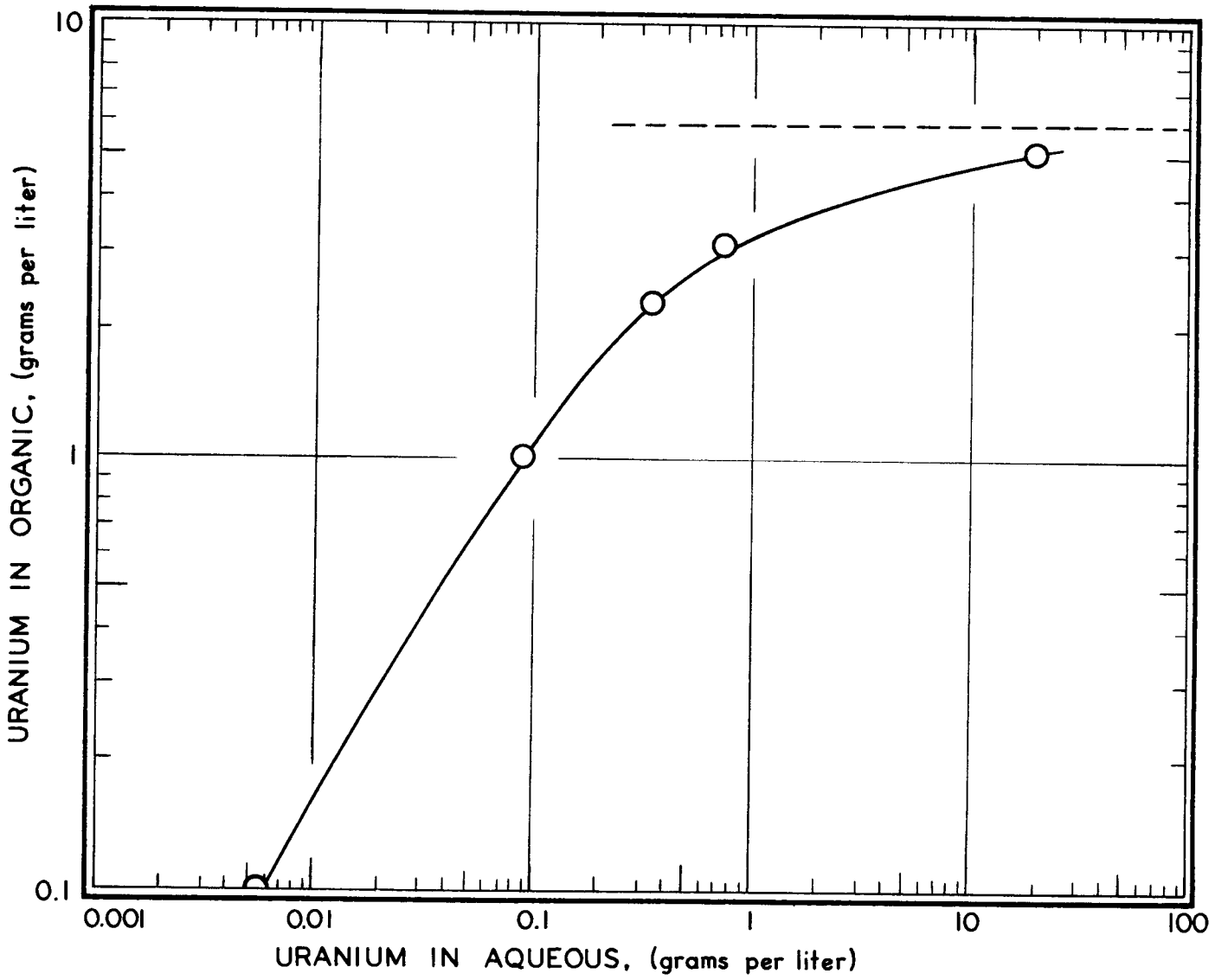

Figure 3

URANIUM EXTRACTION ISOTHERM FROM CHLORIDE SOLUTION

0.05 M Tridecylphosphine Oxide (Batch 292) in Kerosene
0.5 $\underline{M}$ $\bar{Cl}$, pH 0.6, 28°C

Dashed line represents theoretical loading limit (p. 84)
Solid line drawn for theoretical $E_a^o = 16$

property of the phosphine oxide and was not due to any contaminant, as discussed in "Description of Compounds." The uranium loading reached, 5.1 g U/l, was about 86 percent of the theoretical stoichiometric limit. The extraction coefficients are, of course, affected by the decreasing amount of free reagent remaining available at the high loading levels, and in two of the tests they are also affected by the extraction of a significant fraction of the chloride from the aqueous solution. In order to compare the coefficients at high and low loading, it is necessary to estimate the extent of the concentration changes and calculate the coefficients for constant conditions. For this purpose, Table 4 includes the estimated free reagent concentration for each test and the corresponding extraction coefficient for a free reagent concentration of 0.05 M, both calculated on the basis of a combining ratio of two reagent molecules for each uranium. In addition, the decrease in aqueous chloride concentration was estimated (for the third and fifth tests, Table 4) on the basis of two chloride ions extracted with each uranium, and the corresponding extraction coefficient at 0.5 M chloride and 28°C was estimated by means of Figure 1 (extrapolated) and Figure 18. The resulting values, shown in the last column of Table 3, are reasonably constant at 12-20. The average, 16, was used to calculate the theoretical extraction isotherm shown by the solid line of Figure 3. The points shown in this figure give the equilibrium concentrations actually found (the third and fifth points being corrected for temperature and chloride change).

If the extraction of uranium from chloride solutions in tests at low uranium concentrations had been accomplished by a small amount of some strong extractant contaminating the phosphine oxide, instead of by the phosphine oxide itself, the quantity of uranium so extracted would necessarily be limited to an amount equivalent to the small amount of the actual extractant. Thus, the consistent extractions obtained over the range of loading levels, in these tests and also in similar extractions from other solutions described below, confirm that the phosphine oxide itself was the effective extractant, and considerably strengthen the overall confidence in the essential purity of the reagents.

Extraction from Sulfate Solutions

A series of solutions (1 g U/l) with sulfate concentrations of 0.5 to 6.0 molar and at pH levels ranging from 1.9 to the natural pH of the acid solutions have been extracted with tridecylphosphine oxide in kerosene. The results are shown in Table 5.

Table 5

EXTRACTION FROM SULFATE SOLUTIONS

0.004 M Uranium(VI)

Tridecylphosphine Oxide, No. 292, in kerosene

Phase Ratio, aqueous/organic = 1

Agitation - 10 minutes (wrist-action shaker)

Temperature = 26°C

Sulfate (M)	Reagent (M)	Initial pH	E_a^o
0.5	0.1	0.42	0.2
	0.3	0.32	4.0
	"	0.42	3.5
	"	1.11	0.7
	"	1.78	0.3
1.5	0.1	0.47	0.08
	0.3	< 0	18
	"	0.47	1.2
	"	0.97	0.3
	"	1.87	0.1
4.0	0.1	0.33	0.03
	0.3	< 0	24
	"	0.33	0.5
6.0	0.3	< 0	15

Effects of pH and Sulfate Concentration

The data of Table 5 as plotted on Figures 4 and 5 show the effect of sulfate concentration and pH level upon uranium extraction. In contrast to the results in chloride solutions, the extraction coefficients dropped rapidly as the pH rose. This may be due at least in part to increased dissociation of bisulfate to sulfate and, correspondingly, increased sulfate complexing of the uranium. Uranium extraction increased with increasing sulfuric acid concentration up to around 3 or 4 M, but at each constant pH level tested, increase in the sulfate concentration caused the uranium extraction to decrease.

Effect of Phosphine Oxide Concentration

The data of Table 5 plotted on Figure 6 show that the uranium extraction coefficients increased in proportion to a power of the reagent concentration somewhat greater than the square. The power dependence on phosphine oxide concentration of the extraction coefficients from chloride solution (above) and the other types of solutions tested (below) was close to the square, as expected on basis of a reagent:uranium combining ratio of two (cf. p. 84). The higher power dependence in extraction from the sulfate solutions probably does not indicate a shift in the combining ratio, but more likely reflects secondary effects in the complex equilibria in the aqueous sulfate solutions.

Effect of Uranium Concentration

Table 6 shows extractions with several phosphine oxides from aqueous solutions containing 0.004 and ~0.1 M uranium in 0.5 M sulfuric acid solution. From these data, extraction coefficients at constant free reagent concentration have been calculated in the same manner as described above (p. 9). The data for extractions with the tridecylphosphine oxide are shown as an extraction isotherm on Figure 7. The solid line represents the theoretical extraction isotherm calculated for a coefficient of 4.5, while the points give the equilibrium uranium concentrations actually found (corrected to 26°C and pH 0.3).

Extraction from Phosphate Solutions

A series of solutions (1 and 0.1 g U/l) with phosphate concentrations of 0.4 to 5.3 M and at pH levels ranging from 2 to the natural pH of the acid solutions have been extracted with 0.6 M trioctylphosphine oxide in kerosene. The results

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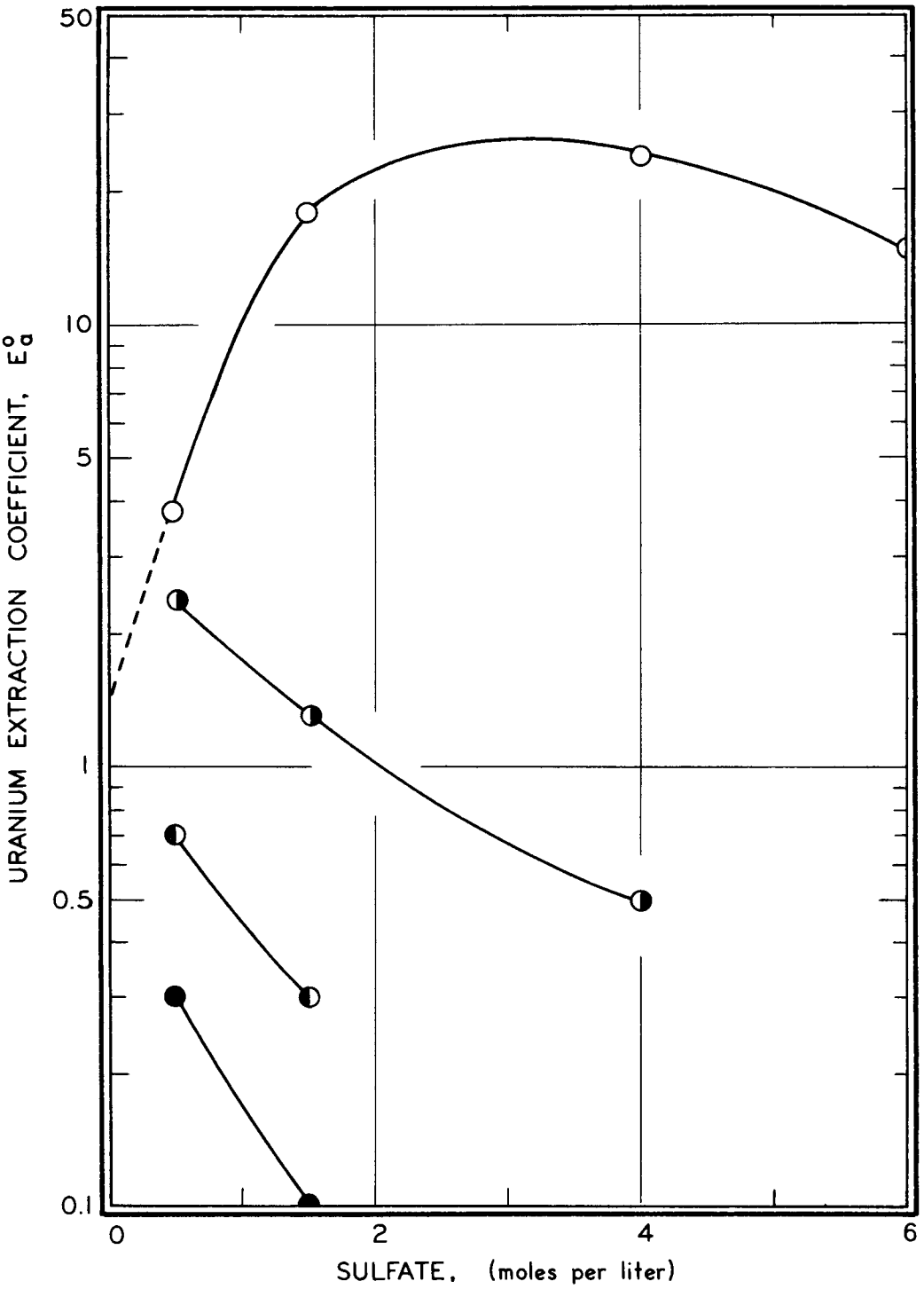

Figure 4

URANIUM EXTRACTION FROM SULFATE SOLUTION

EFFECT OF SULFATE CONCENTRATION

0.3 M Tridecylphosphine Oxide (Batch 292) in Kerosene
0.004 M U(VI), Phase Ratio 1, 26°C

○ pH of unbuffered H_2SO_4
◑ pH 0.5 ◐ pH 1.0 ● pH 1.8

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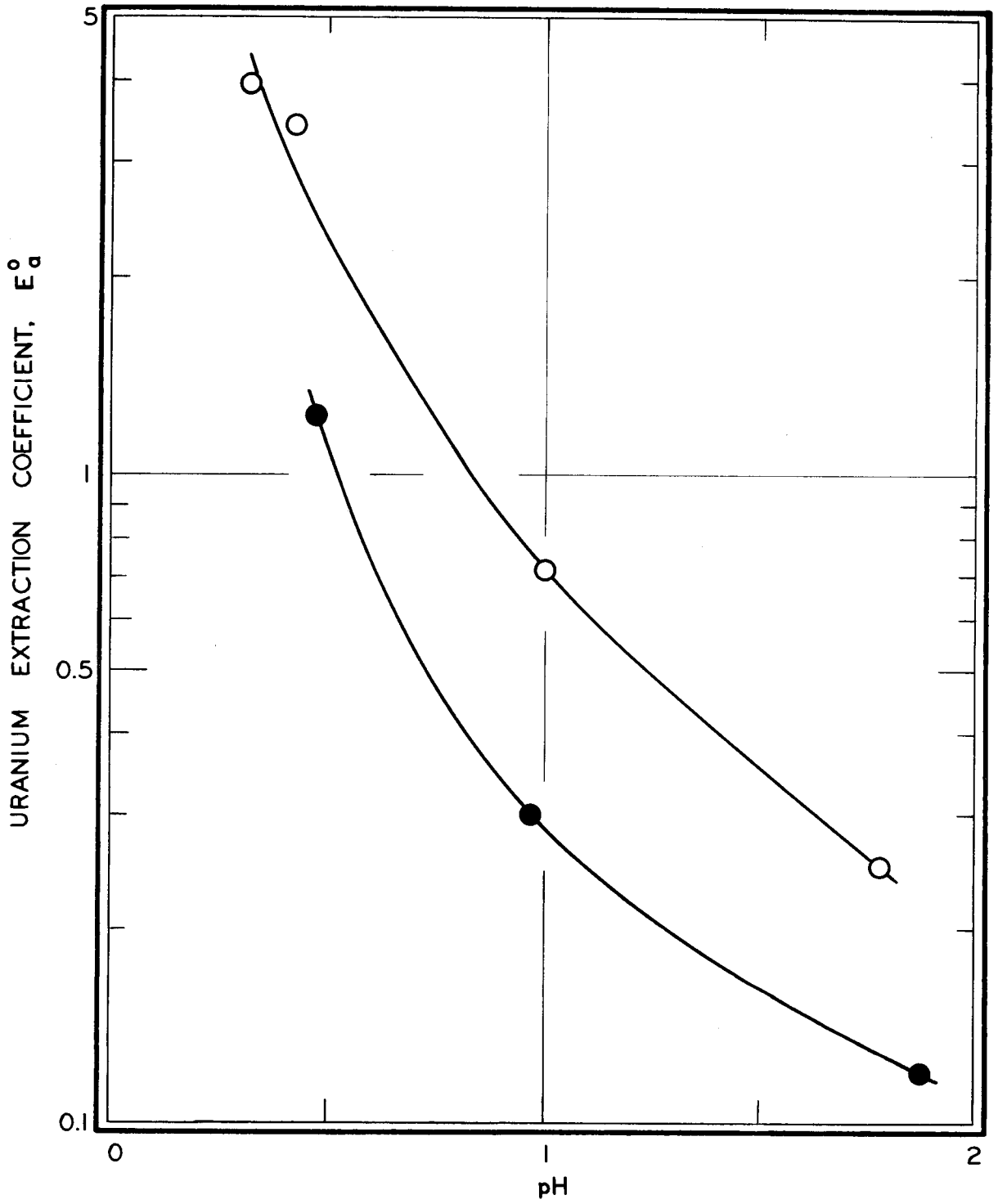

Figure 5

URANIUM EXTRACTION FROM SULFATE SOLUTION

EFFECT OF pH LEVEL

0.3 M Tridecylphosphine Oxide (Batch 292) in Kerosene
0.004 M U(VI), Phase Ratio 1, 26°C

○ 0.5 M SO_4
● 1.5 M SO_4

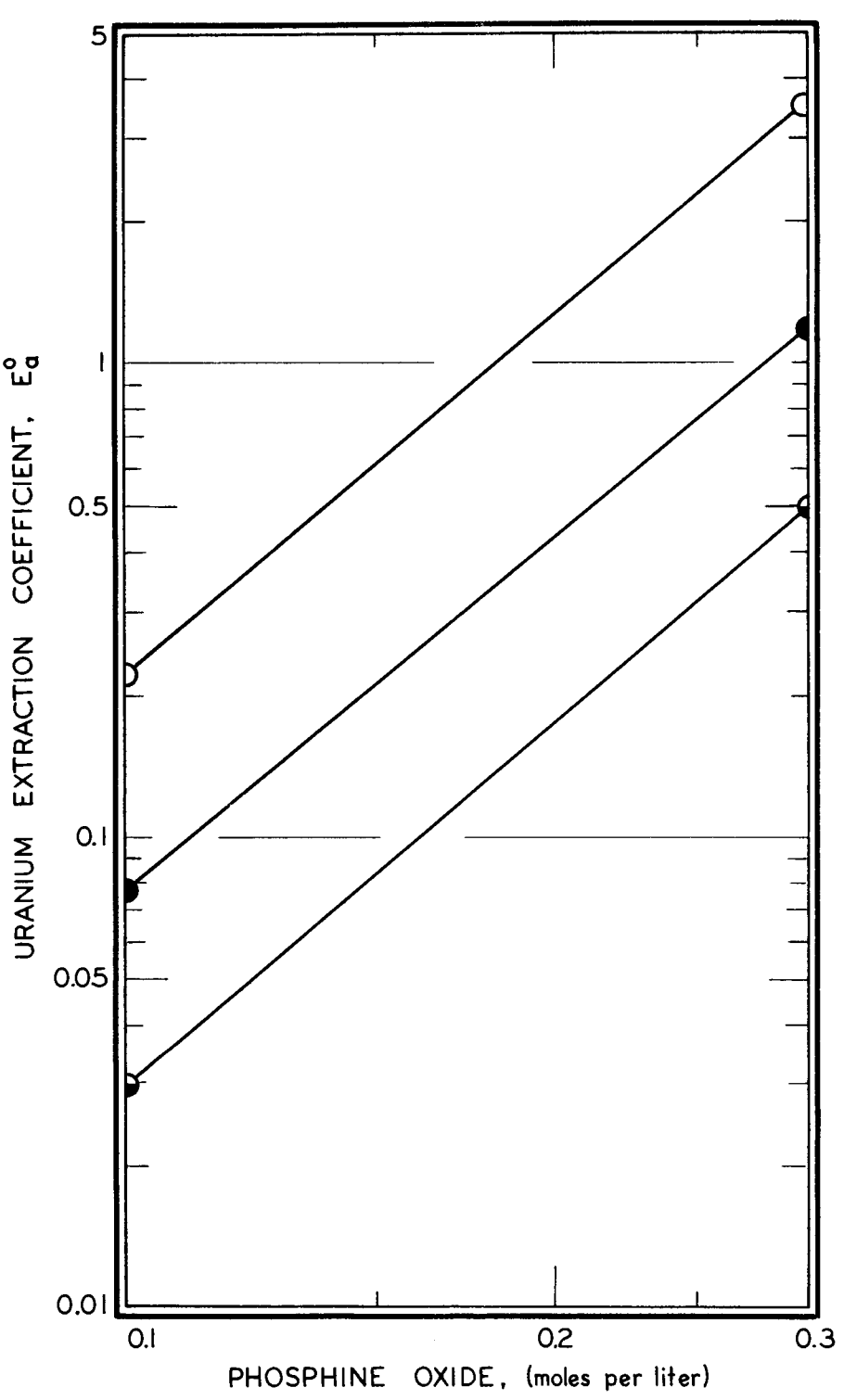

Figure 6

URANIUM EXTRACTION FROM SULFATE SOLUTION

EFFECT OF REAGENT CONCENTRATION

Tridecylphosphine Oxide (Batch 292) in Kerosene
0.004 M U(VI), Phase Ratio 1, 26°C

○ 0.5 M SO_4, pH 0.42
● 1.5 M SO_4, pH 0.47
◒ 4.0 M SO_4, pH 0.33

Table 6

EFFECT OF URANIUM CONCENTRATION ON EXTRACTION FROM SULFATE SOLUTIONS

0.5 M H_2SO_4
0.3 M Phosphine Oxide in kerosene
Agitation - 10 minutes (wrist-action shaker)

Initial (U) Aq M	Phase Ratio a/o	Initial pH	Temp. °C	Uranium Distribution, g/l Aq	Uranium Distribution, g/l Org	Extraction Coefficient[a] E_a^o	Est'd. Free Reagent[b] M	Calcd. E_a^o for 0.3 M Free Reagent 26°C, pH 0.3[b,c,d]
				Tridecylphosphine Oxide, Batch 292				
0.004	1	0.3	26	0.20	0.75	3.8	0.294	4
0.004	15	0.3	28	0.68	2.74	4.0	0.276	5
0.1	20	0.4	25	21.4	20	0.94	0.132	5
				Trioctylphosphine Oxide, Batch 289				
0.004	1	0.3	26	0.146	0.864	5.9	0.293	6
0.1	20	0.4	27	22.2	22.5	1.0	0.110	7
				Tridodecylphosphine Oxide, Batch 288				
0.004	1	0.3	26	0.185	0.825	4.5	0.293	5
0.1	20	0.4	27	22.2	22.3	1.0	0.112	7
				Tri(3,5,5-trimethylhexyl)phosphine Oxide, Batch 287				
0.004	1	0.3	26	0.240	0.760	3.2	0.294	3
0.1	20	0.4	27	22.1	18.9	0.9	0.142	4
				Tri(2-ethylhexyl)phosphine Oxide, Batch 299				
0.004	1	0.3	26	0.890	0.120	0.13	0.299	0.1
0.1	20	0.4	27	23.0	1.7	0.07	0.286	0.1

a) Extraction coefficient affected by loading.
b) Calculated on the basis of a combining ratio of 2 molecules of reagent per uranium.
c) E_a^o for 0.3 M free reagent $= \dfrac{(E_a^o \text{ found})}{\left(\dfrac{\text{M free reagent}}{0.3}\right)^2}$
d) Coefficients corrected to 26°C by means of Figure 18, and to pH 0.3 by means of Figure 5.

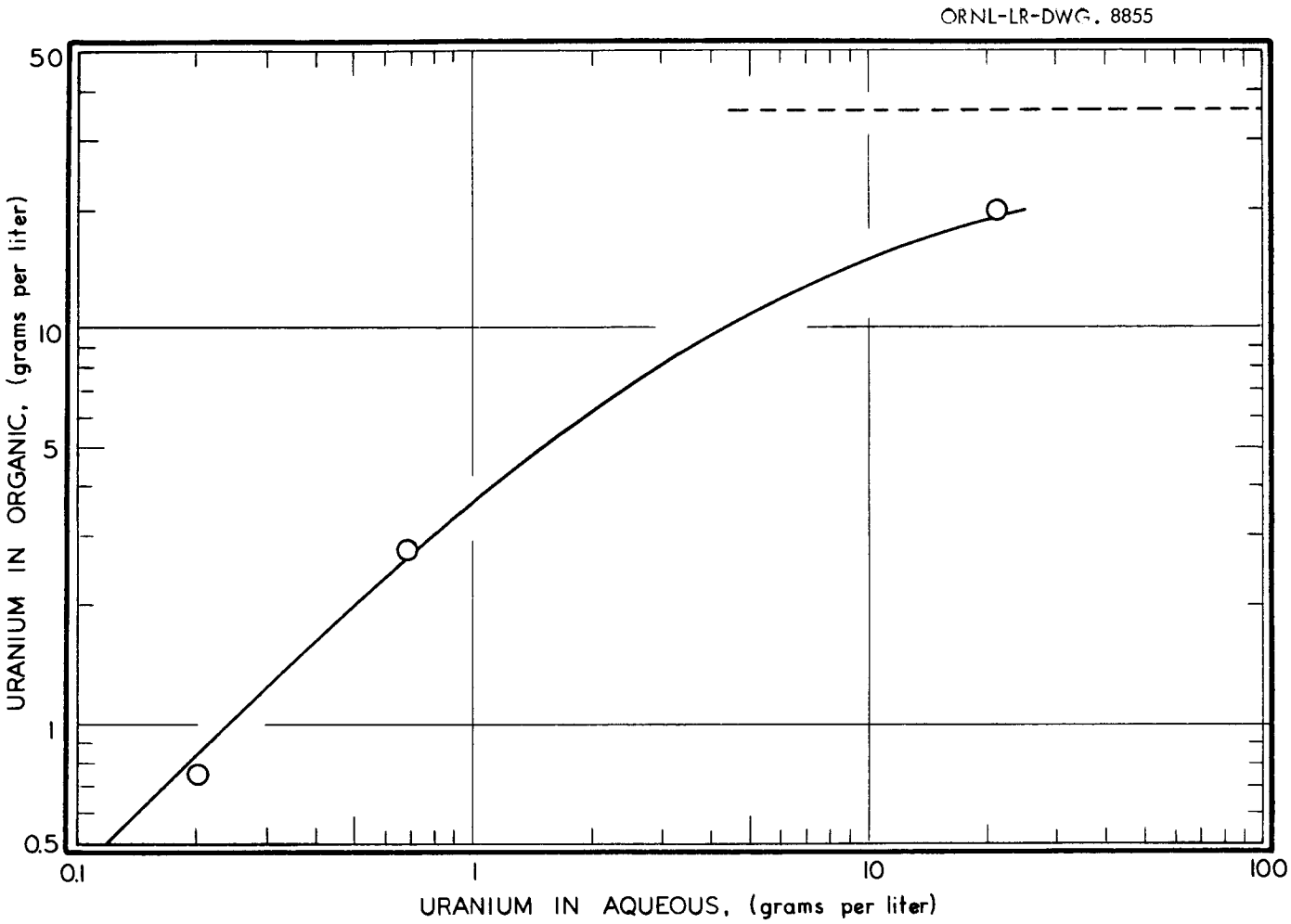

Figure 7

URANIUM EXTRACTION ISOTHERM FROM SULFATE SOLUTION

0.3 M Tridecylphosphine Oxide (Batch 292) in Kerosene
0.5 M H_2SO_4, 26°C, pH 0.3

Dashed line represents theoretical loading limit (p.84)
Solid line drawn for theoretical E_a^o = 4.5 (p. 9)

are shown in Table 7. The reagent concentration was not varied, since 0.6 M is about the upper limit of solubility of trioctylphosphine oxide in kerosene at room temperature (p. 45), and lower reagent concentrations were not of interest because of the low extractions.

Effect of pH

The data of Table 7 plotted on Figure 8 show that the extraction coefficient in phosphate solutions decreased in about the same way as was found with the sulfate solutions above.

Effect of Phosphate Concentration

Table 7 and Figure 9 show the effect of phosphate concentration at pH levels of 1.0 and < 0. (The higher concentrations were set at 3.3 M (20% P_2O_5) and 5.3 M (30% P_2O_5) since these are concentrations encountered in commercial phosphate fertilizer and chemical plants. For the same reason, the corresponding uranium concentration was set at 100 ppm.) Even with the high extractant concentration studied (0.6 M), the extraction coefficients were low and decreased with increasing phosphate concentration, being less than unity when the phosphate concentration exceeded 0.4 M. The behavior in phosphoric acid is in contrast with that in sulfuric acid, where improved extraction accompanied increased acid concentration over a considerable range.

Effect of Uranium Concentration

One extraction isotherm has been run in 1.4 M phosphoric acid with 0.6 M trioctylphosphine oxide in kerosene. As shown by the data in Table 8, the extractions from the solution, even with the high concentration of extractant used, were very poor, the coefficients being about 0.5. (At the very low uranium loading attained, the free reagent concentration remained essentially unchanged, so that no correction of the measured coefficients is required.)

Enhancement of Extraction with Nitrate and Chloride Salts

When using organic reagents whose uranium extracting ability cannot compete favorably with uranium complexing agents already present in the aqueous phase, it is often possible to increase extractions by the addition of favorable salts. For example, the uranium extraction coefficients are ~ 0.1 with

Table 7

EXTRACTION FROM PHOSPHATE SOLUTIONS

Reagent = 0.6 M Trioctylphosphine Oxide, Batches A-1 and A-2
Organic Diluent = Kerosene
Phase Ratio, aqueous/organic = 2
Contact Time = 20 min. (tumbled end-over-end)
Room Temperature

Phosphate (M)	Initial pH	U(VI) (M)	E_a^o
0.4	Acid (1.1)	0.004	1.3
1.4	Acid (0.68)	0.004	0.33*
	1.0	0.004	0.26*
3.3	Acid (0.32)	0.0004	0.15*
	"	"	.18
	"	.004	.15
	1.0	0.0004	0.09*
	"	"	.07
	2.0	0.0004	0.02*
5.3	Acid (< 0)	0.0004	0.04

Tests marked were with Reagent Batch A-2, others with Batch A-1.

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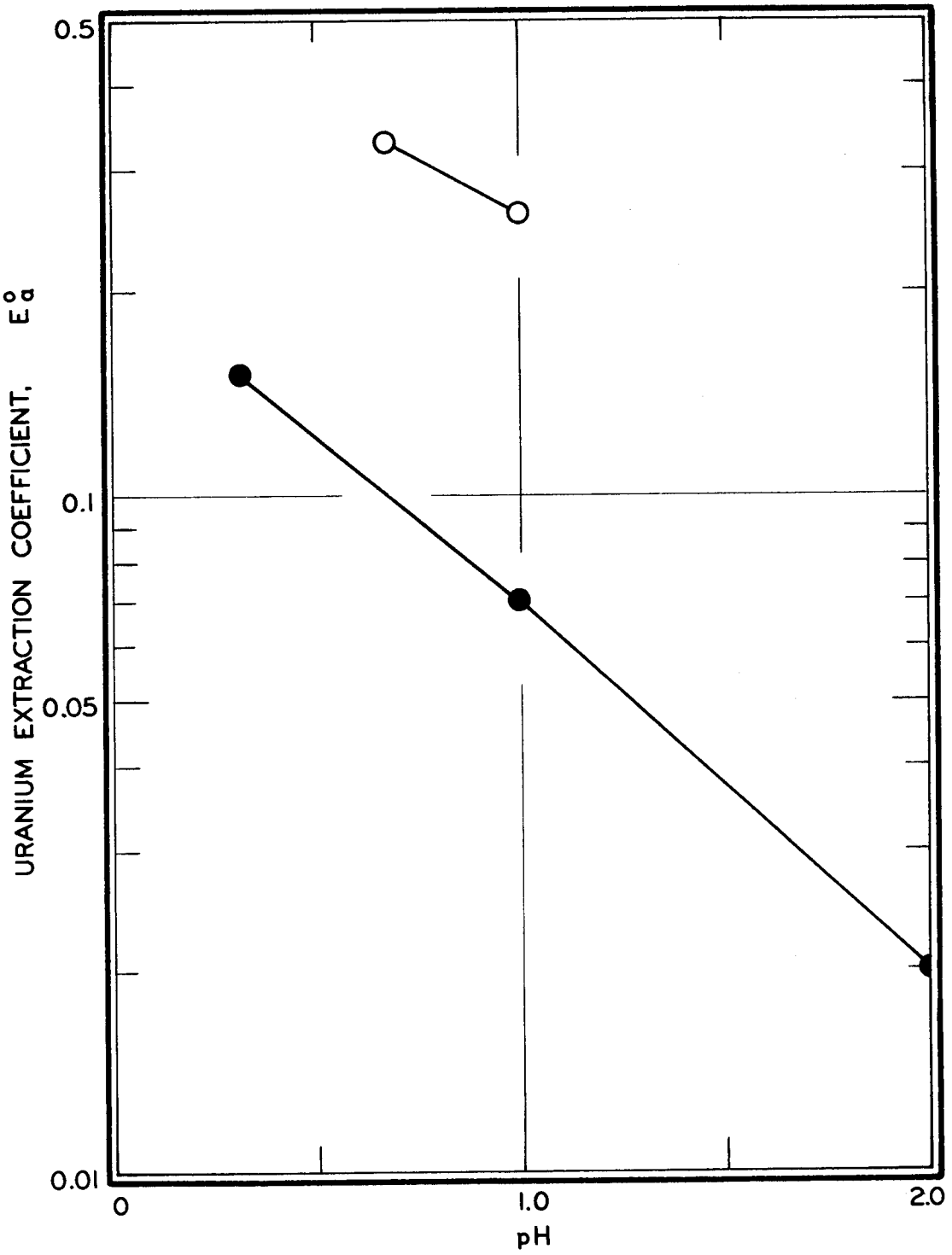

Figure 8

URANIUM EXTRACTION FROM PHOSPHATE SOLUTION

EFFECT OF pH LEVEL

0.6 M Trioctylphosphine Oxide (Batch A-2) in Kerosene
Aqueous/Organic phase ratio 2, Room Temperature

○ 0.004 M U(VI), 1.4 M PO_4
● 0.0004 M U(VI), 3.3 M PO_4

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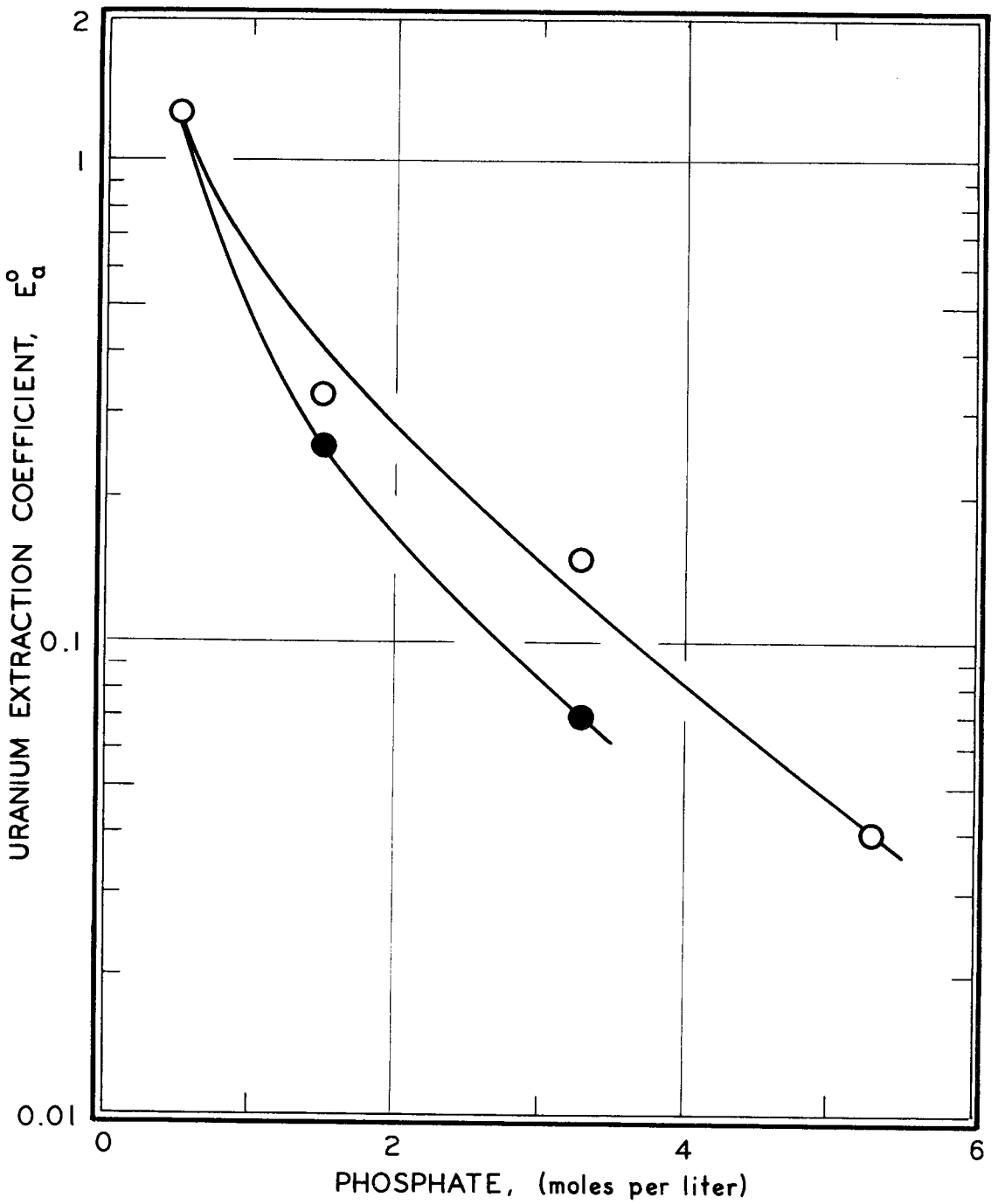

Figure 9

URANIUM EXTRACTION FROM PHOSPHATE SOLUTION

EFFECT OF PHOSPHATE CONCENTRATION

0.6 M Trioctylphosphine Oxide in Kerosene
0.0004 M and 0.004 M U(VI), Aqueous/Organic phase ratio 2, Room Temperature

○ pH of unbuffered H_3PO_4
● pH 1

Table 8

EFFECT OF URANIUM CONCENTRATION ON EXTRACTION FROM 1.4 M PHOSPHORIC ACID

Reagent = 0.6 M Trioctylphosphine Oxide, Batch A-2

Organic Diluent = Kerosene

Contact Time = 20 min.

Room Temperature

Phase Ratio Aqueous/Organic	Initial Uranium (g/l)	Uranium Distribution		E_a^Q
		Aqueous (g/l)	Organic (g/l)	
1	6.6	4.9	1.7	0.35
1	4.9	3.2	1.7	.53
9	1.0	0.99	0.46	.46
5.7	1.0	.96	.43	.45
4	1.0	.91	.42	.46
3	1.0	.86	.43	.51
1	1.0	.65	.37	.56

pentaether (dibutoxytetraethyleneglycol) from solutions in which the equilibrium nitrate concentration is 0.1 M or less. This coefficient is increased remarkably when nitrate salts are added to the aqueous phase, the coefficient with pentaether from 8 M $Ca(NO_3)_2$ (saturated) becoming 300[17]. With 0.55 M tributylphosphate (in hexane) the extraction coefficient is ~0.4 from a solution in which the equilibrium nitric acid concentration is 0.1 M, whereas the presence of 3 M nitric acid provides a coefficient of nearly 10 from a 0.12 M uranyl nitrate solution. In the presence of the interfering ions sulfate or phosphate (0.2 M), the concentration of the nitric acid salting agent must be increased to 6 M to achieve coefficients of ~10 (sulfate solution) and 4 (phosphate solution) with 0.55 M tributyl phosphate[18].

The enhancement of uranium extraction by adding small amounts of favorable anions is particularly effective with phosphine oxides. For example, extractions at pH 1 are fairly low from 0.5 M sulfate with 0.3 M tridecylphosphine oxide (Figure 4), and quite low from 0.4 M phosphate with 0.6 M trioctylphosphine oxide (Figure 9). The extractions can be increased considerably, however, by the addition of sodium chloride or nitrate, the latter being much more effective. The following data compare extractions with 0.1 M tridecylphosphine oxide from the above aqueous solutions.

Additive	Sulfate Solution	Phosphate Solution
None	(0.2)	(<< 1)
0.3 M NaCl	1.3	0.14
0.3 M $NaNO_3$	100	24

The large increase in extraction coefficient with the relatively small addition of nitrate salt is noteworthy, especially when compared with the above tributylphosphate data showing the effect of small concentrations of sulfate and phosphate salts. If the nitrate were added in combination with some other metal ion such as iron or aluminum which also complexes phosphate, then the uranium extraction coefficient would be increased by an additional amount.

Extraction from Sulfate-Nitrate Solutions

Effect of Nitrate Concentration

The effect of nitrate concentration upon the extraction from certain sulfate solutions is shown by Table 9 and Figure 10. For the 0.5 M sulfate, pH 1 solution, the addition of

Table 9

EXTRACTION FROM SULFATE-NITRATE SOLUTIONS

0.004 M Uranium(VI)
Tridecylphosphine Oxide, No. 292, in kerosene

Phase Ratio = 1
Agitation = 10 minutes (wrist-action shaker)

Sulfate M	Phosphine Oxide M	Nitrate M	Initial pH	E_a^o	Temp. °C
0.5	0.03	0.3	0.25	28	25
			1.1	11	25
			1.95	5	25
		1.2	1.00	110	25
	0.1	0.05	0.32	17	27
			1.1	4.6	27
			1.8	2.4	27
		0.1	1.1	18	27
		0.3	1.1	100	27
1.0	0.03	0.3	<0	20	25
			1.02	3.9	25
			1.92	2.5	25
		1.2	1.01	34	25
	0.1	0.1	1.0	6.2	27
		0.3	1.02	31	27
		1.2	1.01	290	27

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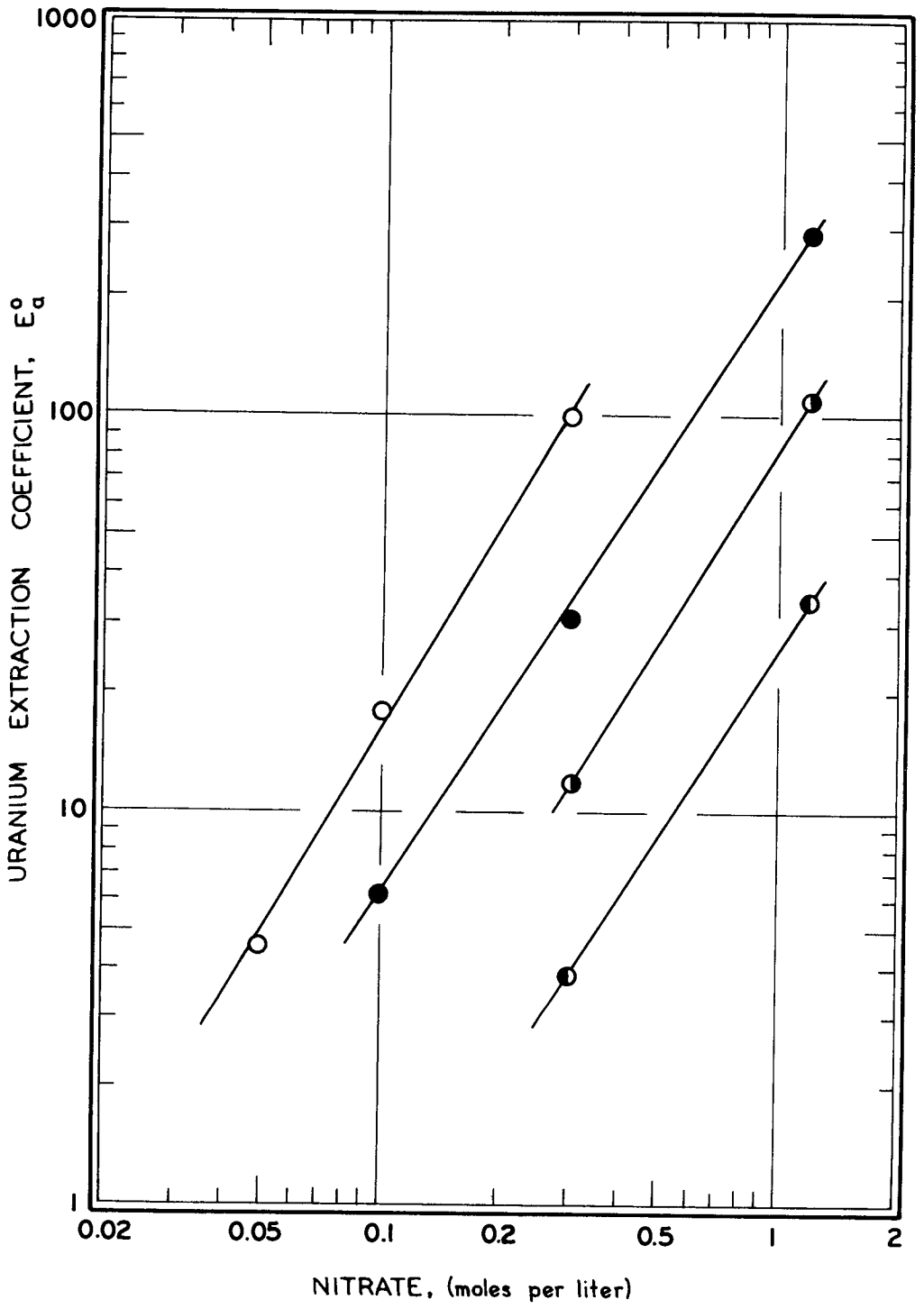

Figure 10

URANIUM EXTRACTION FROM SULFATE-NITRATE SOLUTION

EFFECT OF NITRATE CONCENTRATION

Tridecylphosphine Oxide (Batch 292) in Kerosene
Phase Ratio 1

○ 0.1 M Reagent, 0.5 M SO_4, pH 1.1, 27°C
● 0.1 M Reagent, 1.0 M SO_4, pH 1.0, 27°C
◑ 0.03 M Reagent, 0.5 M SO_4, pH 1.0, 25°C
◐ 0.03 M Reagent, 1.0 M SO_4, pH 1.0, 25°C

0.1 M nitrate salt, or less than 1 percent by weight of nitrate, is sufficient to increase the extraction coefficient from less than 1 to more than 15 when 0.1 M tridecylphosphine oxide in kerosene diluent is used as the extractant.

Effect of pH

The variation in extraction coefficient with pH at different nitrate levels and two phosphine oxide concentrations is described in Figure 11. Again, there is a decrease in extraction with an increase in pH levels from near zero to 2.

Effect of Phosphine Oxide Concentration

Extractions at two reagent concentrations in kerosene (Table 9) and at several reagent concentrations in carbon tetrachloride are plotted on Figures 12 and 13, showing that the uranium extraction coefficients increased approximately as the square of the reagent concentration (cf. p. 84).

Effect of Uranium Concentration

Table 10 shows extractions with tridecylphosphine oxide from aqueous solutions containing 0.004 and ~0.1 M uranium in 0.5 M sulfate, 0.3 M nitrate, at pH 1. Where possible the coefficients corresponding to 0.1 M free reagent, 25°C, were calculated as above (p. 9). The data indicate an inherent extraction coefficient of approximately 100 under those conditions.

Extraction from Phosphate-Nitrate Solutions

Effect of Nitrate Concentration

Table 11 and Figure 14 describe nitrate requirements for extraction of uranium from phosphate solutions with 0.1 M tridecylphosphine oxide in kerosene. More nitrate is needed to achieve useful coefficients in phosphate than in sulfate solutions; for example, twice as much is required to reach a coefficient of 10 in 0.5 M phosphate as in 0.5 M sulfate solution (pH = 1), and five times as much is required to reach a coefficient of 50.

Effect of pH

The dependence of extraction coefficient upon the pH of the phosphate-nitrate solutions is presented in Figure 15

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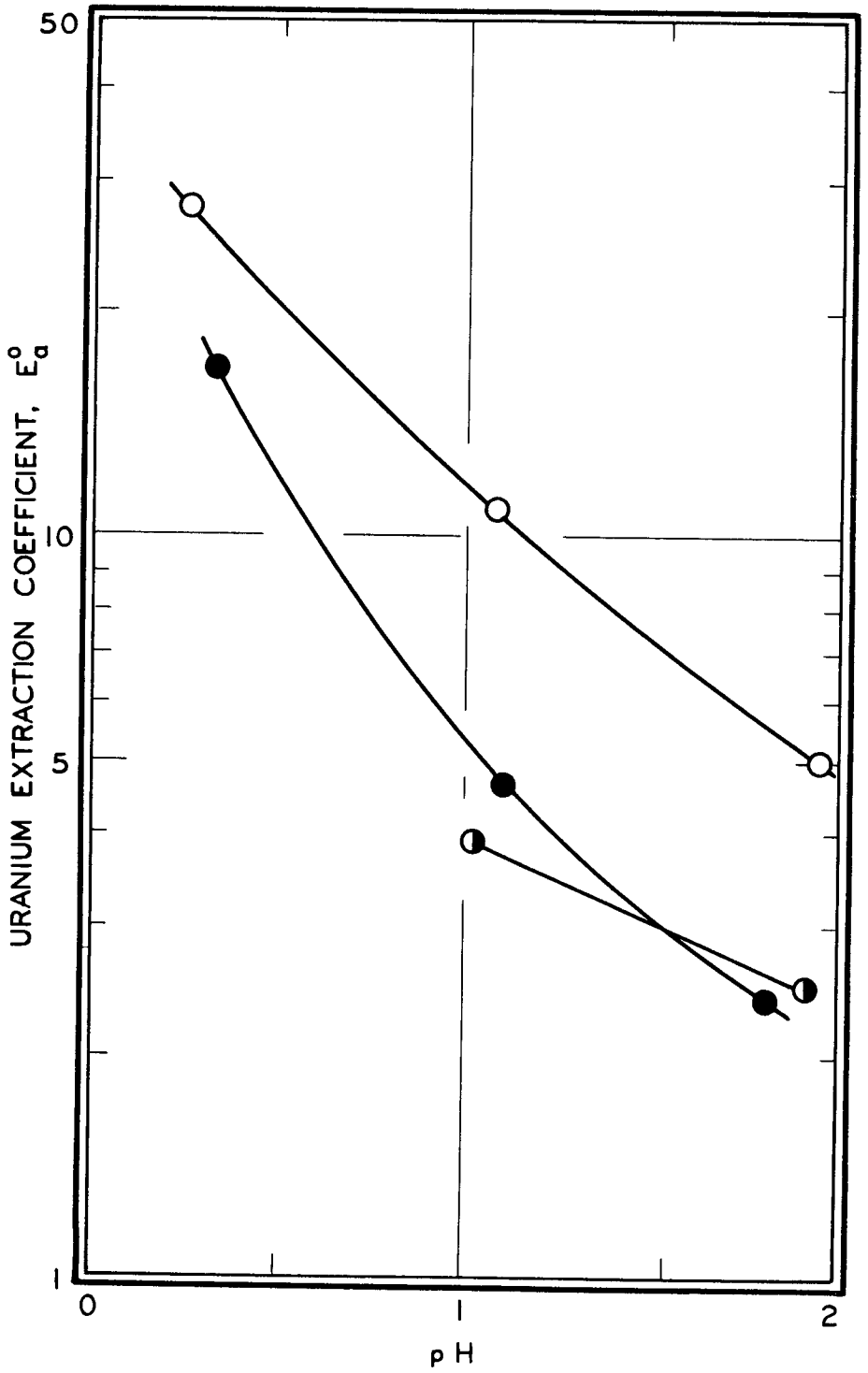

Figure 11

URANIUM EXTRACTION FROM SULFATE-NITRATE SOLUTION

EFFECT OF pH LEVEL

Tridecylphosphine Oxide (Batch 292) in Kerosene
Phase Ratio 1

○ 0.03 M Reagent, 0.5 M SO_4, 0.3 M NO_3, 25°C
● 0.1 M Reagent, 0.5 M SO_4, 0.05 M NO_3, 27°C
◑ 0.03 M Reagent, 1.0 M SO_4, 0.3 M NO_3, 25°C

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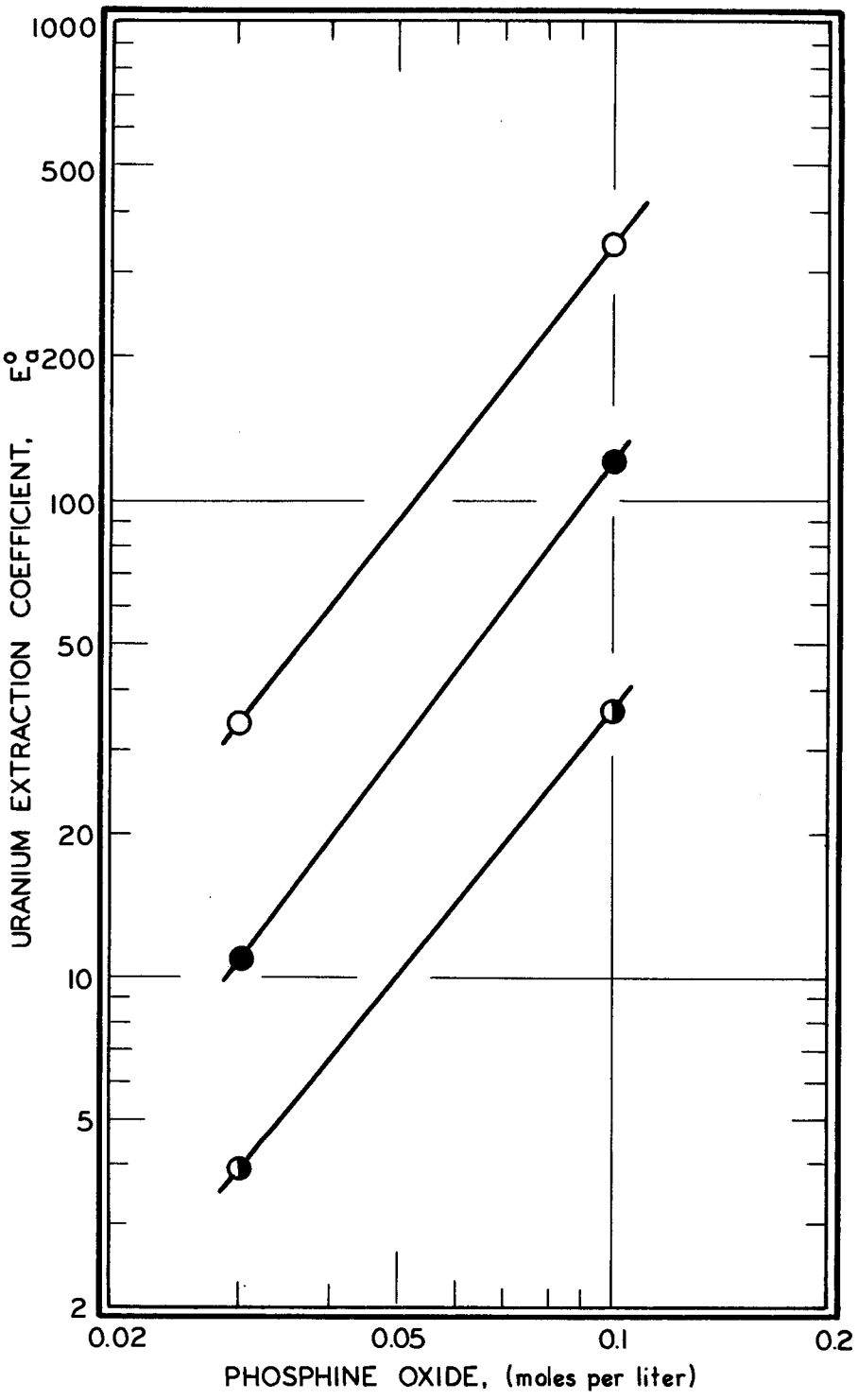

Figure 12

URANIUM EXTRACTION FROM SULFATE-NITRATE SOLUTION

EFFECT OF PHOSPHINE OXIDE CONCENTRATION

Tridecylphosphine Oxide in Kerosene
0.004 M U(VI), Phase Ratio 1, 25°C

○ 1.0 M SO_4, 1.2 M NO_3, pH 1.0
● 0.5 M SO_4, 0.3 M NO_3, pH 1.1
◑ 1.0 M SO_4, 0.3 M NO_3, pH 1.0

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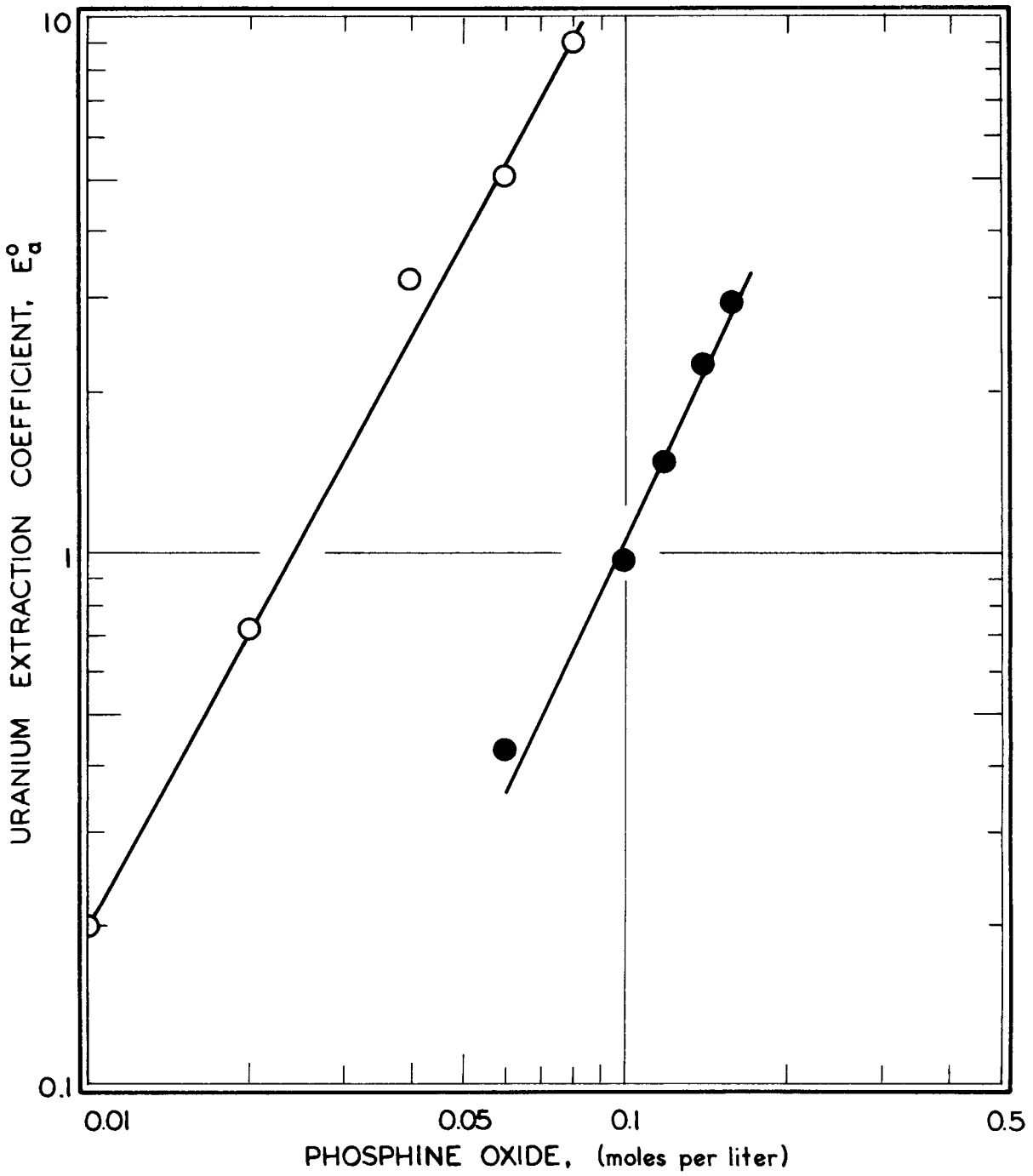

Figure 13

URANIUM EXTRACTION FROM SULFATE-NITRATE SOLUTION

EFFECT OF PHOSPHINE OXIDE CONCENTRATION

Tridecylphosphine Oxide (Batch A) in Carbon tetrachloride
0.004 M U(VI), 0.3 M NO_3^-, pH 1.1
Phase Ratio 1, Room Temperature

○ 0.5 M SO_4 ● 1.7 M SO_4

Table 10

EFFECT OF URANIUM CONCENTRATION ON EXTRACTION FROM SULFATE-NITRATE SOLUTIONS

0.5 M SO_4
0.3 M NO_3
0.1 M Tridecylphosphine Oxide, No. 292, in kerosene
Agitation - 10 minutes (wrist-action shaker)

Initial U (Aq) M	Phase Ratio a/o	Initial pH	Temp. °C	Uranium Distribution g/l		Extraction Coefficient[a] E_a^o	Est'd. Free Reagent[b] M	Calc'd. E_a^o for 0.1 M Free Reagent, 25°C, 0.5 M SO_4, 0.3 M NO_3, pH 1.1[b,c]
				Aq	Org			
0.004	1	1.1	25	0.0098	0.998	102	0.092	120
0.004	20	1.1	28	0.62	6.9	11	0.042	90[d]
0.1	1	1.0	25	12.7	~10	~0.8	e	---
0.1	20	1.0	25	22.5	~10	~0.4	e	---

a) Extraction coefficient affected by loading.

b) Calculated on basis of a combining ratio of 2 molecules of reagent per uranium.

c) E_a^o for 0.1 M free reagent $= \dfrac{(E_a^o \text{ found})}{\left(\dfrac{\text{M Free Reagent}}{0.1}\right)^2}$

d) Calculated E_a^o = 65 at 28°C corrected to 25°C by means of Figure 18.

e) Not calculated, extremely sensitive to uranium concentration in organic phase.

Table 11

EXTRACTION FROM PHOSPHATE-NITRATE SOLUTIONS

0.004 M Uranium(VI)
0.1 M Tridecylphosphine Oxide, No. 292, in kerosene

Phase Ratio, aqueous/organic = 1
Agitation - 10 minutes (wrist-action shaker)
Temperature = 27°C

Phosphate M	Nitrate M	Initial pH	E_a^o
0.4	0.1	1.1	7
	0.3	0.5	75
		1.2	15
	1.2	0.6	130
		1.0	70
1.4	0.1	1.0	0.5
	0.3	1.1	1.2
		2.2	0.1
	1.2	1.1	3
		2.1	0.3

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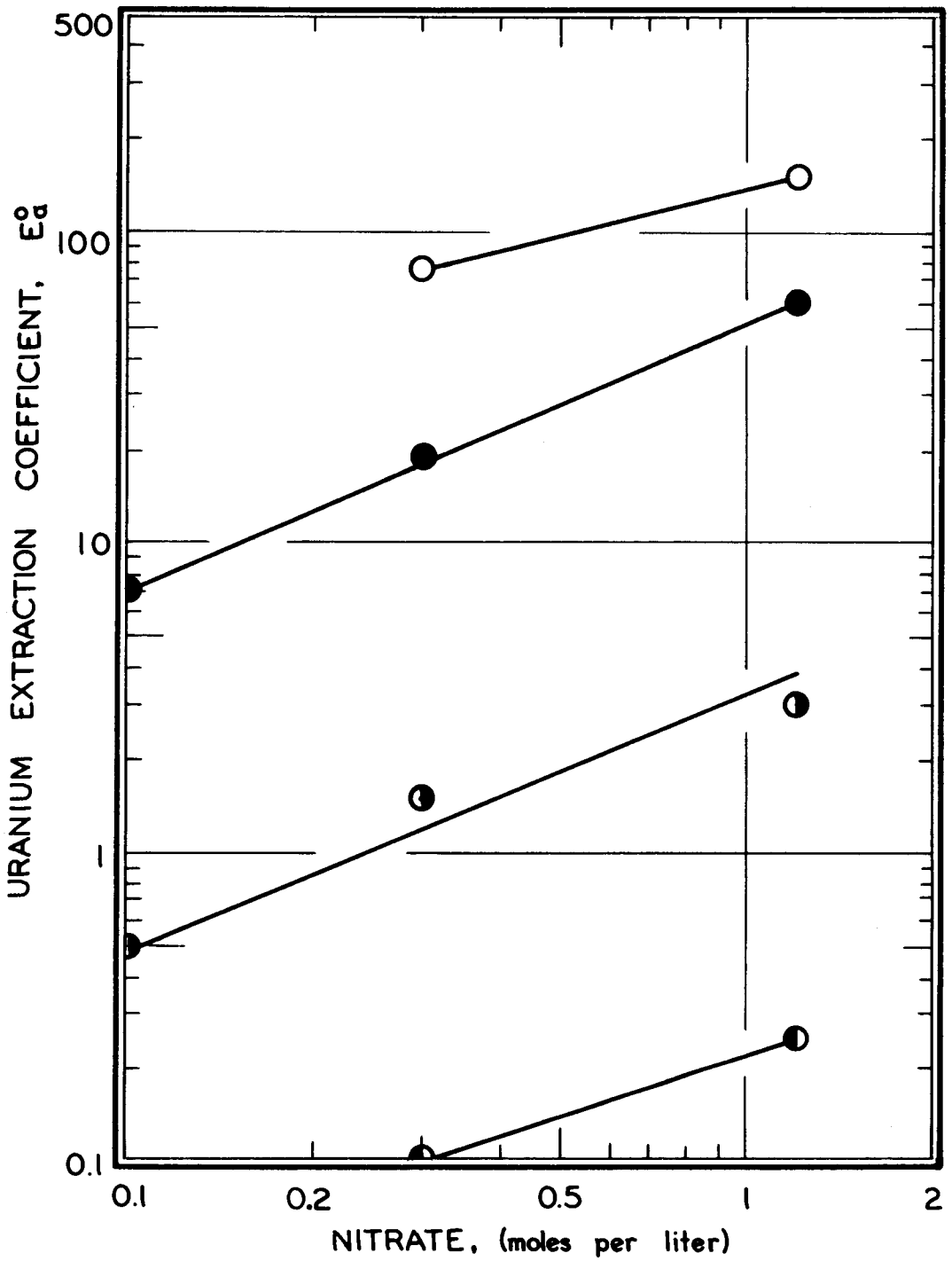

Figure 14

URANIUM EXTRACTION FROM PHOSPHATE-NITRATE SOLUTION

EFFECT OF NITRATE CONCENTRATION

0.1 M Tridecylphosphine Oxide (Batch 292) in Kerosene
0.00$\overline{4}$ M U(VI), Phase Ratio 1, 27°C

○ 0.4 M PO_4, pH 0.5
● 0.4 $\overline{M}$ PO_4, pH 1.1
◑ 1.4 M PO_4, pH 1.0
◐ 1.4 $\overline{M}$ PO_4, pH 2.2

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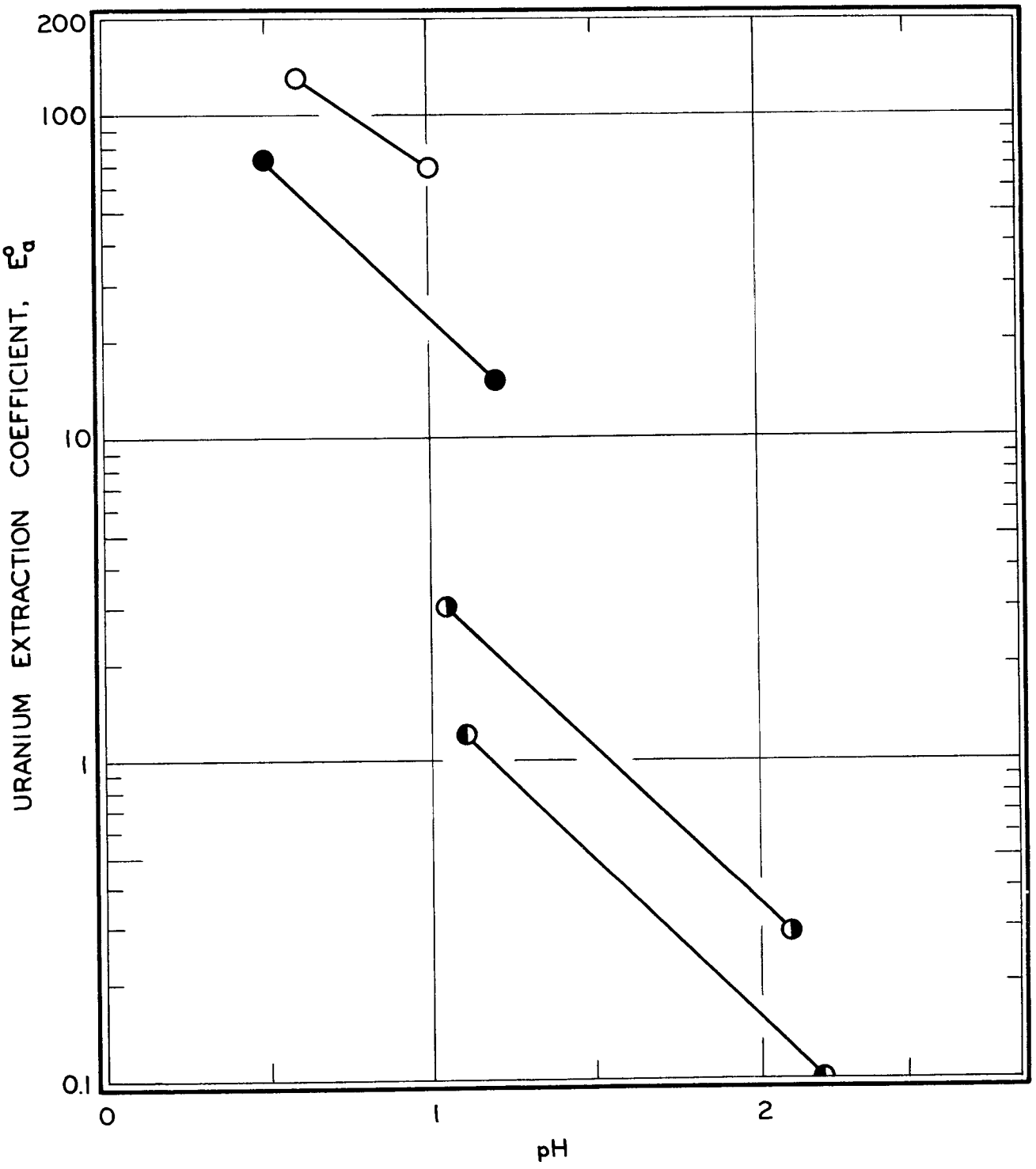

Figure 15

URANIUM EXTRACTION FROM PHOSPHATE-NITRATE SOLUTION

EFFECT OF pH LEVEL

0.1 M Tridecylphosphine Oxide (Batch 292) in Kerosene
0.00$\overline{4}$ M U(VI), Phase Ratio 1, 27°C

○ 0.4 M PO_4, 1.2 M NO_3
● 0.4 $\overline{M}$ PO_4, 0.3 $\overline{M}$ NO_3
◑ 1.4 M PO_4, 1.2 M NO_3
◐ 1.4 $\overline{M}$ PO_4, 0.3 $\overline{M}$ NO_3

(from data of Table 11). Again, the extraction decreased with increase of pH, and the rate of decrease in the range from pH 1 to pH 2 was more severe than in the systems described above.

Effect of Phosphine Oxide Concentration

Extractions at several phosphine oxide concentrations in carbon tetrachloride are plotted in Figure 16, showing that the uranium extraction coefficients increased approximately as the square of the reagent concentration (cf. p. 84).

Effect of Uranium Concentration

The uranium extraction isotherm for 0.4 M phosphate, 0.3 M nitrate solution, pH 1.1, is presented on Table 12. The coefficients corresponding to 0.1 M free reagent, 25°C, were calculated as above (p. 9). The solid line of Figure 17 represents the theoretical extraction isotherm calculated for a coefficient of 20; the points give the equilibrium uranium concentrations actually found (corrected to 25°C). The importance of nitrate is again demonstrated by the fact that this coefficient is more than ten-fold greater than the coefficient from 0.4 M phosphate solution with six times as high a phosphine oxide concentration in the absence of nitrate (Table 7).

Choice of Diluent

All of the experiments described thus far have been performed using either carbon tetrachloride or kerosene as the organic diluent. These and others are compared in Table 13. The best diluents for use with the tridecylphosphine oxide appear to be the aromatic and the kerosene-range aliphatic hydrocarbons. There is also a correspondence between decreased extraction and greater polar character of the diluent. These trends have also been reported for extractions with tributylphosphate[19].

Effect of Temperature on Extraction

The data of Figure 18 show an inverse relationship between extraction coefficient and temperature, the coefficient in the several solutions tested decreasing by one-half in about a ten degree temperature rise within the range tested. This is considerably higher than the temperature effect noted in experiments with tributylphosphate[20].

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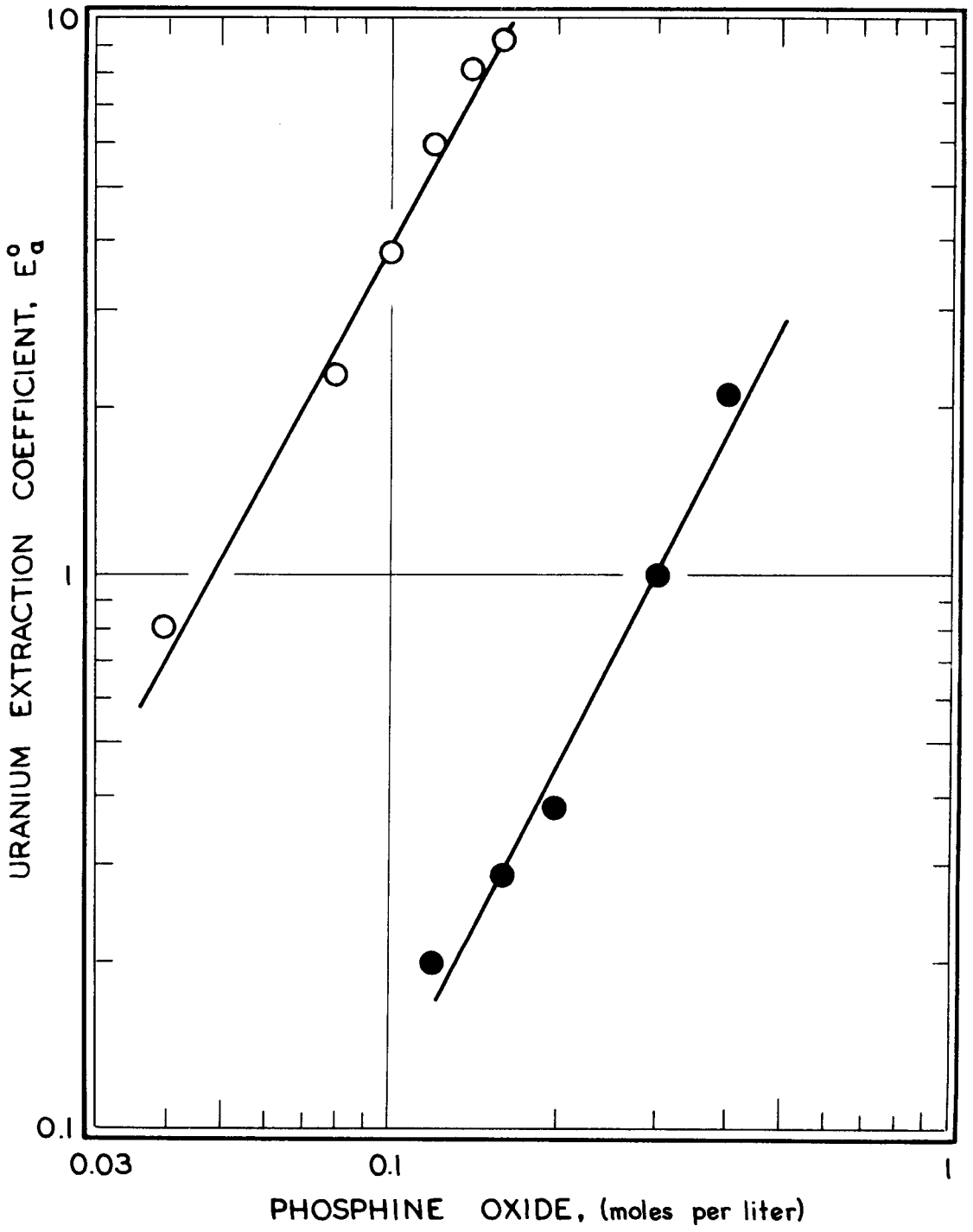

Figure 16

URANIUM EXTRACTION FROM PHOSPHATE-NITRATE SOLUTION

EFFECT OF REAGENT CONCENTRATION

Tridecylphosphine Oxide (Batch A) in Carbon tetrachloride
0.004 M U(VI), 0.3 M NO_3, pH 1.1
Phase Ratio 1, Room Temperature

○ 0.4 M PO_4 ● 1.4 M PO_4

Table 12

EFFECT OF URANIUM CONCENTRATION ON EXTRACTION FROM PHOSPHATE-NITRATE SOLUTIONS

0.4 M PO_4
0.3 M NO_3
0.1 M Tridecylphosphine Oxide, No. 292, in kerosene
Agitation - 10 minutes (wrist-action shaker)

Initial U (Aq) M	Phase Ratio a/o	Initial pH	Temp. °C	Uranium Distribution g/l Aq	Uranium Distribution g/l Org	Extraction Coefficient[a] E_a^o	Est'd. Free Reagent[b] M	Calc'd. E_a^o for 0.1 M Free Reagent, 25°C, 0.4 M PO_4, 0.3 M NO_3, pH 1.1[b,c]
0.004	1	1.2	27	0.067	0.920	15	0.092	22[d]
0.019	1	1.1	25	0.365	4.17	11	0.065	29[e]
0.004	20	1.1	28	0.71	4.43	6.2	0.063	20[f]
0.019	20	1.1	25	4.04	~8	~2	~0.033	~19

a) Distribution coefficient affected by loading.

b) Calculated on basis of a combining ratio of 2 molecules of reagent per uranium.

c) E_a^o for 0.1 M reagent $= \dfrac{(E_a^o \text{ found})}{\left(\dfrac{\text{M free reagent}}{0.1}\right)^2}$

d) Calculated E_a^o = 18 at pH 1.2 and 27°C. Corrected to pH 1.1 and 25°C by means of Figures 15 and 18.

e) Calculated E_a^o = 26 at 0.26 M nitrate (final). Corrected to 0.3 M NO_3 (final) by means of Figure 14.

f) Calculated E_a^o = 16 at 28°C. Corrected to 25°C by means of Figure 18.

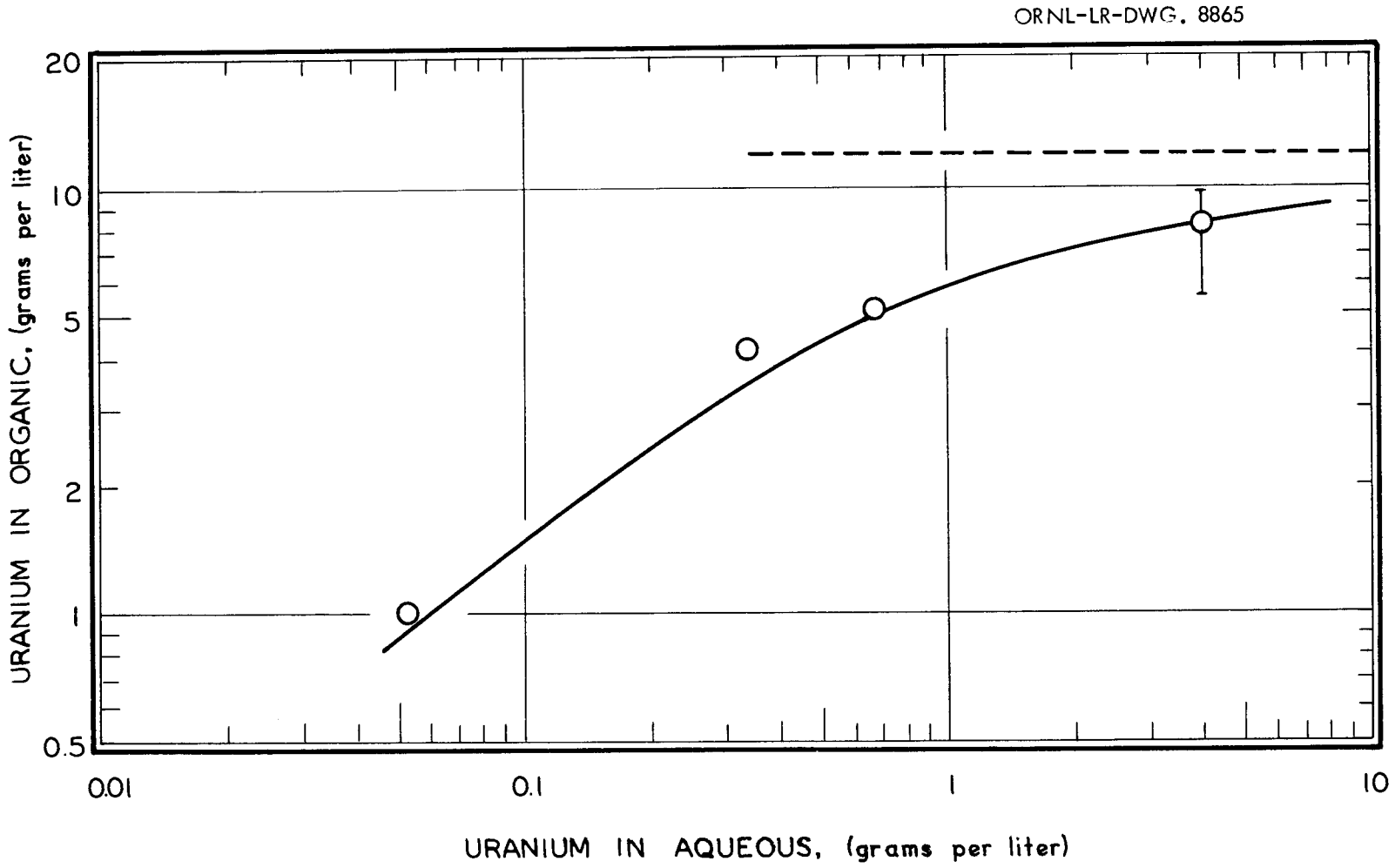

Figure 17

URANIUM EXTRACTION ISOTHERM FROM PHOSPHATE-NITRATE SOLUTION

0.1 M Tridecylphosphine Oxide, Batch 292, Kerosene Diluent
0.4 M PO_4, 0.3 M NO_3, pH 1.1, 25°C

Dashed line represents theoretical loading limit (p.84)
Solid line drawn for theoretical $E_a^o = 20$ (p. 9)

Table 13

CHOICE OF ORGANIC DILUENT FOR URANIUM EXTRACTIONS

0.004 M U(VI)
0.03 M Tridecylphosphine Oxide, No. 292
0.3 M NO_3, 0.5 M SO_4
Initial pH = 1.05
Phase Ratio, aqueous/organic = 1
Agitation - 10 minutes (wrist-action shaker)
Temperature = 29°C

Organic Diluent	E_a^o
Kerosene	7.0
Benzene	7.0
Toluene	6.4
Carbon tetrachloride	4.0
Xylene*	3.5
Di-n-butylether	1.8
Hexone	1.2
Nitrobenzene	0.8
n-Butylacetate	0.2
Isoamyl alcohol	<0.01

*Baker and Adamson reagent xylene, boiling range 137-140°C.

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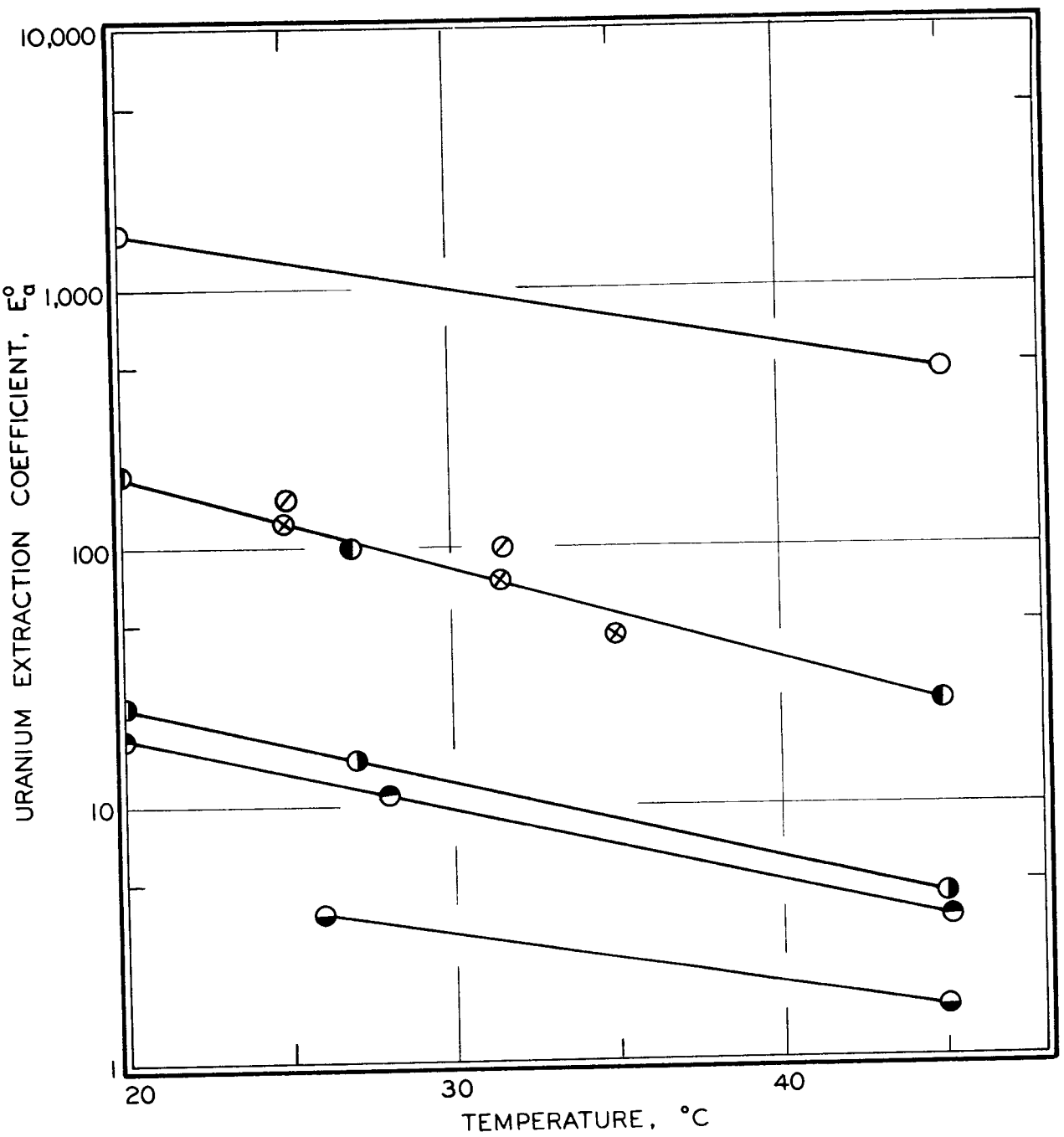

Figure 18

EFFECT OF TEMPERATURE ON URANIUM EXTRACTION

0.004 M U(VI), Phosphine Oxide in Kerosene
10 minutes Agitation (wrist-action)

Tridecylphosphine Oxide (Batch 292), Phase Ratio = 1

○ 0.1 M Reagent, 0.1 M NO_3, pH 1.02
◐ 0.1 M Reagent, 0.5 M SO_4, 0.3 M NO_3, pH 1.1
◑ 0.1 M Reagent, 0.5 M PO_4, 0.3 M NO_3, pH 1.2
◓ 0.05 M Reagent, 0.5 M Cl, pH 0.7
◒ 0.3 M Oxide, 0.5 M H_2SO_4, pH 0.32

0.1 M Trioctylphosphine Oxide (Batch B-1) 0.5 M SO_4, 0.3 M NO_3, pH 1.1

⊘ Phase Ratio, aqueous/organic = 1 ⊗ Phase Ratio, aqueous/organic = 2

Effect of Temperature on the Solubility of Phosphine Oxide

The solubility of tri-n-octylphosphine oxide, Batch B-1, in kerosene increased from about 0.2 M at 18° to about 0.5 M at 32°C, as shown on Figure 19. There was some tendency toward supersaturation at the higher temperatures.

A qualitatively similar temperature dependence was observed with tri-n-decylphosphine oxide in kerosene.

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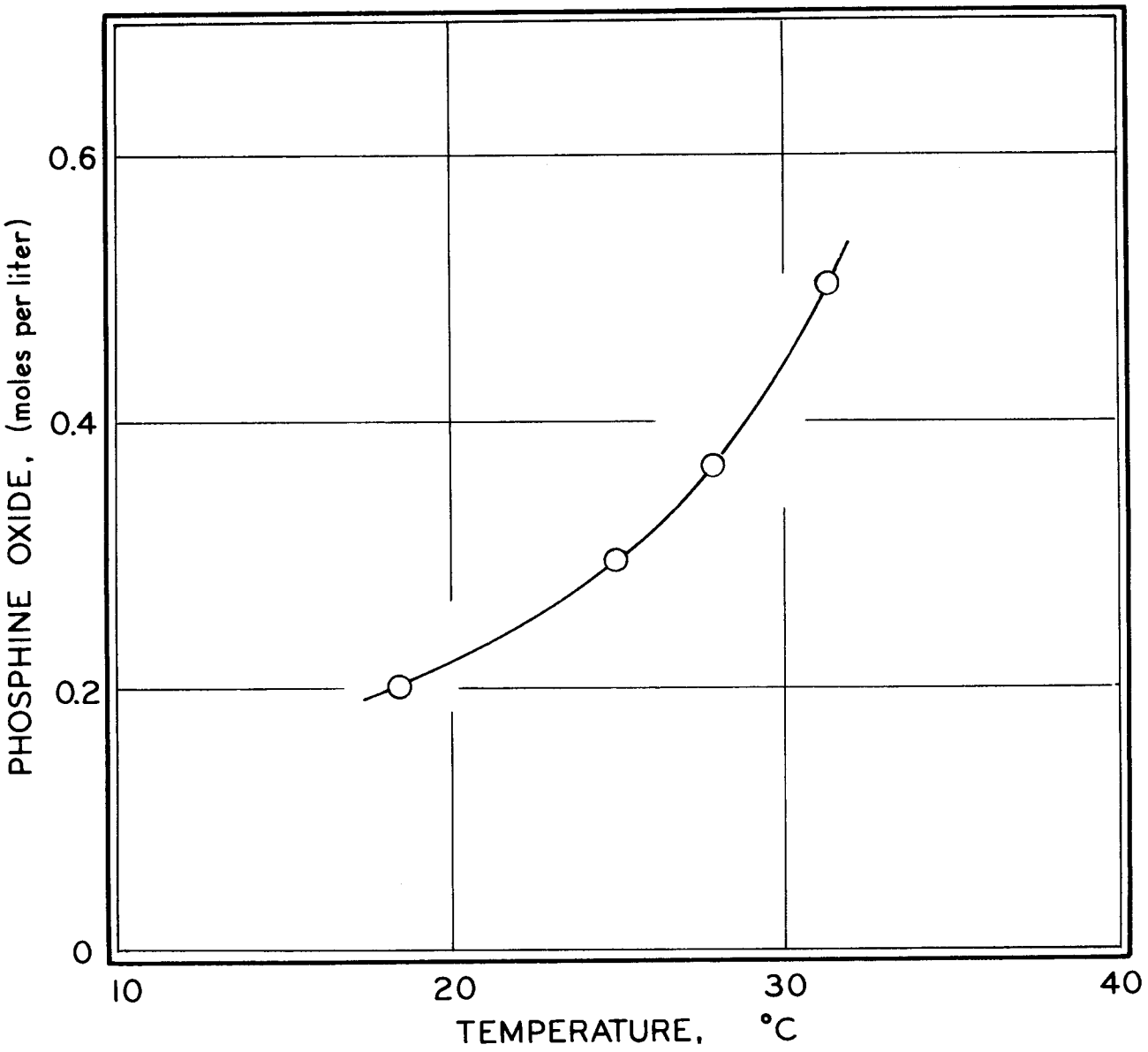

Figure 19

EFFECT OF TEMPERATURE ON SOLUBILITY OF PHOSPHINE OXIDE

Trioctylphosphine Oxide (Batch B-1) in Kerosene

EXTRACTION OF MINERAL ACIDS

The phosphine oxides will extract mineral acids, the extraction ability, similar to that for uranium, being higher under comparable conditions than that reported for tributylphosphate.[11,21] As a comparison under the test conditions used in this investigation, acid extractions with 0.1 M tributylphosphate and 0.1 M tridecylphosphine oxide in kerosene have been made from 0.58 and 3.0 M nitric acid solutions. The respective acid concentrations obtained in the organic phases were 0.004 M and 0.06 M in the tributylphosphate, and 0.07 M and 0.1 M in the phosphine oxide. In the latter case, the concentration of nitric acid in the phosphine oxide phase was approaching saturation loading.

The theoretical combining ratio for nitric acid and tributylphosphate has been reported to be 1:1.[21,22] Further unreported data[23] indicate that it is possible to extract nitric acid from concentrated solutions in an amount somewhat greater than the 1/1 loading ratio with 0.2 M tributylphosphate and still greater with 0.2 M tri(2-ethylhexyl)phosphate (e.g., 1.032 and 1.055). The reason for this increased extraction is not known although it has been established that reagent degradation is not responsible.

The phosphine oxides (like tributylphosphate) extract nitric acid most effectively and hydrochloric, sulfuric and phosphoric acids to lesser extents. The data are shown in Table 14. From pure solutions, the amount of acid extracted reached (e.g.) 0.2 equivalent per mole of phosphine oxide when the aqueous concentration was 0.1 M for nitric acid or 2 M for hydrochloric, sulfuric or phosphoric acid. Again, similar to tributylphosphate, the limiting extraction from higher concentrations of the acids was somewhat greater than one equivalent of acid for each mole of phosphine oxide.

Table 14

EXTRACTION OF MINERAL ACIDS WITH TRIDECYL- AND TRI(2-ETHYLHEXYL)PHOSPHINE OXIDES

Oxide = 0.1 M
Organic Diluent = Kerosene
Contact Time = 2 min.
Room Temperature

Mineral Acid	Conc. (M)	Phase Ratio a/o	Extraction into Organic Phase: Tridecylphosphine Oxide, Batch A g/l	Tridecylphosphine Oxide, Batch A Moles Acid/ Mole Phosphine Oxide	Tri(2-ethylhexyl)phosphine Oxide, Batch D g/l	Tri(2-ethylhexyl)phosphine Oxide, Batch D Moles Acid/ Mole Oxide
HNO_3	0.3	1/1	----	----	1.13	0.56
	0.58	"	4.35*	0.68	----	----
	1.45	"	5.75*	0.91	----	----
	3	"	6.36*	1.01	5.7	0.91
	6	"	----	----	6.5*	1.03
		5/1	7.14*	1.14	----	----
HCl	6	1/1	2.62	0.73	3.2	0.89
	9	"	4.65*	1.30	----	----
H_2SO_4	3	1/1	2.43	0.25	----	----
	6	"	5.5*	0.56	2.9	0.30
H_3PO_4	3	1/1	2.73*	0.28	----	----
	6	"	5.4*	0.55	----	----

*Based on material balance of acid in aqueous and organic phases; other results based on analysis of aqueous phase only.

EXTRACTION OF IRON, ALUMINUM, AND THORIUM

Most uranium-bearing process solutions as encountered from various sources contain, in addition to the uranium values, other metal ions which are frequently at concentrations higher than the uranium itself. Consequently, if a successful separation of uranium from these liquors is to be achieved by solvent extraction techniques, the extractant used must have a higher (preferably much higher) extraction coefficient for uranium than for the other, unwanted materials.

Table 15 lists coefficients for the extraction of iron and aluminum by trioctylphosphine oxide in kerosene from a series of acidic solutions. The corresponding uranium coefficients are included for comparison, showing major differences favorable to the selective extraction of uranium.

A few tests have been made of the extraction of thorium from sulfate solutions. The extractions were low, the coefficients with 0.1 M tridecylphosphine oxide in kerosene being less than 1 from a solution of thorium nitrate (0.02 M) in 0.1 M sulfuric acid (and less than 0.1 from a monazite sand leach liquor containing 0.1 M excess sulfuric acid), even with nitric acid added up to 1.5 M HNO_3. Since a coefficient much higher than 100 would be expected from a corresponding uranium nitrate-sulfate solution (cf. Table 9), efficient separation of uranium from thorium in such a solution may be expected. It should be noted that these results with 0.1 M phosphine oxide in solutions containing sulfate do not contradict the reported high extraction of thorium nitrate with 0.75 M tributylphosphine oxide.(11)

The extraction of vanadium with phosphine oxides is discussed in the following section. Although the extraction of other metal ions has not yet been tested systematically, it might be expected that the relative difference in extraction coefficients for other metals would be qualitatively similar to those experienced with tributylphosphate.(24)

Table 15

URANIUM, IRON AND ALUMINUM EXTRACTION COEFFICIENTS FROM ACID SOLUTIONS WITH TRIOCTYLPHOSPHINE OXIDE

Oxide = 0.2 M Trioctylphosphine Oxide (Batch B-1) in kerosene
Iron and Aluminum = 0.1 M
Phase Ratio, aqueous/organic = 5/1
Room Temperature

Acid Solution	E_a^o Iron	Aluminum	Uranium
Chloride			
4 M HCl	---*	$<4\times10^{-4}$	10^4
0.5 M Cl, pH = 1	0.4**	8×10^{-4}	260
Sulfate			
4 M H_2SO_4	0.007	7×10^{-4}	10
0.5 M SO_4, pH = 1	0.006	4×10^{-4}	0.6
Nitrate			
4 M HNO_3	0.02	$<4\times10^{-4}$	$>10^4$
0.5 M NO_3, pH = 1	0.2	2×10^{-3}	$>10^3$
Phosphate			
4 M H_3PO_4	----	2×10^{-3}	$\sim$0.01
0.7 M PO_4, pH = 1	----	5×10^{-4}	$\sim$0.1

*Three phases formed, with about 20% of the total iron reporting in the "third" phase and about 1% in the "normal" organic phase.

**About 10% of the iron was extracted into the organic phase.

EXTRACTION OF VANADIUM

Since vanadium is frequently associated in nature with uranium, its extraction behavior has also been briefly studied. The following experiments with tridecyl- and trioctylphosphine oxides indicate the effects of reagent concentration, added anions, diluent, and pH levels upon the extraction and stripping of vanadium in the oxidized (+5) and reduced (+4) state.

Extraction of Vanadium(V) from Sulfate Solutions

Effect of Nitrate and pH

Extractions of vanadium(V) from 0.5 M sulfate solution with and without added nitrate are shown in Table 16. In the absence of nitrate, extraction coefficients with 0.2 M trioctylphosphine oxide were far below unity. Addition of nitrate increased the extraction, the coefficients reaching about 5 at pH 1.0 and above 10 at pH 1.5 and pH 2.0 when the nitrate concentration was 1 M. However, at pH 2.5, the coefficients leveled off at about 1 throughout the range from 0.2 to 1 M nitrate. Extractions by 0.4 M tridecylphosphine oxide increased with nitrate in the same way as the extractions by trioctylphosphine oxide at pH 1, with higher coefficients throughout corresponding to the higher reagent concentration.

In no instance did the vanadium extraction coefficient approach the magnitude of the uranium coefficients obtained under corresponding testing conditions.

Chloride

Additions of chloride up to concentrations of 1 M did not increase extractions of vanadium by 0.2 M trioctylphosphine oxide in kerosene, from solutions containing 0.004 M vanadium(V) and 0.5 M sulfate at pH 1.5.

Effect of Phosphine Oxide Concentration

The effect of trioctyl- and tridecylphosphine oxide concentrations on the extraction of vanadium from sulfate solutions has been studied both in the presence and absence of nitrate. The results from these experiments appear in Table 17 and Figure 20. Although the extraction coefficients

Table 16

EFFECT OF NITRATE AND pH ON EXTRACTION OF VANADIUM(V)

From 0.5 M sulfate solution
Room Temperature

Nitrate M	0.2 M Oct_3PO[a] Initial pH = 1.0	1.5	2.0	2.5	0.4 M Dec_3PO[b] Initial pH = 1.0
	Extraction Coefficients, E_a^o				
0	<0.1	0.1	0.1	0.2	0.4
0.05	0.9	0.6	0.8	0.5	---
0.1	---	---	---	---	(3.5)
0.2	2.0	2.0	2.0	1.1	(6.3)
0.3	2.5	4.7	3.2	1.1	(10)
0.5	5.0	6.8	3.2	0.9	---
1.0	4.3	>10	>10	1.1	---

a) 0.2 M Trioctylphosphine oxide (Batch B-1) in kerosene; phase ratio $1^a:1^o$; initial vanadium concentration 0.004 M.

b) 0.4 M Tridecylphosphine oxide (Batch A) in kerosene; phase ratio $2^a:1^o$; initial vanadium concentration 0.04 M.

Table 17

EFFECT OF PHOSPHINE OXIDE CONCENTRATION ON EXTRACTION OF VANADIUM(V)

From 0.5 M sulfate solution
Room Temperature

Phosphine Oxide:	Trioctyl[a]	Trioctyl[a]	Tridecyl[b]
Initial Vanadium Conc.:	0.004 M	0.004 M	0.04 M
Nitrate Conc.:	None	0.15 M	0.16 M
Initial pH:	2.0	1.5	1.0
Phosphine Oxide Conc., M	Extraction Coefficients, E_a^o		
0.1	---	---	0.7
0.2	0.1	(1.5)	1.6
0.3	0.2	4.0	3.4
0.4	---	---	5.1
0.6	0.1	20	---

a) Trioctylphosphine oxide, Batch B-1, in kerosene.

b) Tridecylphosphine oxide, Batch A, in kerosene.

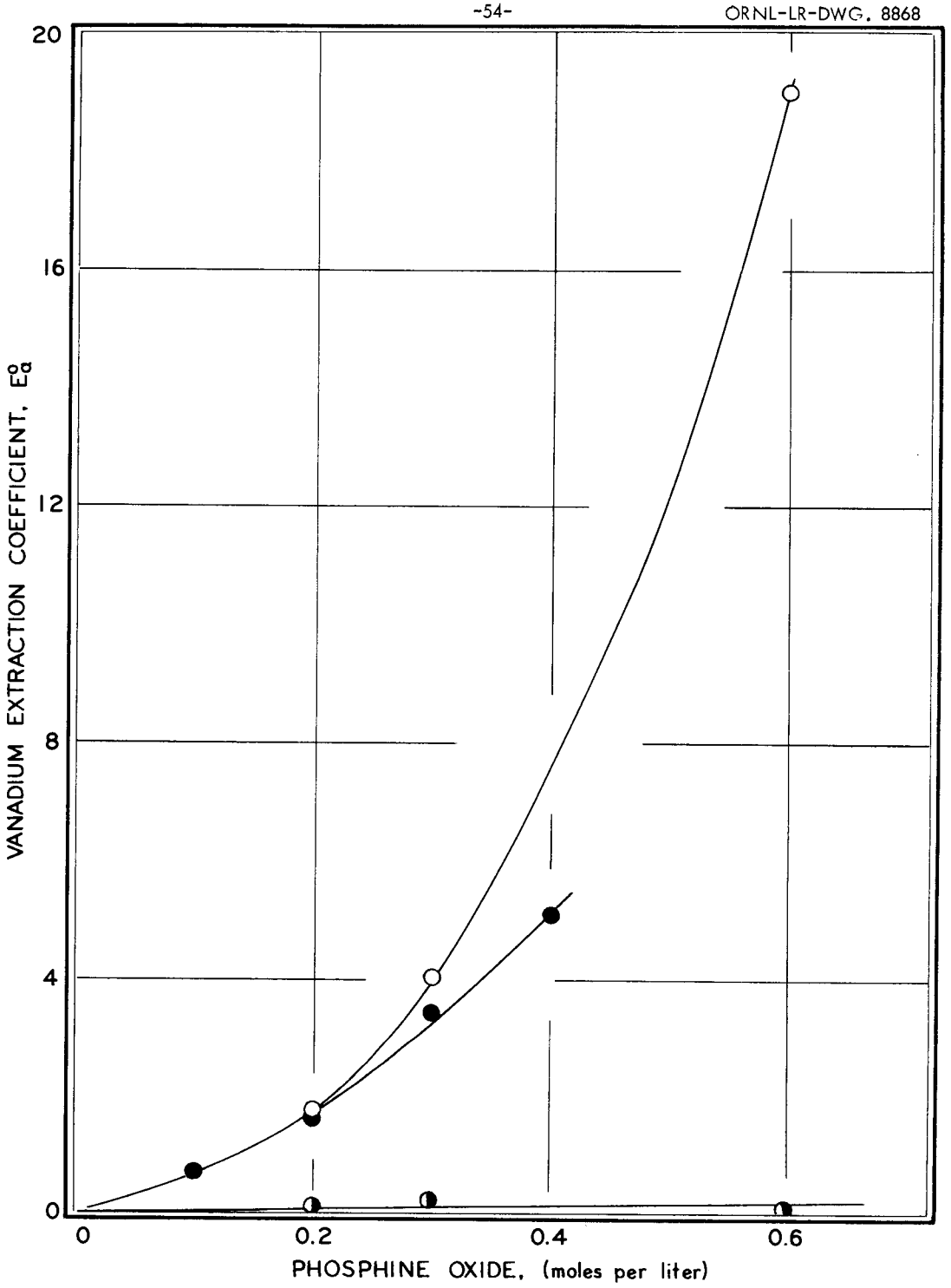

Figure 20

VANADIUM(V) EXTRACTION FROM SULFATE SOLUTION

EFFECT OF REAGENT CONCENTRATION

0.5 M SO_4, Room Temperature

○ Trioctylphosphine Oxide (Batch B-1) in Kerosene
0.004 M V(V), 0.15 M NO_3, pH 1.5, Phase Ratio 1

● Tridecylphosphine Oxide (Batch A) in Kerosene
0.04 M V(V), 0.16 M NO_3, pH 1.0,
Aqueous/Organic Phase Ratio 2

◑ Trioctylphosphine Oxide (Batch B-1) in Kerosene
0.004 M V(V), pH 2.0, Phase Ratio 1

increased with phosphine oxide concentration when nitrate was present, the extractions remained low in its absence with phosphine oxide concentrations up to 0.6 M.

Choice of Diluent

Extraction coefficients from sulfate solutions with trioctylphosphine oxide dissolved in several diluents are reported in Table 18. In general, the diluents used show the same relative performance for both uranium and vanadium extractions (compare Table 18 and Table 13).

Extraction of Vanadium(IV) from Sulfate Solutions

As shown by the results in Table 19, only negligible quantities of vanadium(IV) were extracted from 0.5 M sulfate solution, in the pH range 1-3, by tridecylphosphine oxide in kerosene. The addition of sodium nitrate to this solution at pH 1.5 up to a concentration of 1 molar caused no significant increase in vanadium extraction.

Stripping of Vanadium

Several reagents have been briefly tested as to their ability to strip vanadium from the pregnant organic solvent. For each of these tests an organic solution was used which contained 1.32 grams of vanadium(V) per liter of 0.1 M tridecylphosphine oxide in kerosene. This solution was prepared by prior extraction from a solution containing 0.5 M sulfate and 0.6 M nitrate at a pH of 1.5.

As in the case with uranium (see below), it is possible to strip the vanadium with either acidic or alkaline reagents, as shown in Table 20. Moderately effective stripping was obtained with dilute hydrochloric acid, sulfuric acid, and acidified solutions of sodium chloride and sodium sulfate. More effective stripping was obtained with a dilute solution of sodium carbonate.

Since reduced vanadium was not extracted, an aqueous solution of a reducing agent may be expected to strip the vanadium. Solutions of oxalic acid were tested (Table 20). After contact for several hours (without agitation) at room temperature, a 0.25 M oxalic acid solution had reduced and stripped all the vanadium, and a more dilute solution (10% more than the amount theoretically required to reduce all the vanadium to V(IV)) had stripped 70%.

Table 18

CHOICE OF ORGANIC DILUENT FOR VANADIUM EXTRACTIONS

Vanadium = 0.004 M

Oxide = 0.2 M Trioctylphosphine Oxide (Batch B-1)

Nitrate = 0.5 M

Initial pH = 1.5
Phase Ratio, aqueous/organic = 1, except as noted.
Room Temperature

Organic Diluent	Extraction Coefficient, E_a^o
Benzene	10*
Kerosene	7
Hexone	6
Amsco D-95	3*
Carbon tetrachloride	3
Isopropyl ether	1
Isoamyl alcohol	0.1

*Phase ratio, aqueous/organic = 5.

Table 19

THE EFFECT OF pH UPON THE EXTRACTION OF REDUCED VANADIUM(IV) WITH TRIDECYLPHOSPHINE OXIDE

Vanadium * = 0.02 M

Oxide = 0.2 M Tridecylphosphine Oxide (Batch A)

Organic Diluent = Kerosene

Sulfate = 0.5 M

Phase Ratio, aqueous/organic = 2
Room Temperature

Initial pH	E_a^o
1	0.07
1.5	0.08
2	0.05
3	0.02

*Reduced to V(IV) with Na_2SO_3.

Table 20

STRIPPING OF VANADIUM FROM PHOSPHINE OXIDES

Organic phase = 0.1M Tridecylphosphine Oxide (Batch A) in kerosene, containing 1.32 g vanadium(V) per liter.
Phase ratio, aqueous/organic = 1.
Room temperature.

Stripping Agent	Stripping Coefficient S_o^a	% Vanadium Stripped
1M H_2SO_4	6	86
0.5M H_2SO_4	3	77
0.32M Na_2SO_4 + 0.18M H_2SO_4	4	80
2M HCl	3	73
1M HCl	3	72
0.9M NaCl + 0.1M HCl	2	71
0.5M Na_2CO_3		94
0.25M Oxalic Acid[a]		>99
0.0143M Oxalic Acid[a,b]		70

a) Contact with oxalic acid solution for several hours without agitation.

b) 10% in excess of the amount of oxalic acid theoretically required to reduce all the vanadium to V(IV).

EXTRACTION OF URANIUM FROM LEACH LIQUORS

The experiments which are described in the following sections were designed primarily to give general additional information as to the properties of the phosphine oxides and are not detailed enough to delineate exact processing procedures. In view of uncertainties as to eventual reagent supply and cost, it would be unrealistic at this time to consider more than potential applications. The tests in conjunction with those described previously do serve, however, to demonstrate the versatility of the phosphine oxides as extractants.

For purposes of the following discussion, several uranium raw materials process acid liquors have been classed according to the mineral acid or acids used to leach the ore, the soluble anions present in the ore, the other metals which must be recovered, and the uranium concentration level. Table 21 contains analyses of the several liquors, synthetic and actual, which were used for testing in the following section.

Nitrate-Phosphate Liquor from Leached Zone (TVA)

Sometime ago at the request of the AEC Raw Materials Division, a comparison was made of the effectiveness of some available and potentially available reagents for the extraction of uranium from liquors of the type obtained in the TVA process for utilizing the Florida Leached Zone.[12] About thirty reagents were screened in simple extraction tests from synthetic and actual liquors, ten of which showed sufficient extraction to warrant further testing. Included among the latter were tri(2-ethylhexyl)phosphine oxide and tributylphosphate.

The tri(2-ethylhexyl)phosphine oxide used in these tests was found, subsequently, to contain a neutral uranium-extracting impurity, possibly a dialkylphosphine oxide (or dialkylphosphinous acid). After most of this material had been removed, uranium extractions were lower than had been obtained with the original product (see below), but the resulting extraction coefficients were still high enough to maintain interest in this type of compound for Leached Zone application. Several additional phosphine oxides have since been tested and the results are compared in Table 22. The results show that the normal-alkyl compounds are more effective extractants than the 2-ethylhexyl compound from this liquor. This is in accordance with the data presented

Table 21

ANALYSIS OF LIQUORS (g/l)

	Phosphate-Nitrate			Sulfate-Chloride[1]		Sulfate		
						Marysvale[2]		Green[3]
	Synthetic	TVA-1110	TVA-1111	A	B	1	2	Sludge
U	0.125	0.125	0.110	2.8	1.18	1.27	1.20	23.2
V	-----	-----	-----	2.27	1.34	----	----	6.3
Fe	1.3	1.3	1.2	0.97	1.0	5.8	6.0	4.9
Al	35	39	32	1.65	0.41	3.5	3.4	4.0
Ca	15	18	15	----	----	----	----	0.8
F	-----	-----	-----	----	----	1.7	1.7	----
SO_4	-----	-----	-----	8.8	20	50	50	83
Cl	-----	-----	-----	17	6	----	----	----
PO_4	130	163	120	0.8	----	1.9	2.0	6.4
NO_3	245	290	200	----	----	----	----	----
NH_3	-----	-----	-----	----	----	----	----	5.1
pH		<0	0.1	1.22	1.7	0.8	0.85	0.4

1) Acid liquors from the salt roast-acid leach process.(25)
2) Direct sulfuric acid leach of ore for uranium.
3) Sulfuric acid digest of "green sludge" as conducted in the salt roast-acid leach process.(25)

Table 22

EXTRACTION OF URANIUM FROM

SYNTHETIC PHOSPHATE-NITRATE LIQUOR*

Phase Ratio, aqueous/organic = 3
Room Temperature

0.1 M Trialkylphosphine Oxide in Kerosene	pH	Uranium Extraction Coefficient
2-Ethylhexyl, Batch D	< 0	15
	1	40
n-Octyl, Batch A-1	< 0	150
	1	300
3,5,5-Trimethylhexyl, Batch A	< 0	150
	1	600
n-Decyl, Batch A	<0	90
	1	>1000

*See Table 21 for analysis.

in a previous section of this report suggesting that the structure of the three 2-ethylhexyl groups interferes with the complexing action of the phosphine oxide.

The observed increase in the uranium extraction coefficent with rise in pH is contrary to the pH effect described previously for simple phosphate-nitrate solutions. The effects of pH on the complexing of phosphate by aluminum or calcium may be involved in these extractions to a sufficient extent to account for the difference.

Selective extraction of the uranium in the presence of iron and aluminum has been demonstrated by experiments conducted with tridecylphosphine oxide on a synthetic Leached Zone liquor. The results as summarized in Table 23 show that the ratios of the coefficients for uranium and the contaminants are greater than 10^4.

A comparison of extractions from Leached Zone nitrate liquors with tri(2-ethylhexyl)phosphine oxide and tributylphosphate is shown in Table 24.

Under identical conditions, extractions with the phosphine oxide are considerably higher than those obtained with the tributylphosphate.

Dow Chemical Company in conjunction with the TVA laboratories at Wilson Dam have secured additional information relating to the use of tributylphosphate as an extractant in Leached Zone liquors.[26] In nitrate liquors where the aluminum-calcium ratio is high, low but acceptable coefficients have been obtained with this reagent. However, the Leached Zone ores have a wide spectrum of aluminum-calcium ratios and the tributylphosphate becomes less effective when this ratio decreases. Recent developments indicate that some sulfuric acid may be used to supplement the nitric acid in the leaching step, an additional factor making tributylphosphate less effective.

Comparative extractions by phosphine oxides from these latter varieties of Leached Zone liquors have not been made. From the foregoing discussion, it is apparent, however, that the phosphine oxides should be applicable as extractants over a much wider range of the solution compositions than are the phosphate esters.

Sulfate Liquors from Marysvale Ore

As shown by the results in Table 25, useful and selective extraction of uranium was obtained from synthetic Marysvale

Table 23

EXTRACTION OF URANIUM, IRON AND ALUMINUM

FROM LEACHED ZONE LIQUOR

Reagent - Tridecylphosphine Oxide, Batch A, in kerosene.

Liquor - Synthetic phosphate-nitrate (see Table 21 for composition).

Equal volumes of organic and aqueous phases.

pH < 0

Contact Time = 20 min.

Room Temperature

Conc. Organic Reagent	Extraction Coefficient			Selectivity Factor*	
	U	Fe	Al	Fe	Al
0.05	10	---	.0004	---	10^4
0.10	90	<.001	.0007	10^4	10^5

*Selectivity Factor = $\frac{E^o_{a(\text{uranium})}}{E^o_{a(\text{contaminant})}}$

Table 24

COMPARISON OF EXTRACTION FROM LEACHED ZONE NITRATE LIQUOR WITH TRI(2-ETHYLHEXYL)PHOSPHINE OXIDE AND TRIBUTYLPHOSPHATE

Organic Diluent = Kerosene
Phase Ratio = 1/1
Room Temperature

Reagent Conc. (M)	pH	Liquor	Extraction Coefficient: Tri(2-ethylhexyl)-phosphine Oxide Batch D	Tri(2-ethylhexyl)-phosphine Oxide Batch C*	Tributyl-phosphate
0.05	<0	TVA-1110**	7	10	0.3
0.10	"	"	20	40	1.3
.2	"	"	--	--	2.2
.4	"	"	--	--	10
.6	"	"	--	--	15
1.0	"	"	--	--	17
0.05	0.1	TVA-1111**	20	40	0.06
"	1.1	"	--	55	0.01
0.10	0.1	"	65	65	0.24
"	1.1	"	--	120	0.04

*This is the reagent used for the tests reported in Y-B34-3 (Reference 12). The impurity was found to be 12% calculated as $R_2P(=O)OH$ (phosphinic acid). Batch D contained ~3% acidic material calculated as phosphinic acid.

**See Table 21 for analysis.

Table 25

EXTRACTION OF URANIUM, IRON AND ALUMINUM

FROM SULFATE LIQUOR CONTAINING NO VANADIUM

(Marysvale 1)[a]

Phase Ratio, aqueous/organic = 1
Diluent = Kerosene
Contact Time = 2 min.
Room Temperature

Phosphine Oxide	Conc. (M)	Extraction Coefficients			Selectivity Factor[b]	
		U	Fe	Al	Fe	Al
Tridecyl Batch A	0.4	4.6	---	---	---	---
	0.2	0.7	---	---	---	---
	0.1	0.1	---	---	---	---
Trioctyl Batch A-2	0.6	10	0.035	<.004	10^2	10^3
	0.3	3	0.003	<.003	10^3	10^3

a) See Table 21 for composition.

b) Selectivity Factor = $\frac{E^o_{a(\text{uranium})}}{E^o_{a(\text{contaminant})}}$.

liquors when the concentration of phosphine oxide in the organic diluent was sufficiently high. In accordance with the previous data, the addition of either nitrate or chloride to the system caused a marked improvement in extraction and permitted the use of lower extractant concentrations, nitrate being more effective in this respect than chloride (Table 26 and Figure 21).

The uranium extraction coefficients reported in both Table 25 and Table 26 were somewhat higher than would be predicted from the data reported for pure solutions at the same sulfate level. This difference may be due to the formation of aluminum and iron sulfate complexes to give an appreciable lowering of the effective sulfate activity.

Table 27 and Figure 22 show extraction isotherms with phosphine oxides from the liquor to which sodium nitrate was added in the indicated amounts. When the nitrate concentration was 2%, the organic phase was loaded within very few stages to 10 g U/l or 85% of the theoretical maximum (cf. p. 84). At lower nitrate concentrations, the number of required stages increased appreciably and the loading level was not as high.

Chloride-Sulfate Liquors

Liquors containing both chloride and sulfate are produced in the salt roast, acid leach process for treating Western ores. Depending upon the amount of hydrochloric acid recovered from the off gases, and thus the amount of sulfuric acid required for fortification, the ratio of sulfate to chloride may vary over a considerable range (see, for example, Table 21).

From the data of Table 28, it is apparent that selective extraction of uranium from these liquors may be accomplished using phosphine oxide-diluent mixtures at moderate concentrations. Of the two liquors tested, the better extractions were obtained from the liquor with the lower sulfate to chloride ratio. As expected, the addition of small quantities of nitrate (or to a lesser extent, the further additions of chloride) to the system caused a marked increase in the extraction coefficient. In each case (with or without nitrate) where test conditions were identical, the extractions were greater than those from the Marysvale liquors described above.

Attempts to extract the vanadium from the chloride-sulfate solutions were not made. Such extractions could presumably be accomplished through appropriate adjustment of the pH, nitrate concentration, and phosphine oxide concentration (see above, studies in pure solutions).

Table 26

EFFECT OF CHLORIDE AND NITRATE UPON EXTRACTIONS FROM SULFATE LIQUORS CONTAINING NO VANADIUM

(Marysvale 2)[a]

Reagent = 0.1 M Tridecylphosphine Oxide (Batch A) in kerosene
Phase Ratio, aqueous/organic = 1
Contact Time = 2 min.
Room Temperature

Anion Added			Extraction Coefficients			Selectivity Factor	
Anion[b]	wt/vol %	(M)	U	Fe	Al	Fe	Al
0	0	0	0.1	---	---	---	---
Cl	0.25	0.07	0.5	0.0015	0.015	400	40
"	0.5	.14	1.1	.003	.010	400	100
"	1.0	.28	2.8	.002	.008	1500	400
"	1.5	.42	5	.008	.007	700	700
"	2.0	.56	15	.015	.015	900	1500
NO_3	0.5	0.08	25	0.002	0.004	10^4	$6x10^3$
"	1.0	.16	75	.002	.01	10^4	$7x10^3$
"	1.5	.24	125	.003	.004	10^4	$3x10^4$
"	2.0	.32	200	---	---	---	---

a) See Table 21 for composition.
b) Added as sodium salts.

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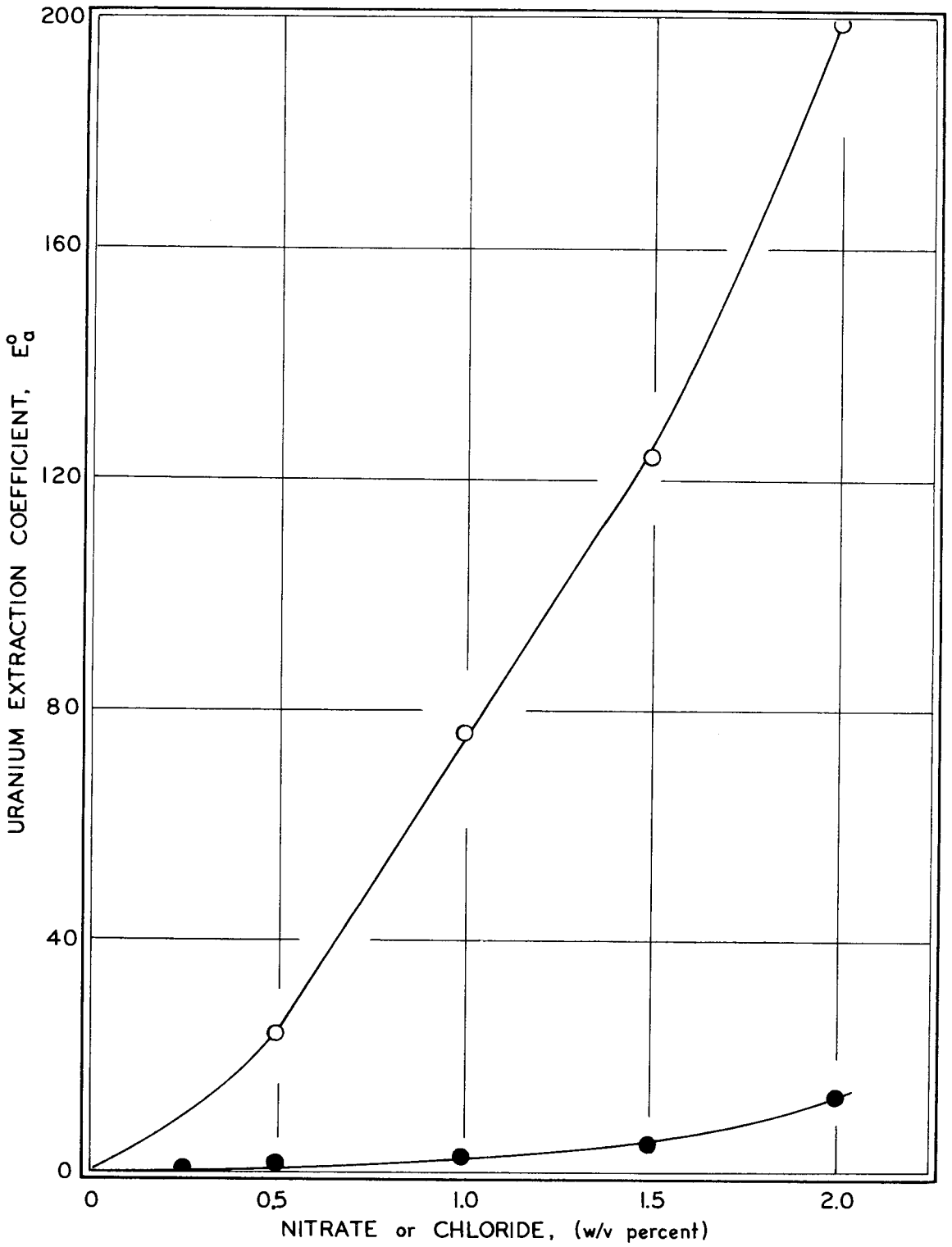

Figure 21

URANIUM EXTRACTION FROM SULFATE LIQUOR (NO VANADIUM)

EFFECT OF CHLORIDE OR NITRATE CONCENTRATION

0.1 M Trioctylphosphine Oxide (Batch A) in Kerosene
Marysvale 2 Liquor, Phase Ratio 1, Room Temperature

○ NO_3 ● Cl

Table 27

EXTRACTION ISOTHERMS FOR PHOSPHINE OXIDES FROM SULFATE LIQUORS (Marysvale Type)

Reagent = 0.1M in kerosene
Contact time = 2 min.
Room temperature

	Tridecylphosphine Oxide, Batch A (Marysvale 1[a], 0.32M NO_3)			Trioctylphosphine Oxide, Batch B-1 (Marysvale 2[a], 0.08M NO_3)		
Contact No.	Uranium Distribution[b] (g/l) Aqueous	Organic	E	Uranium Distribution[c] (g/l) Aqueous	Organic	E
1	0.07	6.0	83	0.04	1.16	31
2	.58	9.4	16	.08	2.28	27
3	1.06	10.4	9.8	.18	3.30	18
4	1.30	10.2	7.8	.31	4.19	14
5	1.28	10.3	8.0	.45	4.94	11
6				.61	5.53	9.1
7				.80	5.93	7.4
8				.87	6.26	7.2
9				.99	6.47	6.5
10				1.1	6.53	5.7
11				1.1	6.59	5.8
12				1.2	6.54[d]	5.3

a) See Table 21 for composition.
b) Experiment performed by contacting 10 ml organic phase with successive 50 ml portions of fresh liquor.
c) Experiment performed by contacting organic phase with successive equal volumes of fresh liquor.
d) Analysis of final organic phase: 6.54 g U/l; 0.0033 g Fe/l; 0.054 g Al/l.

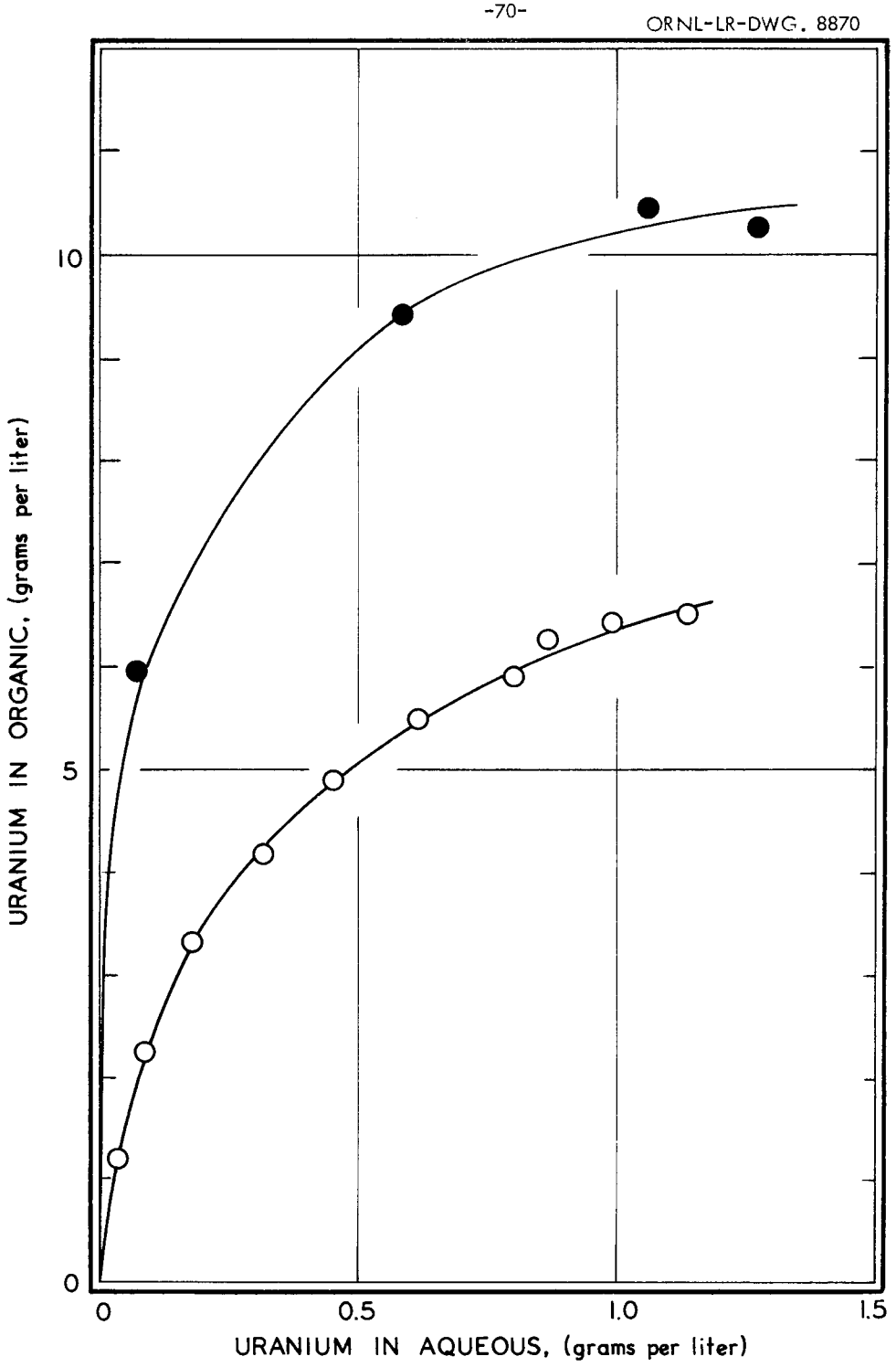

Figure 22

URANIUM EXTRACTION ISOTHERMS FROM SULFATE LIQUORS

Marysvale Type

0.1 M Trialkylphosphine Oxide in Kerosene
Room Temperature

● Tridecylphosphine Oxide (Batch A)
Marysvale 1 Liquor, 0.32 M NO_3

○ Trioctylphosphine Oxide (Batch B-1)
Marysvale 2 Liquor, 0.08 M NO_3

Table 28

EXTRACTION OF URANIUM FROM CHLORIDE-SULFATE LIQUORS

Reagent = Trioctylphosphine Oxide (Batch B-1) in kerosene.
Contact Time = 2 min.
Room Temperature

Liquor[a]	Oxidation State	pH	NO_3 (M)	Phosphine Oxide (M)	Phase Ratio (aqueous/organic)	Extraction Coefficient, E_a^o U	V	Fe	Al
A	Reduced[b]	1.22	0	0.1	1	9	-----	----	----
B	"	1.7	0	0.1	1	1	<0.001	0.01	0.02
B	"	1.7	0	0.2	1	3.5	0.01	0.03	0.02
B	"	1.7	0	0.3	1	8	0.02	0.05	0.02
A	"	1.22	0.3	0.1	1	1500	<0.01	----	----
B	"	1.0	0.3	0.1	3	100	<0.02	0.03	0.02
B	"	1.7	0.3	0.1	3	100	----	----	----
B	Oxidized[c]	1.0	0.3	0.1	3	60	0.2	----	----
B	"	1.5	0.3	0.1	3	70	0.3	----	----

a) See Table 21 for compositions.
b) Treated with Na_2SO_3, essentially complete reduction of vanadium and iron.
c) Treated with $NaClO_3$ in an amount equivalent to 12 times requirement for oxidation of vanadium and iron.

Sulfate Liquors - Moderate Uranium Concentration

It is standard practice in the salt-roast, acid-leach process to reduce stream volumes by completely precipitating all the hydrolyzable metals in the dilute leach liquor with ammonia and redissolving this precipitate ("green sludge") in sulfuric acid such that the liquor volume is about one-tenth of the original. As a result of the volume reduction the final concentration of uranium is ordinarily about 20 g/l. With this concentration level, it is apparent that the cost of adding small amounts of auxiliary reagents (if necessary) such as sodium nitrate or nitric acid would be considerably less important in respect to the overall processing costs than for the more dilute solutions considered above.

Several preliminary extraction results have been obtained from the "green sludge" liquors using 0.2 M tri-octylphosphine oxide in kerosene as the extractant. A summary of the data may be given as follows:

When equal volumes of liquor and 0.2 M reagent in kerosene were used in cascade extractions (organic phase moved against fresh liquor) the organic phase contained 9 g U/l after one extraction stage and 11 g U/l after the 4th stage. Addition of 2% NO_3 as sodium nitrate increased the loading to 17 g U/l and 25 g U/l after the 1st and 4th stages, respectively.

When one volume of the liquor was extracted with five successive equal volumes of organic solution (0.2 M trioctyl-phosphine oxide), the uranium level was reduced to 1 g/l when no added nitrate was used and to 0.01 g/l when 2% NO_3 was added.

STRIPPING OF URANIUM

Stripping of uranium from phosphine oxides can be accomplished by either acidic or alkaline solutions. In alkaline stripping, advantage may be taken of the fact that uranium precipitates in hydroxide solutions or forms soluble complexes in carbonate solutions. Only cursory examination has been made of the feasibility of either acid or hydroxide stripping, and greater emphasis has been placed on the more promising carbonate stripping procedure.

Acid Stripping

Table 29 presents uranium stripping data with several reagents from two solutions of trioctylphosphine oxide in kerosene. In one case the uranium was extracted into the organic solutions from a 0.5 M sulfate solution containing uranium, iron and aluminum at pH = 1 and in the other from a dilute uranyl nitrate solution, both solutions containing about 0.3 M added nitrate. As shown by Table 29, phosphoric and hydrofluoric acids and concentrated sulfate solutions at pH 2 were effective stripping agents due in part to their aqueous uranium complexing properties[27,28,29], but oxalic and acetic acids were not very effective under the conditions used. Dilute hydrochloric acid was not effective, and it may be predicted on basis of the extraction results that chloride salt or more concentrated hydrochloric acid (Table 3) or sulfuric acid (Table 5) would fail to strip the uranium. It is noteworthy that the uranium was not stripped by water, in contrast to practice with tributylphosphate; this is in line with the much greater stability of the reagent-uranium-nitrate complex formed by the phosphine oxides. The data of Table 5 suggest that water might be useful for stripping if sulfate but neither nitrate nor chloride were present; however, this has not been investigated.

Hydroxide Stripping

Stripping with hydroxide solutions appears attractive, since only that amount of reagent would be consumed which is the stoichiometric amount necessary to precipitate the uranium and the small amount of impurities present, and to neutralize any extracted acid.

Tests of stripping with sodium hydroxide solutions were made over a range of concentrations from 2 to 45 weight percent. In each test a great excess of hydroxide was present

Table 29

ACID STRIPPING OF URANIUM FROM TRIOCTYLPHOSPHINE OXIDE

Reagent = 0.1M Trioctylphosphine Oxide, Batch B-1, in kerosene.
Contact time = 2 min.
Room temperature

Stripping Reagent	Phase Ratio (aq/org)	Uranium Stripping Coefficient, S_o^a, From Pregnant Phosphine Oxide Solution Prepared From: Sulfate-Nitrate Solution[a]	Nitrate Solution[b]
Water	2	---	0.06
0.1M HCl	2	---	0.02
0.5M SO_4, pH = 2[c]	1	1.2	0.2
4M SO_4, pH = 2[c]	1	7.3	3.5
4M H_3PO_4	1	---	8.1
4M HF	1	24	19
1M HF	1	3.1	4.3
1M Oxalic Acid	1	---	0.04
4M Acetic Acid	1	0.8	0.11

a) Uranium concentration at 5 g/l, originally extracted from sulfate solution containing: 1.3 g U/l, 5 g Fe/l, 4 g Al/l, 2 g F/l, 50 g SO_4/l, 20 g NO_3/l.

b) Uranium concentration at 2 g/l, originally extracted from uranyl nitrate solution containing about 20 g NO_3/l.

c) $(NH_4)_2SO_4$, pH adjusted with H_2SO_4.

over that theoretically required to precipitate the uranium as $Na_2U_2O_7$. Essentially complete precipitation of the uranium was obtained with 2% sodium hydroxide (0.5 M), about 5 mg U/l remaining dissolved or dispersed in the organic phase. With 5% sodium hydroxide, 5% of the uranium (130 mg U/l) remained in the organic phase. The percent removal continued to fall off as the concentration of the hydroxide stripping solution was increased, to the point that only about half of the uranium was removed by 45% sodium hydroxide. The nature of this retention of the uranium has not yet been investigated, nor have special treatments been tried beyond a test of prolonged contact time (20 hours) and a test of elevated temperature (70°C), neither of which was effective.

Tests were also made of stripping with ammonium hydroxide solutions, again with the quantity of base in great excess over that theoretically required. Here, in contrast to the results with sodium hydroxide, only about half of the uranium was removed by the most dilute reagent (0.73 w/v % NH_3 $\sim$0.4 M). Stripping improved with increasing concentration up to 7 w/v % NH_3; however, less than 90% of the uranium was removed at this concentration, and at concentrations of 15 and 22 w/v % NH_3 (as with the highest concentration of sodium hydroxide) only half of the uranium was removed. It seems probable that the nature of the uranium retention at high base concentrations was the same in both systems, and it might be related to a uranium retention sometimes encountered in stripping with sodium carbonate solutions, described below.

In the sodium hydroxide stripping tests, the precipitates collected mostly at the interface, and were easily removed by centrifugation. All of the ammonia precipitates were difficult to separate, requiring extensive centrifugation (about one hour in a small laboratory centrifuge, 2500 rpm, effective radius 2.5 inches).

Carbonate Stripping

Tests of stripping with sodium carbonate solutions were made over a range of concentrations from 2 to 15 weight percent (0.2 to 1.5 M). Essentially complete stripping of the uranium ($\geq$ 98 percent) was obtained in a single-stage strip at each concentration level tested. Ammonium carbonate was less effective than sodium carbonate at equivalent concentration, e.g., 67% stripped by 0.2 M ammonium carbonate as compared with 99.8% by 0.2 M sodium carbonate (stripping from 0.1 M trioctylphosphine oxide, Batch B-1 in kerosene, phase ratio 1:1, two minutes contact time at room temperature).

In stripping with carbonate solutions, the uranium reports to the aqueous phase as the uranyl tricarbonate complex ion, $UO_2(CO_3)_3^{-4}$. Hence, the uranium concentration in the loaded strip solution would be limited by stoichiometry to one-third the molarity of the sodium carbonate. Actually, a somewhat lower limit is imposed by solubility of the sodium uranyl tricarbonate, which is dependent upon the concentration of carbonate in excess of the amount contained in the tricarbonate ion and the concentration of other anions[30]. The latter includes the anion extracted with the uranyl and also any anions extracted as free acid (cf. p. 47).

This dependence of the solubility upon the excess anion concentration must be considered in choosing a carbonate concentration for the stripping solution. The maximum equilibrium uranium solubility may be estimated from the data of Table 30. However, metastable equilibrium in carbonate solu-

Table 30

SOLUBILITY OF URANIUM IN CARBONATE SOLUTIONS[30]

Excess Anion* (moles/liter)	Uranium Solubility at 25°C (g/l)
0	63
0.5	31
1.0	17
2.0	4

*Carbonate in excess of three moles per mole of uranium, plus all other anions present - e.g., the anion which was associated with uranium in the organic complex, and any acid which may have been extracted at the same time as the uranium.

tions may exist under certain conditions. Should these conditions be met in the stripping process, it is possible that the uranium loading of the carbonate solution may be higher than the predicted equilibrium level.

A stripping cascade with 5% Na_2CO_3 is presented in Table 31. After five equal-volume contacts with fresh preg-

Table 31

STRIPPING CASCADE WITH 5% Na_2CO_3

FROM PHOSPHINE OXIDE

Organic Phase

0.1 M Trioctylphosphine Oxide, Batch B-1, in Kerosene.
6.68 g U/l
0.0033 g Fe/l
Equal volumes of organic and aqueous phases at each 2 minute contact.
Room temperature

Stage	Uranium Distribution (g/l) Organic Phase	Na_2CO_3	% of U Removed From Organic
1	0.01	6.7	99.8
2	0.01	13.3	99.8
3	0.02	20.0	99.7
4	0.6	26.1	91
5	2.0	30.7	70

nant organic solution containing 6.7 g U/l, the concentration of uranium attained in the carbonate solution was 30 g/l. Since the organic phase was originally loaded from a leach liquor containing 1 g U/l, this represented a thirty-fold increase in the concentration of uranium across the system. The excess anion in the resulting solution was about 0.4 M and thus the loading did not exceed the solubility limit predicted in Table 30.

The uranium may be removed from the carbonate solution by well established procedures such as precipitation with sodium hydroxide, followed by regeneration of the carbonate solution. Due to the build-up of salts such as sodium nitrate in the carbonate stream, a constant removal or

"bleeding" of a portion of the stripping solution would be necessary. Alternatively, since the concentration of uranium in the stripping carbonate solution may reach high levels, it may be economically feasible to destroy the carbonate with acid and precipitate uranium from the acid solution.

High Residual Uranium

Anomalously high residual uranium levels (e.g., 100 ppm and higher) have been encountered in some carbonate stripping tests. Such uranium was not removed by contact with fresh carbonate solution, suggesting that it was not an equilibrium concentration but was a quantity in some way "protected" from reaction with the aqueous sodium carbonate. Subsequent tests indicated that the uranium retention is related to the presence in the organic solution of degradation products of the phosphine oxide (or of an unidentified contaminant initially present), since the level of uranium retained increased with aging of the pregnant organic solution. (It should be noted that the quantity of phosphine oxide indicated as lost by this degradation is small, and unimportant in comparison with probable loss rates by, e.g., entrainment.)

Investigation of this anomaly has so far been limited to exploratory tests, chiefly with tri-n-decylphosphine oxide. The few tests with other phosphine oxides indicated that the n-dodecyl compound was similar to the n-decyl, but that the n-octyl, 2-ethylhexyl, and 3,5,5-trimethylhexyl compounds were affected considerably less. The rate of increase of the residual level with aging of the pregnant organic solution was faster at higher temperature, significant increases occurring in hours at 95°C as compared with days at room temperature. A similar although slower effect was found when the barren dilute (0.1 M) phosphine oxide solution was aged before instead of after the extraction, but prolonged aging of the solid phosphine oxide before dissolving it in kerosene appears to have had no effect.

Although repeated contacts with fresh sodium carbonate solution removed little if any of the residual uranium, addition of ethanol or acetone to the system enabled the carbonate solution to remove essentially all of it in one contact. The phosphine oxide so stripped, when re-loaded and stripped again without further use of additive, showed essentially no residual uranium. This indicates that stripping in the presence of the additive removed the substance responsible for the difficulty along with the uranium.

It cannot be predicted from the results so far found whether or not this affect is likely to become significant under process use conditions. The aging times of the pregnant

organic solution at room temperature which led to important levels of uranium retention would correspond to many recycles of the extractant in process use, and the recycling might prove either to increase the effect (as perhaps by accelerated degradation of the phosphine oxide) or to decrease it (as perhaps by means of the repeated scrubbing of the organic solution). If extraction with phosphine oxides is carried on into process development, further investigation of this effect will be appropriate to establish control tests for detecting the impurity responsible, and if necessary, treatment for removing it.

PHYSICAL PROPERTIES OF PHOSPHINE OXIDES IN RESPECT TO THEIR USE AS SOLVENT EXTRACTION REAGENTS

Stability

Kosolapoff[31] states that "tertiary phosphine oxides are the most stable chemical structures in the family of organophosphorus compounds." Experience in the testing program reported here has generally corroborated that the trialkylphosphine oxides are relatively resistant to oxidation, reduction, hydrolysis, etc. However, it has been observed that degradation does occur under treatment with strong oxidizing agents, and also under extended exposure to air at 100°C. The degradation products include the corresponding phosphinic acid. A much slower but presumably similar degradation, also producing phosphinic acid, was observed when dilute solutions of trialkylphosphine oxide (e.g., 0.1 M, in kerosene) were stored for long periods. (Such solutions were exposed to air inside closed containers; none have been stored completely out of contact with air.) On the other hand, no such degradation has been observed in phosphine oxides stored, under similar conditions, as the pure or nearly pure solids.

Although the nature of the degradation and the factors controlling it have not been determined, it does not seem likely that (under the conditions expected to be ordinarily encountered in extraction use) such degradation would impose any important limitation on the effective life of the reagent. No harmful effects from the degradation products on extraction have been observed. Possible effects (probably due to phosphinic acid) on alkaline stripping have been discussed above (p. 78).

Reagent Loss by Distribution to Aqueous Phases

Dr. W. H. Baldwin of the Chemistry Division of ORNL has prepared a P^{32}-labeled tri-n-octylphosphine oxide and has measured its distribution to several aqueous solutions from a 0.2 M solution in n-decane. The data appear in Table 32. The amount of the phosphine oxide distributed to the aqueous phase was in all cases low, < 4 g/l.

As mentioned previously, the phosphine oxides with short alkyl chains, e.g., tributylphosphine oxide, are hygroscopic. Preliminary observations indicated, however, that the losses of these compounds through distribution from an organic phase to aqueous liquors are low.

Table 32

DISTRIBUTION OF P^{32} LABELED PHOSPHINE OXIDE TO AQUEOUS PHASES[23]

Reagent = 0.1 M Trioctylphosphine Oxide in n-decane. Equal volumes of indicated aqueous phase and organic phase at 25°C.

Aqueous Phase	Concentration of Phosphine Oxide Found in Aqueous Phase mg/l
Water	1.1 ± 0.7
1 M HCl	0.2 ± 0.07
0.5 M SO_4 + 0.1 M HNO_3	0.2 ± 0.07
2% Na_2CO_3	3.6 ± 0.06
5% Na_2CO_3	3.6 ± 1.3

Phase Separation

The rate of phase disengagement was not studied per se with either the pure solutions of the process-type liquors. In the various extraction tests, the phase separations appeared for the most part reasonably rapid and clean. The longest-chain compound tested, tridodecylphosphine oxide (in carbon tetrachloride), gave somewhat slower separations than did the decyl and octyl compounds in corresponding tests. In some special instances, described below, precipitation or third-phase formation was encountered.

Separations were also clean in the stripping tests, except in the stripping by direct precipitation with ammonium hydroxide. Here, extensive centrifugation was required to separate the precipitate as formed under the test conditions used (p. 73).

Third Phase Formation

In extraction from solutions containing rather high concentrations of sulfuric or hydrochloric acid, a third liquid phase sometimes separated. This third phase was typically of

small volume, with specific gravity intermediate between the normal aqueous and organic phases, presumably containing relatively high concentration of the phosphine oxide since it carried most of the extracted uranium. Some test conditions that did and did not give three phases with trioctylphosphine oxide in kerosene are compared in Table 33. These

Table 33

COMPARISON OF CONDITIONS GIVING TWO AND THREE LIQUID PHASES

Trioctylphosphine Oxide in kerosene

Phosphine Oxide M	Phase Ratio a/o	Initial Aqueous Phase					No. of Liquid Phases
		Acid	M	pH	Metal Ion	M	
0.3	2	H_2SO_4	6	(acid)	U	0.004	3
"	"	"	4	"	"	"	2
0.6	"	"	4	"	"	"	2
0.3	20	"	0.2	1.0	"	0.1	2
0.2	2	HCl	6	(acid)	U	0.004	3
"	"	"	4	"	"	"	2
0.05	4	"	6 or 4	"	"	"	2
0.2	5	HCl or H_2SO_4 or HNO_3	4	(acid)	Fe	0.1	3
"	"	"	4	"	"	"	2
"	"	HCl, H_2SO_4, H_3PO_4 or HNO_3	4	"	"	"	2
0.6	2	H_3PO_4	3.3	(acid)	U	0.004	2
"	"	"	5.3	"	"	0.0004	2

may be compared with the tests shown in Tables 3, 5 and 14, none of which gave third phases with 0.1 M tridecyl- or tri(2-ethylhexyl)phosphine oxide in contact with rather high concentrations of acids. In general, third phases were not encountered in extractions from nitrate or phosphate solutions,

nor in extractions with phosphine oxide concentrations of 0.1 M or less. The results suggest that the concentration of sulfuric or hydrochloric acid was the principal controlling variable, and it is possible that the nature and amount of metal ion may have had an appreciable influence.

A test with 0.3 M tributylphosphine oxide and 6 M sulfuric acid, similar to the first test listed in Table 33, also gave a third phase. In an extraction with 0.2 M tributylphosphine oxide from a synthetic "Marysvale leach liquor" (Table 21), a small amount of viscous, uranium-containing material was detected, which may have been a third liquid phase. In extractions with 0.1 M tributylphosphine oxide from 0.1 M nitrate, 0.5 M sulfate - 0.3 M nitrate, and 0.4 M phosphate - 0.3 M nitrate, third phase formation was observed when kerosene was used as the diluent, but not when carbon tetrachloride was used. Third-phase formation has been reported with 0.75 M tributylphosphine oxide in carbon tetrachloride in extraction from a solution containing 0.1 M uranium and 2 M sulfuric acid but not from a 0.1 M uranyl sulfate solution without excess acid, nor from a 0.1 M uranyl nitrate solution with 3 M nitric acid.(11)

Third-phase formation has been reported with the structurally-similar reagent tributylphosphate, 30% solution in Amsco-140, in extractions from 6 M sulfuric or perchloric acid solutions.(16) Confirmatory tests in this laboratory showed a third phase with sulfuric acid at 8 M but not at a little less than 6 M. Results were similar with either Amsco-140 or kerosene, with zero or 0.003 M uranium present, and with either sulfuric or hydrochloric acid.

Precipitation of uranium from dilute nitrate solution by triphenylphosphine oxide has been mentioned above (p. 8). Uranium was not precipitated from any of the solutions tested by the trialkylphosphine oxides, with the possible exception of tridodecylphosphine oxide. A small amount of precipitate appeared to be formed in a single test of extraction this this reagent from dilute nitrate solution; however, no precipitate was observed in other tests under nearly the same conditions.

IDENTIFICATION OF COMPLEX SPECIES

Because of the similarity in structure of the trialkylphosphine oxides and the trialkyl phosphates, it is reasonable to expect the formation of similar complexes with acids and with uranium, the much higher extraction power shown by the phosphine oxides resulting from the greater stability of their complexes. Formulas for the uranyl nitrate and nitric acid complexes with tributylphosphate have been shown[22] to be

$$\left[UO_2 \cdot (NO_3)_2 \cdot (TBP)_2\right]$$

and

$$\left[TBP \cdot HNO_3\right]$$

Although it has not been within the scope of the present study to conduct the detailed experiments necessary to identify the complex species and determine their formation constants, several of the data already presented indicate that the complexes with phosphine oxides are indeed similar to these.

Phosphine Oxide-Uranium Combining Ratio

Both the maximum uranium loading obtainable and the dependence of extraction power on reagent concentration give information about the reagent-uranium combining ratio. Although most of the extraction tests have not been carried to maximum loading, the loading reached in a test with a pure solid phosphine oxide (p. 87) was probably very close to maximum. This showed 1.9 moles of phosphine oxide per mole of uranium.

Extractions with Varying Reagent Concentrations

In general, when $\underline{x}$ moles of reagent combine with 1 mole of uranium to form an extractable complex, and extraction coefficients are measured over a range of reagent concentrations with the composition of the aqueous phase held constant, the extraction coefficients are expected to increase as the $\underline{x}$ power of the free reagent concentration. Accordingly, the plot of log E_a^o versus log of free reagent concentration at equilibrium is expected to give a straight line of slope $\underline{x}$. Several of the extractions from tests reported here have been so plotted, the test conditions and the measured slopes being given in Table 34. The slopes for the extractions from

Table 34

PHOSPHINE OXIDE-URANIUM COMBINING RATIO AS INDICATED BY SLOPES OF EXTRACTION COEFFICIENT-PHOSPHINE OXIDE CURVES

Aqueous Solution				Organic Solution		Measured Slope
Anion	Conc. Anion (M)	Conc. NO_3 (M)	pH	Trialkylphosphine Oxide	Diluent	
Cl	1.5	0	0.6	Octyl, Batch B-1	Kerosene	2.2
	0.5	0	0.7	Decyl, " 292	"	2.2
SO_4	4.0	0	<0	Octyl, " B-1	Kerosene	2.1
	4.0	0	0.3	Decyl, " 292	"	2.6
	1.5	0	0.5	" " "	"	2.5
	0.5	0	0.4	" " "	"	2.6
	1.0	1.2	1.0	Decyl, " 292	Kerosene	1.9
	1.0	0.3	1.0	" " "	"	1.9
	0.5	0.3	1.1	" " "	"	2.0
	0.5	1.2	0.5	Octyl, " B-1	"	2.1
	1.7	0.3	1.1	Decyl, " A	CCl_4	2.1
	0.5	0.3	1.1	" " "	"	1.9
PO_4	1.5	1.2	0.5	Octyl, " B-1	Kerosene	2.0
	1.4	0.3	1.1	Decyl, " A	CCl_4	2.0
	0.4	0.3	1.1	" " "	"	1.8

chloride, sulfuric acid, sulfate-nitrate, and phosphate-nitrate solutions were close to 2, indicating a combining ratio of 2. The slopes for the extractions from sulfate solutions at pH 0.3-0.5 were higher. This probably does not indicate a shift in combining ratio, but more likely reflects secondary effects in the complex equilibria in the aqueous sulfate solutions.

Anion-Uranium Combining Ratio

On the basis of requirement of electrical neutrality, the uranium would be expected to enter the organic phase as a neutral complex (e.g., $UO_2(NO_3)_2$, UO_2SO_4). In addition, the dependence of the uranium extraction coefficient upon anion concentration indicates the same type formulas.

Chloride and Nitrate

The extraction coefficients at chloride concentrations of 0.5 and 1.5 M from Table 3 have been plotted as described above. The slopes ranged from 1.7 to 2.3, in fair accordance with the formula

$$\left[(R_3PO)_2UO_2Cl_2\right].$$

The only experiments which show extraction dependence upon nitrate concentration have been conducted in solutions which also contain sulfate and phosphate salts. When these are present the slopes obtained are less than 2 but greater than 1. Since it is expected that nitrate would behave in a manner identical with chloride, the difference of these slopes from 2 is probably attributable to a simultaneous extraction of uranium nitrate and uranium sulfate species, or uranium-nitrate-phosphate species whose structure cannot be determined from these data.

Sulfate and Phosphate

Similarly treated, the extraction data of Table 5 for 0.5 and 1.5 M H_2SO_4 gave a slope close to 1, consistent with the formula $(R_3PO)_2UO_2SO_4$. Solutions at higher pH are complicated by the changing ratio of sulfate to bisulfate, so that the complexing of uranium in the aqueous phase may be changing.

The equilibria in phosphate solutions are even more complex and no attempt has been made to identify the extractable species.

TRIDECYLPHOSPHINE OXIDE AS A SOLID EXTRACTANT

Cursory studies have been made using tridecylphosphine oxide as a solid extractant. A small amount (2.35 g) of the phosphine oxide was slurried with 13 successive 50 ml portions of a uranyl nitrate solution containing 1 g U/l at pH = 1. At the 8th stage the uranium extraction was 96%, but after this stage it dropped off rapidly so that at the 13th stage the extraction was only 35%. The final uranium loading was exceptionally high, being 268 mg U per g dry phosphine oxide, equivalent to 1.9 moles phosphine oxide per mole uranium. The loading at the 8th stage was equivalent to 3.4 moles phosphine oxide per mole uranium.

Physical behavior of the phosphine oxide during this test was complex. After the second stage the phosphine oxide, now yellow with uranium, collected as a ball with a gummy consistency. During subsequent stages it become more fluid until the eleventh stage when separation into yellow viscous globules was observed. These hardened upon standing for two days, and additional slurrying with fresh liquor caused them to agglomerate. Since other phosphine oxides have not been tested in this manner, it is not certain that this behavior is typical of all solid phosphine oxides.

Stripping was accomplished with an efficiency of 83% in one stage by treatment of the loaded phosphine oxide with 50 ml of 10% Na_2CO_3. The material was ground and then contacted with the basic stripping solution for 6 hours.

SUMMARY

A number of symmetrical phosphine oxides have been prepared and examined for their ability to extract uranium from acidic nitrate, chloride, sulfate and phosphate solutions and mixtures thereof. Most of the compounds tested showed high affinity for uranium, excellent extractions being obtained from nitrate and chloride solutions, and under the proper conditions, from sulfate solutions. The extractions from sulfate or phosphate solutions could be remarkably increased by the addition of very small amounts of nitrate salts and to a lesser degree by the addition of chloride salts. These tests included compounds with straight-chain alkyls, branched-chain primary alkyls, phenyl alkyls, and phenyl. In the series of straight-chain alkyls, similar coefficients were found with the n-octyl, n-decyl, and n-dodecyl compounds.

Evidence was found that the phosphine oxide-uranium-anion complex is similar in nature to that reported for tributylphosphate (i.e., $2TBP \cdot UO_2 \cdot 2NO_3$), but much more stable. Because of the resulting ability of the trialkylphosphine oxides to extract uranium from aqueous solutions in which the trialkylphosphates are ineffective, such as dilute chloride solutions, or sulfate or dilute phosphate solutions containing little or no salting agent, particular attention was paid to these systems. Exact comparisons made in several cases showed extraction coefficients with the trialkylphosphine oxides to be several orders of magnitude greater than those with the trialkylphosphates.

A general itemized account of the results from tests with the pure uranium systems studied may be given as follows:

1) All of the alkylphosphine oxides tested (as, typically, 0.1 M solutions in inert organic diluents) extracted uranium from dilute nitrate solution, most of them very strongly. One of the two branched-chain compounds tested, the 3,5,5-trimethylhexyl compound, gave extraction coefficients similar to those with the longer straight-chain compounds, but the 2-ethylhexyl compound gave much lower extraction, perhaps because of strain or steric effects due to branching too close to the center of the molecule. The only aryl compound tested, triphenylphosphine oxide, gave a uranium precipitate which was nearly insoluble in several common solvents. This did not occur with the aryl-substituted alkyl compounds tested, and the coefficients obtained with the γ-phenylpropyl compound were similar to those with the n-butyl compound.

2) Uranium extractions were strongest from nitrate solutions and the effectiveness of the reagents decreased in

chloride, sulfate and phosphate solutions in that order. Extractions were increased by an increase of nitrate, chloride, or sulfuric acid concentration (up to 3-4 M sulfuric acid), but decreased with increasing sulfate salt, phosphate salt, or phosphoric acid concentration.

3) Useful extractions could be obtained even from sulfate and dilute phosphate solutions by increasing the reagent concentration or by the addition of relatively small amounts of nitrate or chloride.

4) The uranium extraction coefficients varied in general with the square of the phosphine oxide concentration, indicating reagent-to-uranium combining mole ratio of 2. This ratio was also indicated by the maximum uranium loading obtained.

5) Extractions from sulfate and phosphate solutions, with or without added nitrate, decreased with increase in pH. Typically, the extraction coefficients at pH 2 were about a third as great as the corresponding coefficients at pH 1. On the other hand, little if any effect of pH was found in extractions from chloride solutions.

6) Extractions decreased with increasing temperature.

7) The best diluents for the alkyl phosphine oxides are the simple aromatic hydrocarbons (benzene, toluene, xylene) and the kerosene-type aliphatic hydrocarbons. Other diluents tested showed decreased extraction with higher polar character of the diluent.

8) The uranium was effectively stripped from the solvent by contacting with solutions of sodium carbonate and of sodium hydroxide, less effectively with solutions of ammonium carbonate and hydroxide. When the hydroxides were used the uranium was precipitated directly from the organic phase. Stripping was also accomplished by use of dilute phosphoric or hydrofluoric acid solutions, or concentrated sulfate solutions at low acidity. Stripping with water alone was not feasible when the uranium had been extracted from liquors containing significant concentrations of nitrate. Water stripping has not yet been studied in the absence of nitrate.

9) Very selective extractions of uranium were obtained from solutions containing high concentrations of iron, aluminum and vanadium. Other metals have not been studied as yet, but it seems reasonable to expect that on a relative basis the selectivity of the phosphine oxides will be comparable to the trialkyl phosphates.

10) Although the coefficients were low, the extraction of vanadium(V) from sulfate liquors was possible if the conditions were properly adjusted, i.e., by addition of a small amount of nitrate to the system, use of high phosphine oxide concentrations, and adjusting the aqueous pH to 1.5-2. Vanadium(IV) was inappreciably extracted under all conditions tested.

11) Phosphine oxides extracted mineral acids from aqueous solutions, nitric acid most effectively and hydrochloric, sulfuric, and phosphoric acids to lesser extents. From pure solutions, the amount of acid extracted reached (e.g.) 0.2 equivalent per mole of phosphine oxide when the aqueous concentration was 0.1 M for nitric acid or 2 M for hydrochloric acid, sulfuric, or phosphoric acid. The limiting extraction from high concentrations of the acids was about one equivalent per mole of phosphine oxide.

12) The long chain trialkylphosphine oxides showed a negligible loss by distribution to acidic or alkaline solutions.

In addition to the studies with pure uranium systems, cursory examinations were made of the uranium extractions by phosphine oxides from several types of uranium raw material liquors. The results from these tests may be briefly listed as follows:

1) Efficient and selective extraction of uranium was obtained from the Florida Leached Zone liquors prepared by the TVA process. Under identical conditions, extractions with the phosphine oxides were considerably higher than those with tributylphosphate. In view of the greater stability of the organic-uranium-nitrate complex, it would be presumed that the phosphine oxides would be effective extractants over a much wider range of solution composition than the trialkylphosphates.

2) Useful and selective extraction of uranium was obtained from sulfate leach liquors (from Marysvale ore) if the concentration of phosphine oxide in the organic diluent was sufficiently high. The addition of nitrate (or chloride) to the system caused a marked improvement in extraction and permitted the use of lower extractant concentrations.

3) Selective extraction of uranium was obtained from chloride-sulfate liquors as produced in the salt roast, acid-leach process for treating Western ores. Since chloride was present in these liquors, lower concentrations of phosphine oxide were required than for the Marysvale liquors, the extractions improving with increasing chloride to sulfate ratios.

4) Efficient and selective removal of uranium was obtained from the "green sludge" liquors typical of those encountered in certain plants using the salt roast, acid-leach method. Due to the relatively high concentration of sulfuric acid, these sulfate liquors were particularly amenable to the phosphine oxide extraction.

FUTURE WORK

Further consideration will be given to the possible application of phosphine oxides to uranium processing problems. In addition to liquid-liquid extraction methods, the compounds will be examined as to their use in slurry extraction and "non-aqueous" (or "lyometallurgical") extraction methods. In the latter method, it might be possible to take particular advantage of the "nitrate effect," since a sufficiently high concentration of nitrate would be obtained in the small amount of aqueous phase present by the addition of a correspondingly small amount of nitrate, and thus the cost for nitrate would be relatively low per pound of uranium.

Since the phosphine oxides have proved favorable to the formation of strong uranium complexes, compounds with similar structure will be investigated. It would be helpful, for instance, if compounds could be found which gave a greater extraction of uranium from sulfate solutions without the aid of nitrate or chloride. Preliminary studies of the phosphoramides and an α-aminophosphinate have shown promise.

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APPENDIX A

PREPARATION OF PHOSPHINE OXIDES

The phosphine oxides described in this report were prepared by the reaction of phosphorus oxychloride with a Grignard reagent,

$$3RMgBr + POCl_3 \longrightarrow R_3PO + 3MgBrCl$$

following a procedure given by Kosolapoff.(1)

Reagents:

Magnesium - Baker and Adams Magnesium Turnings.

Ether - Mallinckrodt anhydrous diethyl ether, dried over sodium.

Alkyl Bromides - 3,5,5-Trimethylhexyl bromide - Matthieson and Bell.

2-Ethylhexyl bromide - prepared from 2-ethylhexanol, Carbide and Carbon Chemicals Co.

All others - Eastman Organic Chemicals, White Label Grade.

All were redistilled before use.

Phosphorus Oxychloride - Baker and Adams Reagent Grade, redistilled.

The magnesium and dry ether were placed in a flask equipped with stirrer, dropping funnel, and reflux condenser. The alkyl bromide was dissolved in dry ether, and a small portion of the solution was added to the reaction flask. Once the reaction started, it was maintained at vigorous reflux by adding the remainder of the alkyl bromide solution at a suitable rate. After all had been added, it was usually necessary to reflux the mixture for an hour or two for dissolution of most of the magnesium.

The phosphorus oxychloride, diluted with dry ether, was slowly dropped into the Grignard solution, considerable heat being evolved in the process. The resultant mixture was hydrolyzed with ice water while being stirred and cooled. Sufficient water was added to form two distinct layers.

Some of the phosphine oxides remained in solution, while others formed as crystalline solids scarcely soluble in cold ether. In the latter case, the product was washed with ether and then purified by recrystallization from ether or aqueous alcohol. In the former case, the ether layer was usually washed with water, then with 5 percent sodium hydroxide solution to convert any by-product acids (phosphonic or phosphinic) to their sodium salts, then again with water or dilute ethanol to remove these salts. This treatment was repeated until no further organic material was found in the washes. Products were obtained by fractional distillation, usually under reduced pressure. Some batches were further treated by heating with aqueous hydrochloric or nitric acid or by prolonged exposure to a stream of moist air, to remove "combined acidity" (an unidentified neutral contaminant thought to be a dialkylphosphine oxide) by conversion to phosphinic acid which was then removed by washing with sodium carbonate and water. The batches listed in Table A-1 were treated as follows:

Phenyl: Recrystallized from dilute alcohol to constant melting point.

ß-Phenylethyl, γ-phenylpropyl: Recrystallized once from diethyl ether.

Butyl, octyl (A-1 and A-2), decyl (A), dodecyl (A), 2-ethylhexyl (C and 194): Distillation cuts of narrow range.

Octyl (B-1), 2-ethylhexyl (D), 3,5,5-trimethylhexyl (A): Distillation cuts further purified by oxidative-hydrolytic treatment.

Octyl (289), dodecyl (288), 2-ethylhexyl (299), 3,5,5-trimethylhexyl (287): Prepared from (respectively) octyl (B-1), dodecyl (A), 2-ethylhexyl (194), and 3,5,5-trimethylhexyl (A), by extended treatment at steam temperature with moist air, followed by washing with sodium carbonate solution and aqueous alcohol.

Decyl (292): Treated alternately with moist air at steam temperature and with sodium carbonate and aqueous alcohol washes until iodometric titration showed little more "combined acidity" and then distilled at reduced pressure.

Table A-1

INDICATED PURITY OF SOME PHOSPHINE OXIDES

Trialkylphosphine Oxide	Batch No.	% P		% Acid Content[a]	
		Theor.	Found	Free[b]	"Combined"
n-Butyl	300-C[e]	14.19		0.2	<1[d]
n-Octyl	A-1	8.01	7.96	0.1	<0.5[c]
	A-2		7.96	0.1	0.5[c]
	B-1		8.05	0.1	9[d]
	289			0.03	0.3[d]
n-Decyl	A	6.58	6.58	0.13	<0.5[c]
	292			0.43	0.6[d]
n-Dodecyl	A	5.58	5.53	0.22	0.5[c]
	288			0.16	<0.1[d]
2-Ethylhexyl	C	8.01	8.6	5.9	12[c]
	D		8.2	0.2	3[c]
	194[f]			1.7	13[d]
	299			0.3	1[d]
3,5,5-Trimethylhexyl	A	7.23	7.30	0.07	3[c]
	287			0.05	0.4[d]
Phenyl	A	11.13	11.00	0.03	<0.1[d]
ß-Phenylethyl	A	8.55	8.67	1.6	0.8[d]
γ-Phenylpropyl	A	7.66	7.76	0.08	<0.1[d]

a) Acid content calculated as % dialkylphosphinic acid.
b) Free acid determined by direct titration.
c) Determined by conversion to phosphinic acid with moist air.
d) Determined according to iodometric procedure given in Appendix C.
e) Prepared by W. H. Baldwin, ORNL Chemistry Division.
f) Prepared by Virginia-Carolina Chemical Corp.

The purity of the products was estimated by alkaline titration to detect any free acid present, by iodometric titration (see Appendix C) to determine "combined acidity," by analysis of carbon, hydrogen, and phosphorus, and by microscopic examination of some of the crystalline products. (An attempt was made to determine the phosphine oxide directly by titration as a weak base in acetic acid or in chloroform[2], on the basis of the reported partial ionic nature of the phosphoryl bond, but no discernable titre was obtained.)

The phosphorus analyses and the contents of free phosphinic acid and of "combined acidity," for the reagent batches used in the tests covered in this report, are listed in Table A-1. Samples of the octyl Batch A-1, decyl Batch A, and dodecyl Batch A compounds were examined under the petrographic microscope by Dr. T. N. McVay, a consultant with the ORNL Ceramics Laboratory. He reported that the samples were well-formed acicular crystals with the only observable inclusions probably being gas. He also determined the refractive indices of these samples by the use of immersion oils.

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APPENDIX B

PHYSICAL PROPERTIES OF PHOSPHINE OXIDES

The physical properties of the phosphine oxides are shown in Table B-1. Three of the compounds, tributylphosphine oxide, tri(2-ethylhexyl)phosphine oxide and triphenylphosphine oxide, have also been prepared and reported elsewhere.

The tributyl derivative as described by Shell[1] has a melting point of 63-65°, comparing well with the 62-63 reported in Table B-1. The boiling point given in the same reference is 156° at 5 mm. The boiling point as listed by Kosolapoff[2] is 300° at 760 mm. This compound is very hygroscopic, but its solubility[3] in water is reported to be 0.18 M at 25°C. A much smaller distribution to the aqueous phase would be expected in solvent extraction application. The phosphine oxides of higher molecular weight used in these experiments have not shown similar hygroscopic properties.

The tri(2-ethylhexyl) compound has been prepared by Shell[1] and by Virginia-Carolina Chemical Corporation[4]. Data for the boiling points, refractive indices and densities have been reported and are compared in Table B-2 with the

Table B-2

COMPARISON OF TRI(2-ETHYLHEXYL)PHOSPHINE OXIDE AS PREPARED AT DIFFERENT INSTALLATIONS

	B.P.	Density	Refractive Index
ORNL	200-15 at 2-3 mm	0.880 at 30°	1.465 at 25°
V-C	161-90 at 0.3 mm	0.867 at 20°	1.465 at 25°
Shell	212 at 5 mm	0.893 at 20°	1.457 at 25°

corresponding data for the material used in this report. The boiling points appear to be consistent with pressure. There are considerable differences in the reported densities of the various products. Refractive indices for the ORNL and V-C

Table B-1

PHYSICAL PROPERTIES OF SOME TRIALKYLPHOSPHINE OXIDES

Trialkylphosphine Oxide	Batch No.	Mol Wt	Physical Appearance	Boiling Point, °C	Melting Point °C	Density g/cc	Refractive Index
n-Butyl	300-C[a]	218	White Crystals[b]	127-133/1 mm	62-63	---	---
n-Octyl	A-1	387	White Crystals	180-188/<0.1 mm	51-52	---	α=1.500, γ=1.532
	A-2		" "	185-205/<0.1 mm	53-54	---	---
	B-1		" "	290/50 mm	52-53	---	---
	289		" "	---	48-50	---	---
n-Decyl	A	471	White Crystals	278-283/3-4 mm	40-42	---	α=1.504, γ=1.556
	292		" "	255-258/0.3-0.5 mm	46-48	---	---
n-Dodecyl	A	555	" "	235-240/<0.1 mm	44-45	---	1.500
	288		" "	---	46-48	---	---
2-Ethylhexyl	C	287	Viscous straw-colored liquid	165-200/12 mm	---	---	---
	D		" "	205-215/2-3 mm	---	0.880^{30}	1.465^{25}
	194[c]		" "	161-190/0.3 mm	---	0.867^{20}	---
	299		" "	---	---	---	---
3,5,5-Trimethylhexyl	A	429	" "	185-190/<0.1 mm	---	0.865^{30}	1.463^{25}
	281		" "	---	---	---	---
Phenyl	A[a]	278	White Crystals[d]	---	150-151	---	---
ß-Phenylethyl	A	362	" " [e,f]	---	150-152	---	---
γ-Phenylpropyl	A	405	" " [f]	---	84-85	---	---

a) Prepared by W. H. Baldwin of the ORNL Chemistry Division.
b) Diliquescent.
c) Prepared by Research Division, Virginia-Carolina Chemical Corp., Richmond, Virginia.
d) Recrystallized from aqueous alcohol.
e) Moderately soluble in butyl acetate and in chlorobenzene, soluble to <0.1 M in carbon tetrachloride, insoluble in kerosene.
f) Recrystallized from diethyl ether.

compounds agree closely but are quite different from that reported by Shell, for which no purity estimate was quoted. After hydrolysis the V-C material was found to contain about 14 percent acid calculated as di(2-ethylhexyl)phosphinic acid.

The melting point for triphenylphosphine oxide, 150-151°C, compares well with 152-154°C as listed by Kosolapoff[2].

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APPENDIX C

IODOMETRIC PROCEDURE FOR DETERMINATION OF "COMBINED ACIDITY" IN PHOSPHINE OXIDES*

The method is based on the reaction of iodine with dialkylphosphinous acids in a properly buffered solution according to the following equation:

$$R_2POH + I_2 \longrightarrow R_2P(=O)I + HI$$

The reaction occurs in a benzene solution containing potassium iodide and pyridine. Successive determinations show deviations of ~2 percent. The absolute accuracy of the method has not been established.

Procedure

a) Place in a 50 ml Erlenmeyer flask

~1 g phosphine oxide
10 ml benzene
10 ml 0.1 N I_2 in 2% KI
2 ml pyridine

b) Shake vigorously for 16 hours (Burell "wrist-action" shaker was used in this work).

c) Titrate excess iodine in mixed phases with standard sodium thiosulfate.

d) Titrate original iodine in the 10 ml benzene - 10 ml iodine - pyridine mixture.

e) Subtract titer (c) from titer (d).

f) Calculate percent dialkylphosphinous acid in the following manner:

$$\% \text{ Dialkylphosphinous acid} = \frac{ml_{titer} \times N_{Na_2S_2O_3} \times \frac{M.W._{R_2POH}}{2}}{\text{Sample weight (mg)}} \times 100$$

*Modification of procedure used by Virginia-Carolina Chemical Corp. for the qualitative determination of dialkyl hydrogen phosphites.