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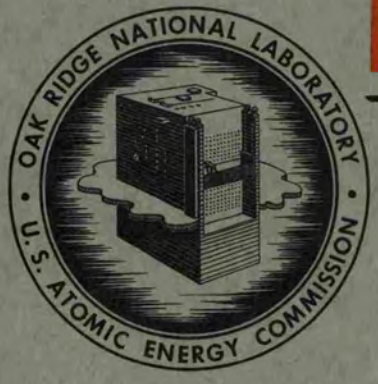

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Chemical Development Section C

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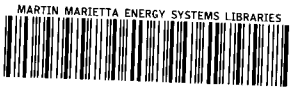

ABSTRACT

Dialkylphosphoric acids in combination with trialkylphosphates, dialkyl alkylphosphonates, trialkylphosphine oxides and other neutral organophosphorus compounds have uranium extraction abilities as much as two orders of magnitude stronger than the cumulative abilities of the individual reagents. With the possible exception of plutonium, other metals tested, e.g., iron, aluminum, vanadium, molybdenum, titanium, show no synergistic enhancement of extraction coefficient. Of the acids tested, only dialkylphosphoric acids showed a synergistic enhancement. Extractions can be achieved from sulfate and phosphate solutions in addition to nitrate solutions. Effects of anion concentration, pH and dialkylphosphoric acid concentration are parallel with and without the neutral additive. High neutral additive concentrations decrease uranium extraction. The reagents allow high uranium concentration from very low-grade liquors and are usable with liquors usually difficult to extract. Several useful reagent combinations can be prepared from commercial reagents.

CONTENTS

1.0 INTRODUCTION

This report describes the remarkable synergistic* enhancement of extraction coefficients obtained in the solvent extraction of uranium with combinations of certain organophosphorus compounds. Specifically, it has been found that dialkylphosphoric acids in combination with certain neutral organophosphorus compounds, e.g., trialkylphosphates, dialkyl alkylphosphonates and trialkylphosphine oxides, have much stronger uranium extraction ability, stronger sometimes by as much as two orders of magnitude, than would have been expected from the combined abilities of the individual reagents.

The evaluation and development of various organic compounds as reagents for the solvent extraction of uranium and other metals from raw materials and process solutions has received considerable emphasis during recent years at this laboratory and at other installations under contract to the Atomic Energy Commission. Solvent extraction has long been used for the refining of uranium from ore concentrates, but the reagents and methods were necessarily restricted to systems using highly salted acidic nitrate solutions and were unsuitable for treatment of the more complex liquors resulting from leaching of uranium ores with sulfuric or hydrochloric acids. As a consequence, it has been necessary to develop new reagents having possibilities for wider application.

Several processes for the extraction of uranium, vanadium, thorium, molybdenum, etc., have been developed at Oak Ridge National Laboratory as a result of this investigation. Two of the processes, the dialkylphosphoric acid extraction (Dapex) process (1,2,3,4,5,6,7) and the amine extraction (Amex) process (3,4,6,8-14), have been receiving considerable attention from the uranium processing industry and the Dapex process is now operating successfully on commercial scale at four Western plants.

In early 1951, Dow Chemical Company conducted extraction experiments with alkylphosphoric acid mixtures in phosphate systems which led to the development of a process for the recovery of uranium from commercial phosphoric acid with mixtures of the alcoholysis products of phosphorus pentoxide (15). Subsequently, a process was proposed by the same laboratory for the recovery of uranium from Western ore leach liquors and slurries with long-chain monoalkylphosphoric acids (16), and this process is in use at two plants. Other extraction reagents that have been studied include combinations of tributylphosphate with thiocyanates (17) at the Raw Materials Laboratory, Winchester, Massachusetts, and the acetone-hydrochloric acid reagents for lyometallurgical leaching proposed by Battelle Memorial Institute. (18)

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*"Synergism is the cooperative action of discrete agencies such that the total effect is greater than the sum of the two effects taken independently."

The ORNL Dapex process embodies (a) extracting the desired metals with a solution of a dialkylphosphoric acid, typically, di(2-ethylhexyl)phosphoric acid (D2EHPA), in a suitable diluent such as kerosene which may be modified with small amounts of chemical modifiers and (b) stripping the metals from the organic extract with either alkaline or acid aqueous solutions. The ability to strip all extracted metal ions completely with alkaline solutions and with high efficiency of reagent utilization is an important feature of the Dapex process.

The chemical modification of the kerosene, mentioned above, is recommended to prevent separation of the dialkylphosphate salt as a separate phase when using an alkaline stripping cycle. Initially, long chain alcohols were used for the chemical modification, but these suffer the drawback of decreasing the extraction coefficient of the reagent. This reduction of extraction coefficient would impose some limitation, though not a serious one, upon the general applicability of the process.

An investigation followed to find new reagents not having the property of decreasing the extraction ability and yet being suitable for the modification of the organic phase. Some compounds in several classes (neutral organophosphorus compounds, ketones, acetates and alkyl chlorides) did prove able to maintain miscibility, and of these a series of neutral organophosphorus compounds proved particularly useful. They provided synergistic enhancement of the uranium coefficient in the reagent combination while the other classes of reagents did not.

The present report can only touch upon many of the possibilities offered by this versatile group of synergistic extractants. Many variations in type and structure of both neutral and acid components have been tested, permitting some correlations of properties and structure. The bulk of the work reported here has been done with combinations of D2EHPA and the neutral additives tributylphosphate (TBP) and dibutyl butylphosphonate (DBBP). These reagents are representatives of several which are presently available in commercial quantities.

Testing has been accomplished by batch equilibrations of the aqueous and organic phases in separatory funnels. Larger scale and continuous testing have been (4,19) and will be reported elsewhere. Variables studied were effects of reagent class and structure, reagent concentration, diluent, pH level, anion type and concentration, uranium concentration, and temperature. Methods for stripping extracted metals from the organic phase have been tested. Extractions of metal ions other than uranium have also been examined both to determine their behavior in uranium extraction systems and to establish possibilities for their own extraction and separation by solvent extraction with synergistic reagents. Some observations are described which relate to the mechanism by which synergistic extractions take place.

Recently, workers at Mallinckrodt Chemical Works have reported the observation of a synergistic effect in extractions involving small amounts of dibutylphosphate (DBP) in a predomi-

nantly tributylphosphate organic phase (20). They propose a complex such as the following,

$$UO_2(NO_3)_2 \cdot DBP \cdot TBP$$

The systems described in this report correspond to quite different concentration levels (~0.1-0.4 M acid reagent and ~0.05-0.5 M neutral reagent as against Mallinckrodt's <0.001 M DBP in ~1 M TBP). At the high concentration levels of dialkylphosphoric acid used in the present investigations an increase in relatively high tributylphosphate levels causes a marked decrease in the observed synergistic enhancement.

Dow Chemical Company in recent reports (21) has described enhancement of coefficients in extractions with mixtures of certain amines and D2EHPA. Results of tests at this laboratory on similar combinations are compared in this report.

2.0 SUMMARY

In examining the important variables (e.g., organic and aqueous phase compositions) affecting uranium extraction by synergistic reagents, most of the results have been obtained with combinations of D2EHPA with TBP, DBBP, or tributylphosphine oxide (TBPO). Less detailed evaluations are also included for a variety of reagent combinations in which both neutral and acidic components were varied.

The enhancement achieved by the synergistic additives rose and then fell as the concentration of neutral reagent increased at a constant D2EHPA level. The maximum was reached with lower concentrations of the reagents giving the stronger enhancements. From 1.5 M H_2SO_4 the maximum enhancement was about 4-fold (over extraction with D2EHPA alone) with 0.1-0.2 M TBP, about 10-fold with 0.05-0.1 M DBBP, and about 50-fold with 0.05 M TBPO. For any combination of reagents the position of the maximum appeared to depend closely upon these absolute concentrations of neutral additive rather than upon the concentration of D2EHPA.

Uranium extraction by dialkylphosphoric acids at low uranium loading is represented by the equation (22)

$$UO_2^{++} + 2(HX)_2 \rightleftharpoons UO_2H_2X_4 + 2H^+$$

where $(HX)_2$ is the dimerized dialkylphosphoric acid. The synergistic enhancement can be explained in terms of adding the neutral reagent to the above complex.

$$UO_2^{++} + (HX)_2 + N \rightleftharpoons UO_2H_2X_4N + 2H^+$$

where N is the neutral synergistic additive. Interactions between the dialkylphosphoric acid and the neutral additive (23) also occur.

$$N + (HX)_2 \rightleftharpoons N(HX)_2$$

$$N + 1/2(HX)_2 \rightleftharpoons N(HX)$$

The maximum in the extraction coefficient and its subsequent decrease result from a competition of these reactions.

Highest uranium extraction coefficients were obtained when aliphatic hydrocarbons were used as diluents. The concentration of TBP required to give the maximum extraction decreased as the more favorable diluents were used and, necessarily, the initial slopes of the extraction curves (extraction coefficient vs TBP concentration) were increasingly steep in this same direction.

Uranium extraction increased with pH. The rate of increase with the TBP-D2EHPA and DBBP-D2EHPA combinations was approximately the same as for D2EHPA alone.

The degree of enhancement by a particular neutral reagent was nearly the same from nitrate, chloride, sulfate or phosphate aqueous solutions. Thus, with the synergistic combinations, as with D2EHPA alone, extraction was best from nitrate and was impaired by chloride < sulfate < phosphate.

Extractions from the acid solutions were reversible.

Equilibrium extraction curves (extraction isotherms) for D2EHPA-TBP and D2EHPA-DBBP systems reflect the enhanced extractions in their initial slopes before any loading limitation is encountered. The higher extraction at low uranium levels provides more efficient reduction of raffinate uranium level per stage, i.e., lower raffinates can be obtained in a set number of stages, or fewer stages are required to obtain a specified low raffinate. It also provides an obvious advantage in extraction to obtain high uranium loadings from a very low-grade aqueous liquor, or in application to liquors unusually difficult to extract.

An increase in temperature of the extracting solutions caused a decrease in synergistic extraction coefficients. With many of the reagents the drop corresponded to a loss of one-half of the extracting ability of the reagents in a temperature interval of about 15°. The data with TBP and DBBP, etc., fit the empirical expression

$$\log E_{T_2} = \log E_{T_1} - 0.0207(T_2 - T_1)$$

Plutonium(IV) and (VI) was the only element besides uranium (VI) indicating a synergistic enhancement of coefficient. Uranium(IV), vanadium(IV), aluminum and molybdenum showed little if any enhancement of extraction coefficient when tested with D2EHPA-neutral phosphorus compound mixture. Iron(III), titanium, and thorium (individually) were extracted either less strongly or less rapidly with the mixture than with D2EHPA alone, and iron (III) extraction from a U-Fe mixture was considerably depressed by addition of DBBP to D2EHPA.

Preferred reagents for stripping are sodium and ammonium carbonate solutions. Uranium and other metals are stripped efficiently under conditions prescribed for the Dapex process. The

neutral synergistic additives modify the kerosene diluent so that the corresponding salt of D2EHPA remains compatible with the kerosene. Equations are given in the Appendix for the calculation of minimum requirements for a number of modifiers.

Acid stripping is also possible, but less effective than basic stripping. The highest stripping coefficients obtained with sulfuric and hydrochloric acids were too low for practical use. Hydrofluoric and phosphoric acids at high concentrations (>5 M) stripped 0.1 M D2EHPA--0.1 M TBP effectively.

Losses of modifier to the aqueous liquors and strip solutions were low (e.g., ~25 ppm TBP and DBBP to both acidic liquors and 1 M Na_2CO_3 strip solutions, and lower losses with commercial, higher molecular weight neutral reagents). The D2EHPA losses to ordinary aqueous liquors were <1 ppm, to 10 M HCl were <2 ppm, and to 1 M Na_2CO_3 were 40-50 ppm.

Of other reagent combinations examined, nearly all of the neutral organophosphorus compounds (phosphites, phosphates, phosphonates, phosphinates, phosphine oxides, diphosphonates and a phosphonoacetate) enhanced the uranium extraction coefficient with D2EHPA by a factor of at least 2. Compounds with chains which were severely branched close to the central phosphorus atom had lower coefficients than those which were composed of straight chains. Comparison of straight-chain compounds of different classes showed that efficiency increased as the number of carbon-phosphorus bonds in the reagent increased (i.e., phosphate, phosphonate, phosphinate, phosphine oxide).

In addition to D2EHPA, other dialkylphosphoric acids, e.g., di(n-octyl), di(3,5,5-trimethylhexyl) and bis(di-isobutylmethyl), showed synergistic enhancement when used in combination with neutral organophosphorus reagents. Their enhanced coefficients were in the same relative order as their coefficients without the neutral additive.

In a few tests with selected primary, secondary and tertiary amines in combination with D2EHPA, synergistic enhancement was observed when a long chain primary amine was used, but adverse effects resulted with the secondary and tertiary amines.

Some tests are described on systems in which two synergistic additives were used with D2EHPA and in which one synergistic additive and a long-chain alcohol were present. In the first case, it is possible to calculate the coefficients obtained by the mixture of reagents from the extraction abilities of the separate synergistic combinations, but the effect of the alcohol upon the synergistic reagent seems to bear no relation to its effect on D2EHPA alone.

Combinations of the same neutral reagents with acid reagents other than dialkylphosphoric acids sometimes lead to a decrease in the uranium extraction coefficient, e.g., addition of 0.1 M TBP to 0.1 M mono(2,6,8-trimethylnonyl-4)phosphoric acid, DDPA, decreased the uranium extraction coefficient by 85 per cent. Com-

binations with other monoalkylphosphoric acids and with 2-ethylhexylphosphonic acid showed a similar decrease, but little or no effect was noted when phosphinic acids were tested.

Availability of reagents, the complexing strength desired, and the physical performance are all criteria which can determine the choice of a particular reagent combination. These choices can be made from several commercial reagents, e.g., several dialkylphosphoric acids, trialkylphosphates, and dialkyl alkylphosphonates, used in limited amounts, and one trialkylphosphine oxide.

3.0 SYNERGISTIC REAGENT COMBINATIONS WITH D2EHPA

Effective synergistic reagent combinations can use a variety of dialkylphosphoric acids. In general, the performance with the different dialkylphosphoric acids is similar except for degree of synergistic enhancement. Most of the experiments described in this section used D2EHPA because of its commercial availability and because it is the reagent of choice in several commercial solvent extraction plants. Synergistic combinations with other dialkylphosphoric acids and some reagents which give opposite or antagonistic effects are described in later sections (4.2, 5.0).

A variety of neutral compounds can be used in synergistic reagent combinations, e.g., trialkylphosphates $(RO)_3PO$, dialkyl alkylphosphonates $(RO)_2RPO$, alkyl dialkylphosphinates $(RO)R_2PO$, and trialkylphosphine oxides R_3PO. When such a series is prepared with identical alkyl groups, e.g., n-butyl, the effectiveness increases in the order listed. This pattern has previously been observed (24,25) when the neutral reagents alone were used to extract uranium from suitable solutions. Again, discussions in this section of the report are limited to available reagents except for a few comparative tests with tributylphosphine oxide. Further attention is given to other commercial and research-sample-only neutral reagents in a later section (4.1).

3.1 Effect of Composition of Organic Phase

Effects of reagent concentration and diluent are discussed in this section. Most of the uranium extractions were made from an aqueous medium of 1.5 M sulfuric acid. Extraction coefficients from dilute (<1 g U/l), high-pH solutions are frequently too high for accurate analysis of the raffinate phase by the fluorescence method, although a few of these high coefficients are included. The lower coefficients from the high-acid solution afford a better basis for reagent comparison.

3.1.1 Reagent Concentrations

When a synergistic additive is added in increasing amounts to D2EHPA, uranium extraction coefficients first rise and then fall. Table 3.1 and Figs. 3.1 and 3.2 show behavior of D2EHPA combinations with TBPO, DBBP and TBP. For D2EHPA in the range

Table 3.1 Effect of Reagent Concentrations in the Synergistic Extraction of Uranium from 1.5 M Sulfuric Acid

Aqueous phase: 1.5 M H_2SO_4, 0.004 M U(VI)
Organic diluent: kerosene
Agitation: 10 min (wrist-action shaker)
Phase ratio, aqueous:organic = 1
Temperature: TBP and TBPO tests, 25-26°C; DBBP tests, 32-34°C

Synergistic Additive	M	Uranium Extraction Coefficient with Di(2-ethylhexyl)-phosphoric Acid (M)				
		0	0.05	0.1	0.2	0.4
None	-	-	0.5	3	9	40
Tributylphosphate (TBP)	0.05	0.00004	1.6	10	29	-
	0.1	0.00005	2.3	12	33	140
	0.2	0.00013	2.2	12	38	-
	0.3	-	-	9	26	130
	0.4	-	-	-	23	90
	0.5	0.0002	1.1	6	-	70
Dibutyl butylphosphonate (DBBP)	0.02	-	-	15	-	-
	0.05	0.0001	5.1	26	70	-
	0.08	-	-	31	-	-
	0.1	0.00009	5.1	30	98	-
	0.2	0.0001	4.1	24	90	-
	0.5	0.0007	1.3	8	36	-
Tributylphosphine Oxide (TBPO)	0.025	-	23	140	310	-
	0.05	-	25	190	530	-
	0.1	*	13	120	660	-
	0.2	-	-	50	280	-

*3rd phase, 48% extracted.

0.05-0.4 M TBPO gave the most synergistic enhancement (50--70-fold) and TBP the least (~4-fold), with DBBP being intermediate (~10-fold).

At a constant level of neutral reagent, the uranium extraction coefficient varied nearly with the square of the uncomplexed D2EHPA concentration and, in this respect, the behavior of the synergistic combination is similar to that of D2EHPA alone, as examined by Baes, Zingaro, and Coleman. (22) The D2EHPA was shown to be dimeric in n-hexane solutions in the range 0.025-2.1 M. Later experiments by Baes and Baker (23) showed dimerization in n-octane down to at least 0.001 M. Extractions of uranium to the point where the D2EHPA extract contains from 5-10 moles of acid reagent for each mole of uranium were adequately described by the following equation:

$$UO_2^{++} + 2(HX)_2 \rightleftharpoons UO_2X_4H_2 + 2H^+ \qquad (1)$$

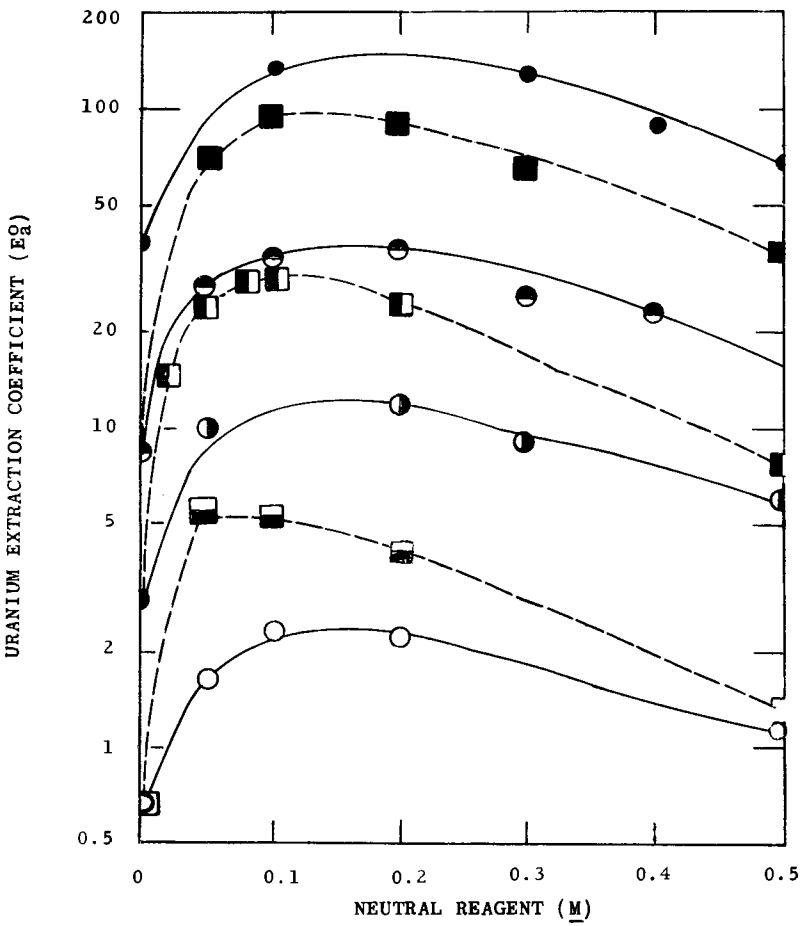

Fig. 3.1 Effect of Reagent Concentration on Synergistic Uranium Extractions.
Aqueous phase: 1.5 M H_2SO_4, 0.004 M U(VI).
Organic phase:

	TBP	DBBP
0.05 M D2EHPA	○	◒
0.1	◑	◧
0.2	◓	■
0.4	●	—

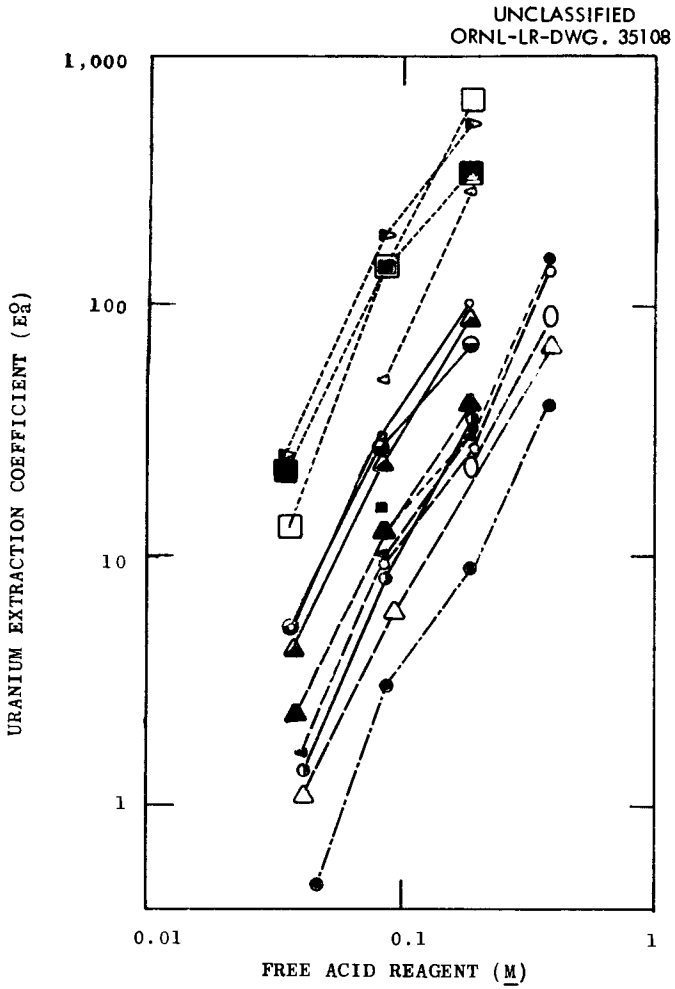

Fig. 3.2 Effect of Uncomplexed D2EHPA Concentration on Uranium Extraction Coefficient.
Aqueous phase: 1.5 M H_2SO_4, 0.004 M U(VI).
Neutral reagent used with D2EHPA in kerosene diluent:

M	TBP	DBBP	Bu_3PO
0.02	–	▪	■
0.05	◂	◒	▷
0.1	●	○	□
0.2	▲	△	▽
0.3	○	—	-
0.4	○	—	-
0.5	△	◑	-

D2EHPA alone – ——●——

where $(HX)_2$ represents the D2EHPA dimer. Thus, under conditions of these low uranium loadings in the organic phase, the uranium extraction would vary with the second power of the concentration of uncomplexed reagent in the organic phase and calculation of this concentration from analytical data showing uranium extraction necessitates subtracting 4 moles of D2EHPA for each mole of uranium from the initial reagent. Such calculations have been made with the data of Table 3.1 and these show a very close agreement with second-order dependence on the D2EHPA. This is shown by Fig. 3.2 in which the plot of the log of extraction coefficient vs. the log of the free D2EHPA concentration has a slope of 2 at each level of neutral reagent. In addition, at a particular D2EHPA level, the initial increase in uranium extraction coefficient shows a first-order dependence upon the concentration of neutral additive. These factors suggest the following complexing reaction

$$UO_2^{++} + 2(HX)_2 + N \rightleftharpoons UO_2H_2X_4N + 2H^+ \qquad (2)$$

where N is the neutral additive, e.g., TBP.

Baes and Baker (23) have examined the competing solvent interactions which cause the eventual decrease in extraction coefficient. Isopiestic molecular weight and infrared measurements show interaction between D2EHPA and tri(n-octyl)phosphine oxide (TOPO) in n-octane. The interactions represent the stepwise addition of two moles of TOPO to the D2EHPA dimer.

$$TOPO + (HX)_2 \rightleftharpoons (TOPO)(HX)_2 \qquad K = 100 \pm 50 \qquad (3)$$

$$TOPO + 1/2(HX)_2 \rightleftharpoons (TOPO)(HX) \qquad K = 30 \pm 5 \qquad (4)$$

These or similar reactions between D2EHPA and other neutral additives thus compete with the uranium complexing reaction (Eq. 2) and account for the maxima in the curves of Fig. 3.1.

The position of the maximum in each curve with a particular neutral reagent depended closely upon the absolute concentration of the neutral reagent and much less upon the concentration of acid reagent or upon any simple ratio of the two. The maximum was achieved with lower concentration of those neutral reagents which gave greatest enhancement, e.g., ~0.05 M TBPO, ~0.08 M DBBP and 0.1-0.2 M TBP. The slight shift of the maximum to higher concentration of neutral reagent when more acid reagent was added appeared to be consistent with the extraction reactions proposed (Eqs. 1-4).

Uranium extraction coefficients 100-fold greater were obtained when the DBBP-D2EHPA combination was tested in 0.5 M SO_4, pH 1 solution (Fig. 3.3). The concentration dependencies remained essentially unchanged, i.e., the curves peaked at about 0.08 M DBBP and the coefficients with 0.1 M D2EHPA were about 4 times higher than those with 0.05 M D2EHPA.

3.1.2 Diluent

Highest uranium extraction coefficients were obtained when aliphatic hydrocarbons, e.g., kerosene, nonane, hexane, were used

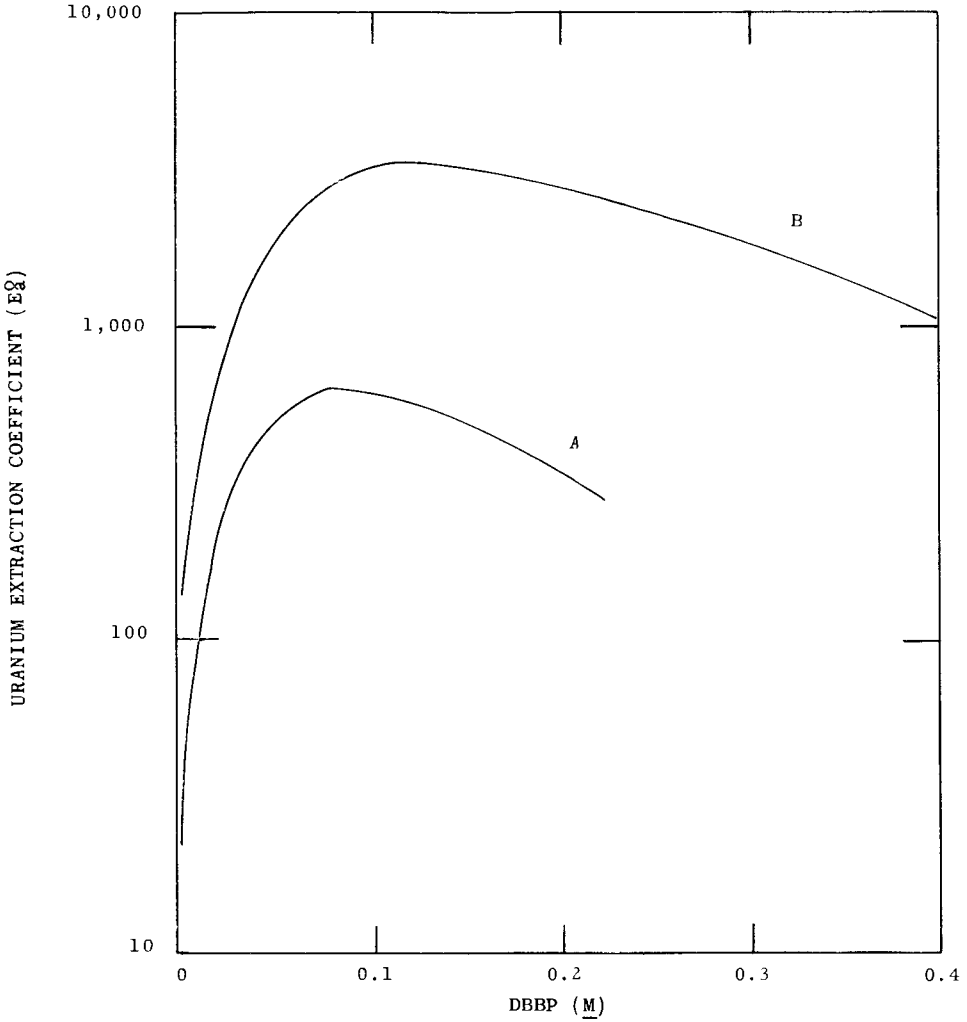

Fig. 3.3 Effect of Reagent Concentration on Synergistic Extraction. DBBP with A - 0.05 M D2EHPA, B - 0.1 M D2EHPA, in kerosene. Aqueous phase initially 0.5 M SO_4, pH 1, 0.004 M U(VI). Aqueous/organic phase = 1, 10 min agitation, 26°C.

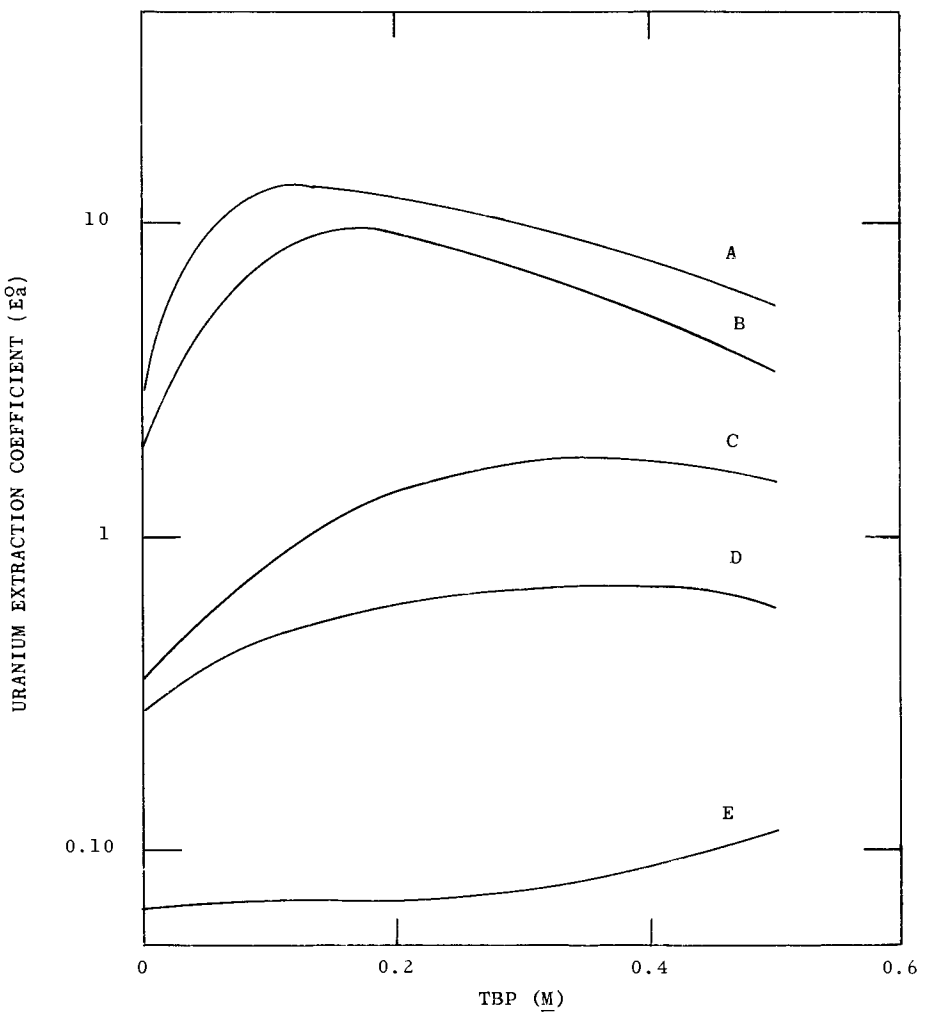

Fig. 3.4 Effect of Diluent on Synergistic Extraction. Organic Phase - 0.1 M D2EHPA + TBP in: A - kerosene, nonane, or Napoleum 470; B - hexane; C - carbon tetrachloride; D - benzene; E - chloroform. Aqueous phase initially 1.5 M H_2SO_4, 0.004 M U(VI). Aqueous/organic phase ratio = 1, 10 min agitation, 25-27°C.

as diluents. Carbon tetrachloride, benzene and chloroform were less effective in that order (Fig. 3.4). The initial slope of enhancement (E_a^o vs neutral additive) decreased as poorer diluents were used. Each curve except that with chloroform passed through a maximum.

3.2 Effect of Composition of Aqueous Phase

The range of uranium extraction ability available with various synergistic combinations allows their possible use in systems ordinarily difficult to extract, e.g., sulfate, phosphate. Some consideration has already been given to the effect of pH and sulfate level (3.1.1). These variables will be considered here in more detail and other systems, e.g., nitrate, chloride and phosphate will be examined.

3.2.1 pH Level

In synergistic extraction systems as in previous examinations of Dapex systems (1,2), uranium extraction increases with increasing pH level (Fig. 3.5). The rate of increase with the TBP- and DBBP-D2EHPA combinations is approximately the same as for D2EHPA alone and represents a fractional dependency between first and second power on pH, the usual behavior in systems where the hydrogen ion is involved in several equilibria, e.g., Eqs. 1 and 2, and the sulfate--bisulfate equilibria.

3.2.2 Sulfate Concentration

The effect of sulfate concentration, mentioned briefly in Sec. 3.1.1, was examined over the range 0.5 to 6.0 M and except for the synergistic enhancement of uranium coefficient, the TBP- and DBBP-D2EHPA combinations behaved similarly to D2EHPA alone (Fig. 3.6). In general, the coefficients decreased with increased sulfate, showing nearly a first order dependency on sulfate from 0.5 to 1.5 M and nearly second order in 1.5 and 6.0 M sulfuric acid and 0.5 to 1.5 M sulfate, pH 1 solution. Again, as with pH dependence, this range of sulfate dependency is consistent with equilibria in the sulfate system.

3.2.3 Nitrate, Chloride, and Phosphate Systems

As in extractions with D2EHPA alone, uranium extractions with D2EHPA-TBP from different aqueous solutions decreased in the order nitrate > chloride > sulfate>phosphate (Table 3.2 and Fig. 3.6). The factor of enhancement on additives of the TBP was nearly the same in each of these systems.

The extraction coefficient showed a different acid dependence for each acid, however. The dependence was near first order for HNO_3, first to second for H_2SO_4, second to third for HCl, and third to fourth for H_3PO_4, as shown by the slopes of the curves of Fig. 3.7.

Spot checks of the reversibility of these extractions were made in the hydrochloric and phosphoric acid systems. The paren-

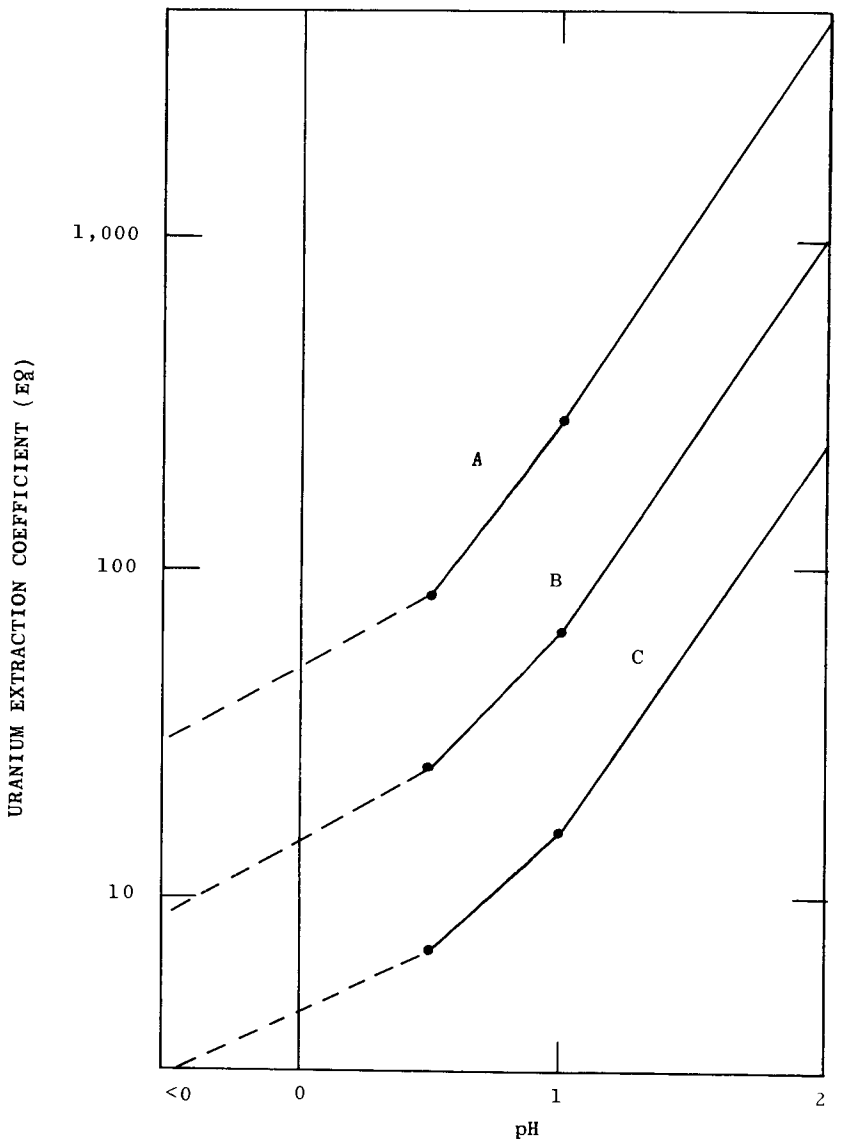

Fig. 3.5 Effect of Sulfate Concentration and pH on Synergistic Extraction. A, 0.1 M D2EHPA + 0.12 M DBBP; B, 0.1 M D2EHPA + 0.11 M TBP; C, 0.1 M D2EHPA; all in kerosene diluent. Aqueous phase: 1.5 M SO_4, 0.004 M U(VI) initially, (pH <0 = pH of unbuffered 1.5 M H_2SO_4). Aqueous/organic phase ratio = 1, 10 min agitation, 26°C.

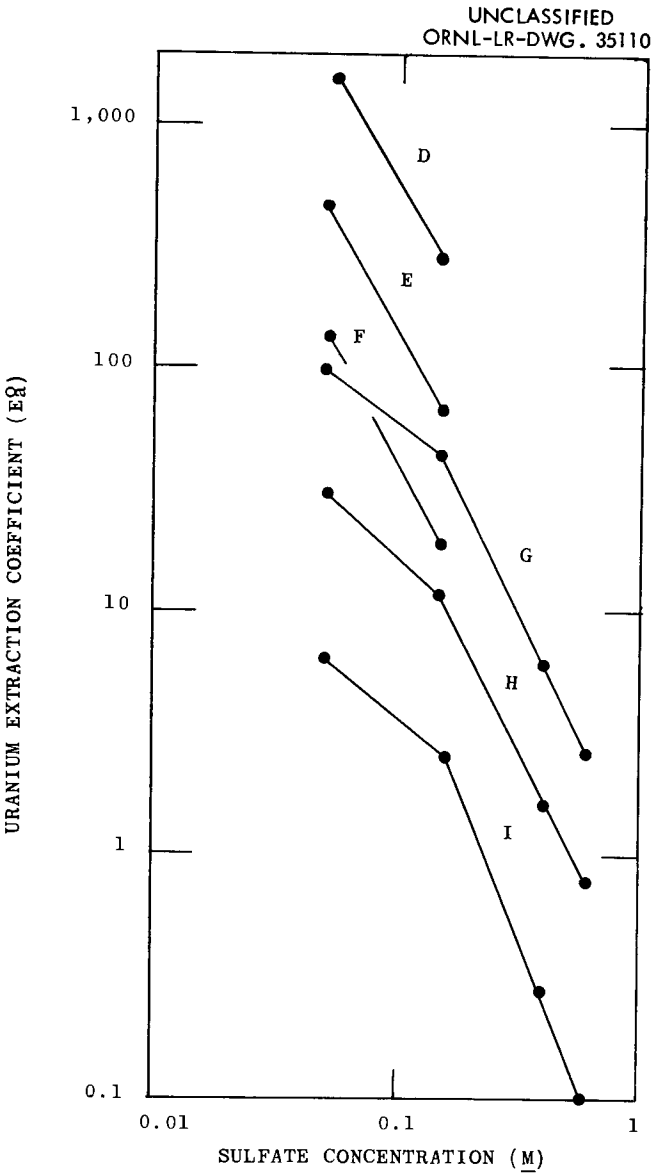

Fig. 3.6 Effect of Sulfate Concentration and pH on Synergistic Extraction. Aqueous phase initially at pH 1: D, 0.1 M D2EHPA + 0.1 M DBBP; E, 0.1 M D2EHPA + 1 M TBP; F, 0.1 M D2EHPA. Aqueous phase initially at pH of unbuffered H_2SO_4: G, 0.1 M D2EHPA + 0.1 M DBBP; H, 0.1 M D2EHPA + 0.1 M TBP; I, 0.1 M D2EHPA. All 0.004 M U(VI) initially in aqueous with kerosene diluent. Aqueous/organic phase ratio = 1, 10 min agitation, 26°C.

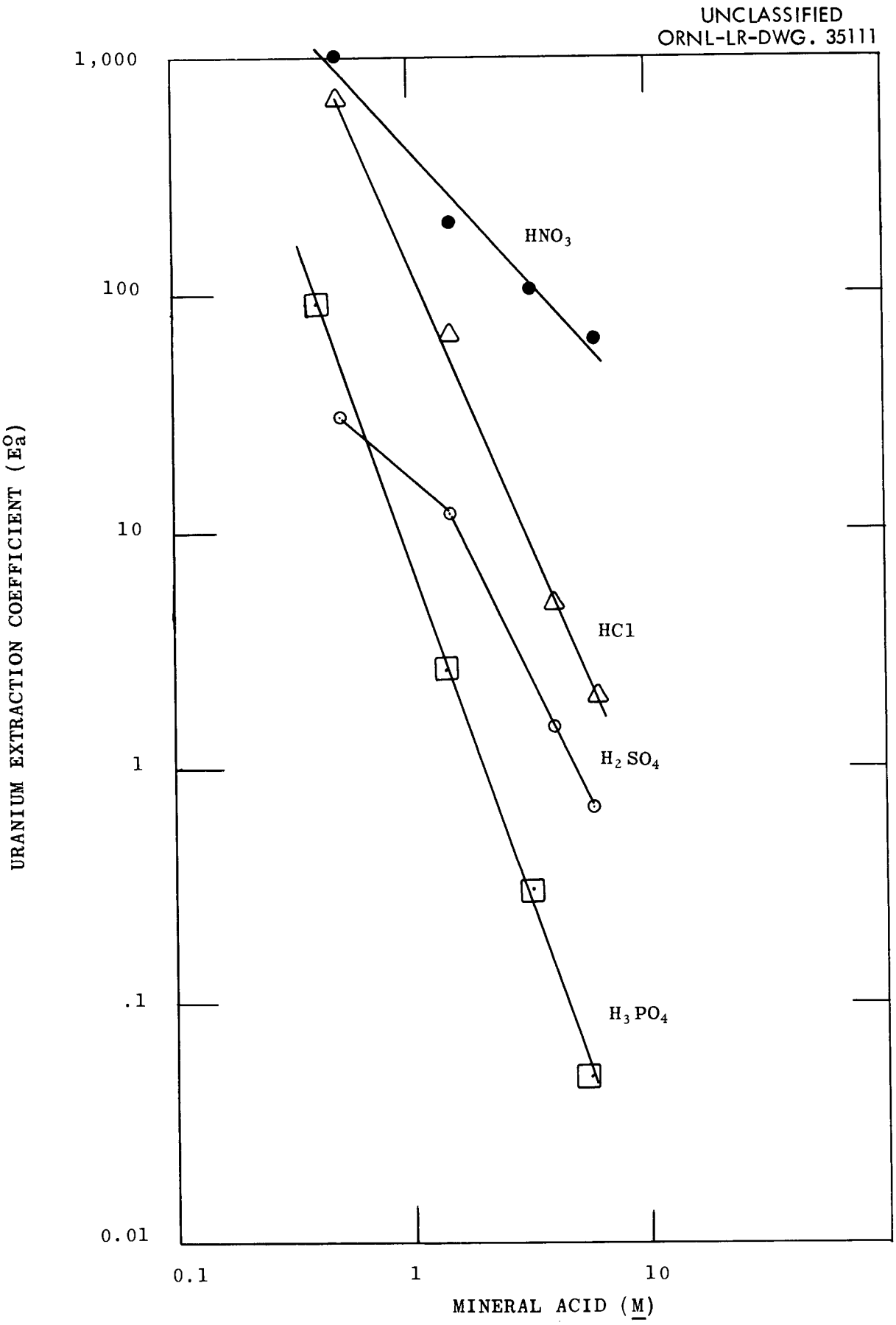

Fig. 3.7 Effect of Mineral Acid Concentration on Synergistic Extractions with 0.1 M D2EHPA-0.1 M TBP in kerosene. Initial aqueous phase = 0.004 M U(VI). Aqueous/organic phase ratio = 1, 10-min agitation, 26°C.

Table 3.2 Synergistic Extraction of Uranium from Nitric, Hydrochloric, and Phosphoric Acids

Organic extractant: 0.1 M di(2-ethylhexyl)phosphoric acid with and without 0.1 M tributyl phosphate in kerosene

Aqueous phase: 0.004 M U(VI) at the pH of the unbuffered acid, excepting 3.3 M and 5.3 M phosphoric acid in which the uranium is 0.0004 M

Agitation: 10 min (wrist-action shaker)

Room temperature

Phase ratio, aqueous/organic: 1

Aqueous Phase		Uranium Extraction Coefficient (E_a^o)			
Acid	M	0.1 M D2EHPA	0.1 M TBP	0.1 M D2EHPA + 0.1 M TBP	Enhancement Factor
HNO_3	0.5	240	0.08	1000	4
	1.5	70	0.5	200	3
	4.0	35	1.3	90	3
	6.0	15	1.2	65	4
HCl	0.5	140		700	5
	1.5	13		70	5
	4.0	0.8		5	6
	6.0	0.15 (0.2)[a]		2 (2)[a]	10
H_3PO_4	0.4	25		90	4
	1.4	0.8 (0.5)[a]		2.5[b]	3
	3.3[d]	0.11 (0.06)[a]		0.3[c] (0.25)[a]	3
	5.3[e]	0.008 (0.01)[a]		0.03 (0.05)[a]	3

[a] Estimated from stripping coefficient ($E_a^o = 1/S_o^a$).

[b] At pH 1, $E_a^o = 3.4$; vs 1.3 without TBP.

[c] At pH 1, $E_a^o = 0.6$, at pH 2, $E_a^o = 1.4$; while without TBP $E_a^o = 0.16$ and 0.4, respectively.

[d] With 0.25 M D2EHPA--0.09 M TBPO, $E_a^o = 16$ from 3.3 M H_3PO_4.

[e] With 0.4 M D2EHPA--0.14 M TBPO, $E_a^o = 3$ from 50 M H_3PO_4.

thetical data in Table 3.2 show extraction coefficients calculated from corresponding stripping data (cf. Table 3.7). The coefficients for the forward and back reactions were in fair agreement.

A few extractions with a TBPO-D2EHPA combination from 3.3 and 5.3 M phosphoric acid (corresponding to concentrations in commercial process phosphoric acid) show uranium extraction coefficients greater than 1 (Table 3.3). With 0.25 M D2EHPA--0.09 M TBPO, the coefficient was 16 from 3.3 M acid, and coefficients of near 3 were obtained with 0.4 M D2EHPA--0.14 M TBPO from 5.3 M H_3PO_4. These concentrations of TBPO were close to the enhancement maximum, giving enhancements of 30- to 40-fold.

Table 3.3 Uranium Extraction from Phosphoric Acid Solution

Uranium(VI) concentration: 0.0004 M (100 ppm)
Kerosene diluent
Agitation: 10 min (wrist-action shaker)
Room temperature
Aqueous/organic phase ratio: 1

Phosphoric Acid (M)	D2EHPA (M)	Tributylphosphine Oxide (M)					
		0	0.05	0.09	0.14	0.18	0.37
3.3	0.25	0.44	-	16	-	-	-
5.3	0.1	0.008	0.6	0.3	-	-	0.2
	0.3	0.08	1.4	2.0	2.3	2.0	-
	0.4	0.12	1.6	2.1	2.9	2.9	-

3.3 Effect of Uranium Concentration

Uranium extraction isotherms contrasting the behavior of D2EHPA alone, D2EHPA-TBP and D2EHPA-DBBP are shown in Fig. 3.8. When the concentration of uranium in the organic phase increases significantly the effective concentration of the free extractant decreases, and the extraction coefficient decreases. While the curve for D2EHPA alone was close to the usual shape, those of the synergistic combinations were initially steeper and straighter, then began to bend more abruptly than is usual and continued to rise only slightly. The resulting pronounced "knee" in each curve was in the region of a uranium-to-D2EHPA mole ratio of 1/4, suggesting enhanced stability of the complex described in Eq. 2. Eventual saturation of the organic phase occurred at a level corresponding to a uranium-to-D2EHPA ratio of 1/2.

The principal significance of synergistic combinations in process use stems from the higher coefficients obtained at the raffinate end of the extraction apparatus. The higher coefficients at the raffinate end allow reduction of uranium to a lower level in the waste stream in a given number of stages and also permit useful extraction from liquors which might ordinarily be difficult to treat. There will be significant increase of loading at the product end only in cases of extraction so difficult that operation does not reach the "knee" at the extraction isotherm.

The data of Table 3.4 from which the isotherms were drawn show serious depression of the uranium coefficient due to the low concentration of the free extractant, when the uranium level in the organic phase exceeds 1 g/liter or a uranium-to-D2EHPA mole ratio of 1/25. Hence, uranium extraction coefficients intended for intercomparison should be measured at low levels of uranium in the extractant phase.

Uranium extractions under conditions where the D2EHPA-to-uranium ratio was never lower than 250 showed the characteristic

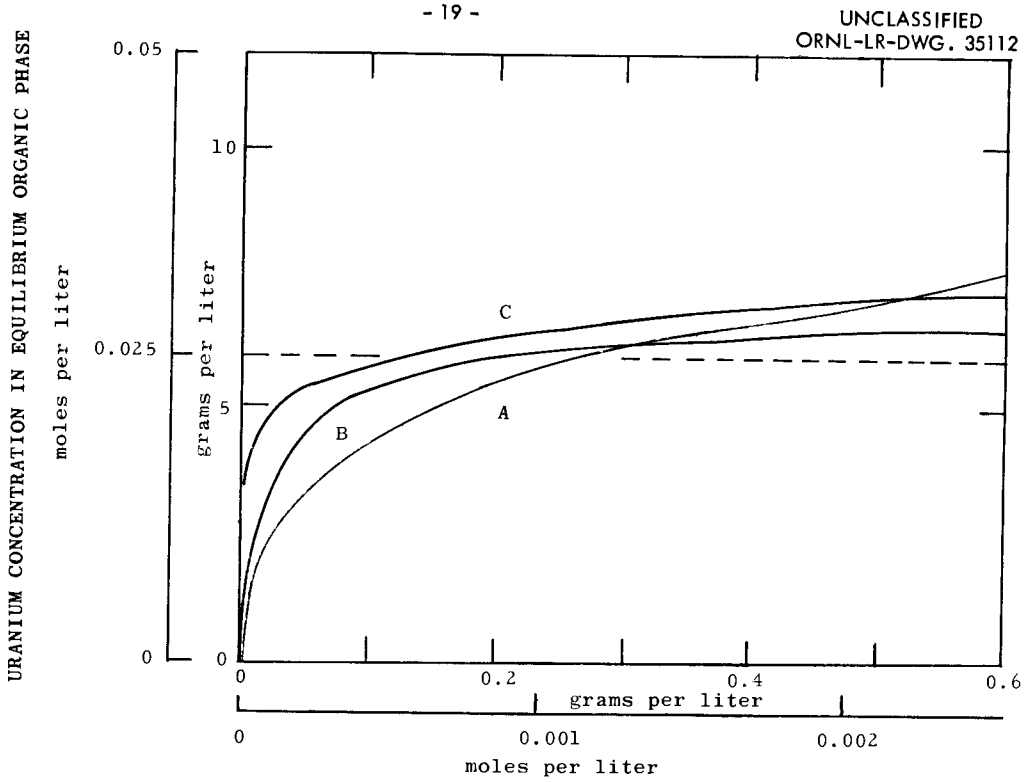

Fig. 3.8 Uranium Extraction Isotherms. A, 0.1 M D2EHPA; B, 0.1 M D2EHPA + 0.1 M TBP; C, 0.1 M D2EHPA + 0.1 M DBBP; all in kerosene. Aqueous phase: initially 0.005 M U(VI), 0.5 M SO_4, pH 1.3. 10-min agitation, 26°C.

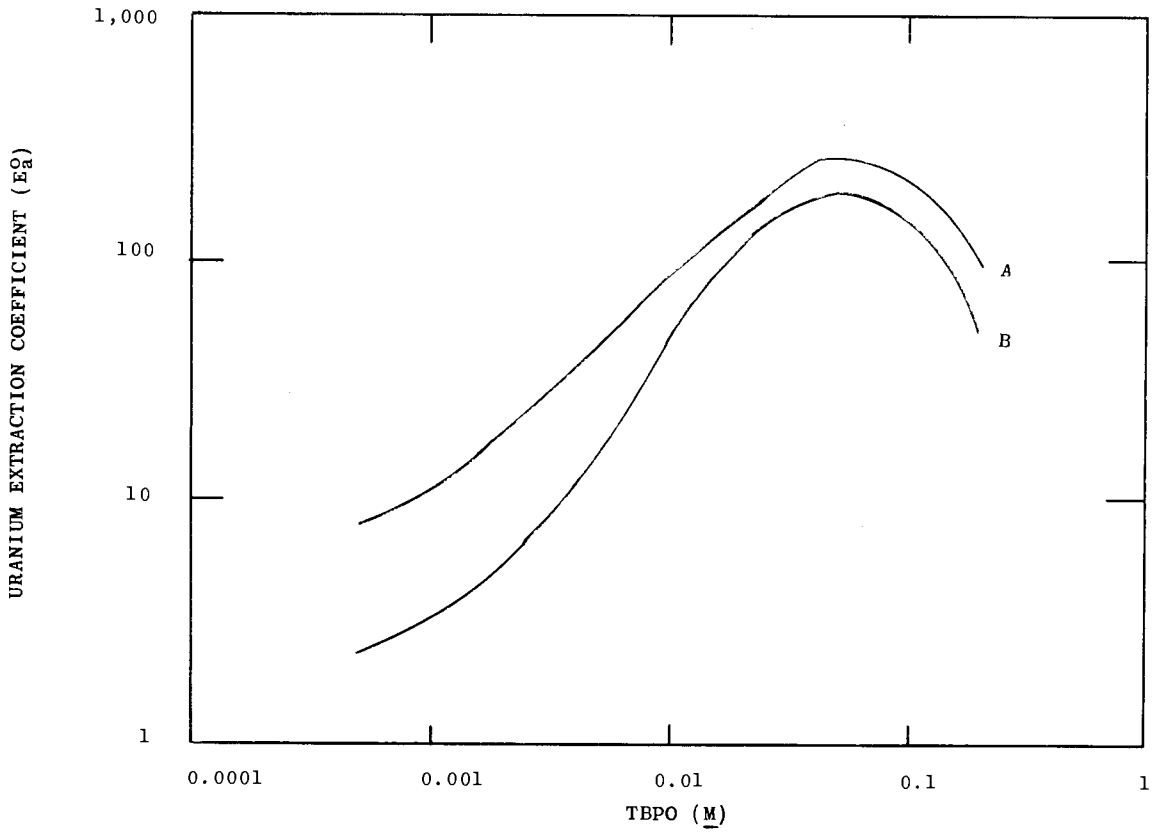

Fig. 3.9 Effect of Uranium Concentration on Synergistic Uranium Extractions. Aqueous phase: initially 1.5 M H_2SO_4 and A, 0.0004 M U(VI) or B, 0.004 M U(VI). Organic phase: 0.1 M D2EHPA and TBPO in kerosene. Aqueous/organic phase ratio = 1, 10-min contact time, 26°C.

Table 3.4 Uranium Extraction Isotherms

Aqueous phase: 0.005 M U(VI), 0.5 M SO_4, pH 1.3
Organic phase: 0.1 M D2EHPA in kerosene, modified as indicated
Agitation: 2 min (wrist-action shaker)

No Additive			0.11 M TBP			0.1 M DBBP		
U (g/liter)			U (g/liter)			U (g/liter)		
Aqueous	Organic	E_a	Aqueous	Organic	E_a	Aqueous	Organic	E_a
0.003	0.65	217	0.001	0.55	550	0.001	2.2	2200
0.0086	1.1	128	0.002	1.2	600	0.004	3.3	825
0.030	2.4	80	0.007	2.4	340	0.012	4.5	375
0.073	3.1	42	0.022	3.6	165	0.083	5.7	70
0.14	4.4	31	0.065	5.0	77	0.37	6.8	18
0.22	5.7	26	0.27	6.1	23	1.1	7.5	7
0.36	6.9	19	0.59	7.3	12			
			1.2	7.3	6			

curve of coefficient vs. neutral reagent (Fig. 3.9). Curves for the initial aqueous concentration of 100 ppm and 1000 ppm uranium both passed through a maximum extraction with 0.1 M D2EHPA at 0.08 M TBPO. The curves coincided at their maxima when the coefficients were corrected for D2EHPA-uranium loading as described in Sec. 3.1.1, but there remained a difference at low TBPO levels. Here, however, the TBPO-to-uranium ratio was also low, possibly preventing full utilization of the synergistic potential.

3.4 Effect of Temperature

The uranium extraction ability of synergistic combinations near the enhancement maximum decreased with increasing temperature (Fig. 3.10, cf. Table 4.1). For many of the reagents, the log of the coefficient dropped linearly with temperature by a factor of one-half in each 15°C interval over the range 25-50°C. This is to be contrasted with a drop by one-half in 25°C with D2EHPA alone, and in 10°C with trioctylphosphine oxide alone. The data, with TBP and DBBP, fit the empirical equation

$$\log E_{T_2} = \log E_{T_1} - 0.0207(T_2 - T_1) \qquad (5)$$

3.5 Extraction of Other Metal Ions

Vanadium(IV), aluminum, and molybdenum sulfates showed little if any enhancement of extraction coefficient on addition of neutral phosphorus compounds to D2EHPA (Table 3.5). With iron (III), titanium, and thorium sulfates, either the extraction

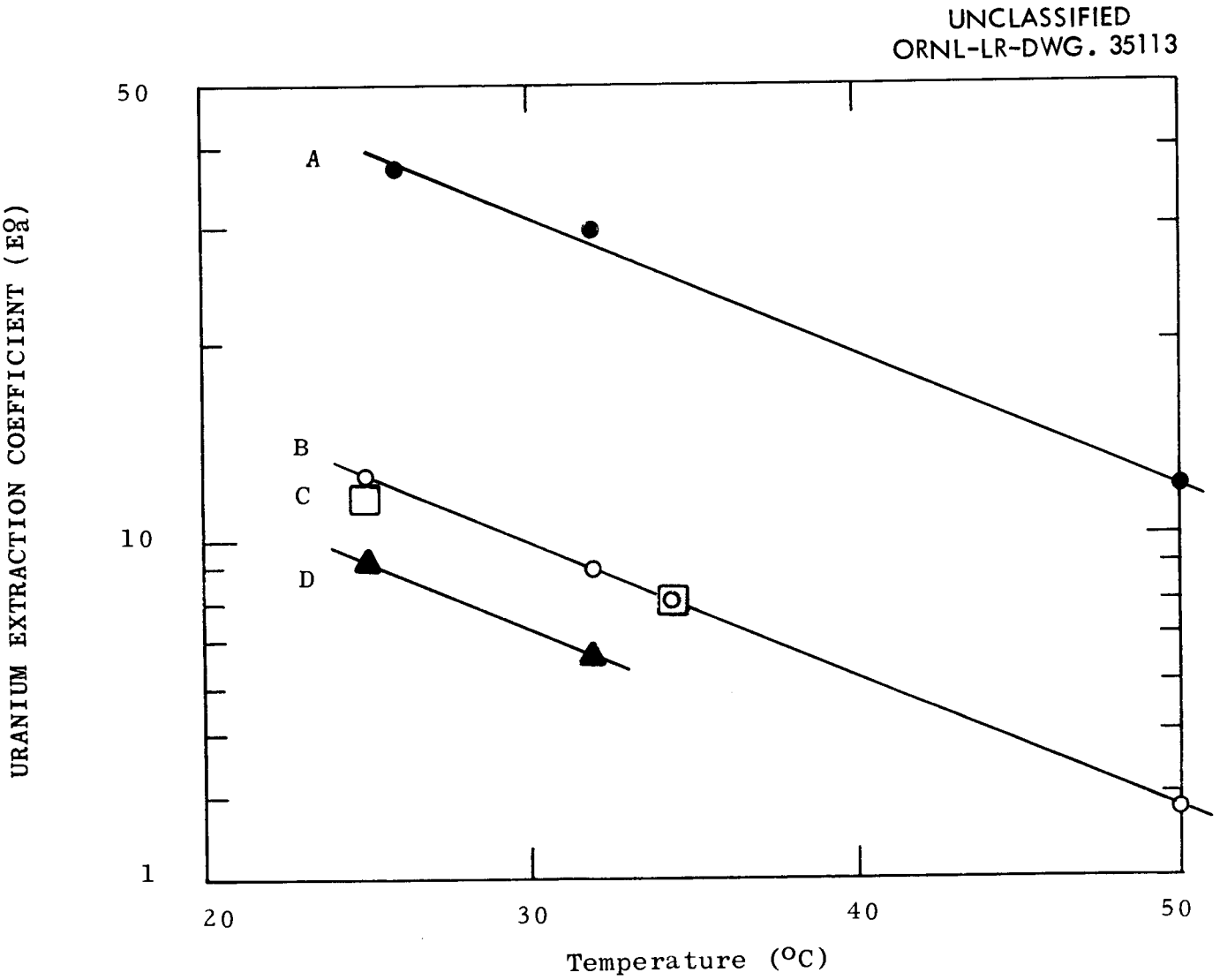

Fig. 3.10 Effect of Temperature on Extraction With Synergistic Reagent Combinations. Aqueous phase: 1.5 M H_2SO_4, 0.004 M U(VI). Organic phase: 0.1 M D2EHPA in kerosene, synergistic additive as indicated - A, 0.1 M DBBP; B, 0.1 M TBP; C, 0.2 M TBP; D, 0.05 M TBP. Aqueous/organic phase ratio = 1, 10-min agitation.

Table 3.5 Extraction of Metals Other than Uranium by D2EHPA and D2EHPA Plus Neutral Reagents

Aqueous phase: 0.01-0.02 M metal ion, 0.3-0.5 M SO_4, pH 1.2-1.4
Organic phase: 0.1 M D2EHPA in kerosene modified as indicated
Temperature: 24-26°C

Phase Ratio (a/o)	Contact[a] Time (min)	Metal Ions Individually	Extraction Coefficient (E_a^o) D2EHPA Alone	D2EHPA + 0.1 M TBP	D2EHPA + 0.1 M DBBP
1/1	30	V(IV)	0.8	-	0.8
		Al	0.01	0.01	0.01
		Mo	3.4	2.5	4.9
		Fe(III)	3.1	2.3	1.7
		Ti	5.9	-	2.5
		Th	1.0	0.6	-
		U(VI) + Fe(III)			
1/5[b]	10	U	90		1700
		Fe	0.33		0.14
	1000	U	80		1400
		Fe	>50		25
5/1[c]	10	U	2.8		2.5
		Fe	0.27		0.035
	1000	U	2.8		2.5
		Fe	0.25		0.016

[a]Wrist-action shaker.
[b]Mole ratio, U_{org}:D2EHPA at equilibrium, 1:24.
[c]Mole ratio, U_{org}:D2EHPA at equilibrium, 1:2.7 with D2EHPA alone, 1:2.9 with synergistic combination.

coefficients or the extraction rates were decreased. The ability of iron(III) to compete with uranium extraction was considerably less with D2EHPA-DBBP than with D2EHPA alone, at both low and high loading. Thus, the selectivity as well as the extraction power for uranium is enhanced with the synergistic extractant, with respect to iron, and probably also with respect to the other metals which showed little or no enhancement when tested individually.

Extraction of uranium(IV) from 0.5-6 M hydrochloric acid was not enhanced by addition of 0.1 M TBP to 0.1 M D2EHPA (Fig. 3.11). The extraction coefficient of uranium(IV) with or without the neutral reagent was about 5 times higher than that of uranium(VI) from similar solutions when extracted with 0.1 M D2EHPA alone, and was about the same as the synergistically enhanced uranium (VI) coefficient obtained with 0.1 M D2EHPA--0.1 M TBP.

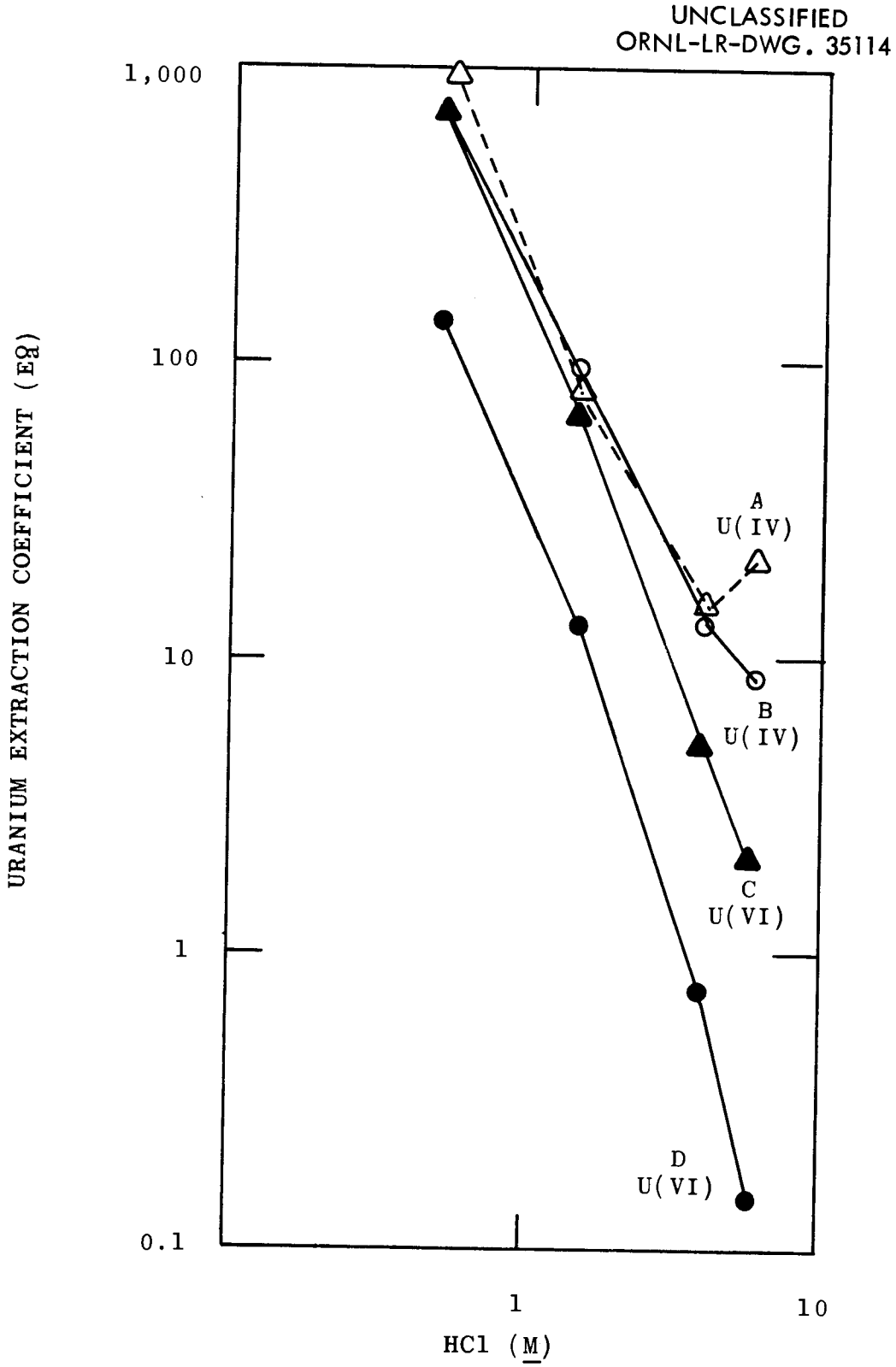

Fig. 3.11 Comparison of Extraction of Uranium(IV) and Uranium(VI). Organic phase: 0.1 M D2EHPA alone, B and D; and with 0.1 M TBP, A and C, all in kerosene. Initially 0.004 M U in aqueous phase. Aqueous/organic phase ratio = 1, 10-min agitation, 26°C.

The extraction of plutonium(VI) from sulfuric acid solution and of both plutonium(IV) and plutonium(VI) from nitric acid solution showed some synergistic enhancement on addition of phosphine oxide to D2EHPA. (26)

3.6 Stripping Extracted Metals from the Organic Phase

Methods for stripping uranium and other extracted metals from pregnant D2EHPA extractant were discussed in a previous report. (2) The generally preferred method is to strip with sodium or ammonium carbonate solution.[1] Miscibility of the resulting dialkylphosphate salt is maintained by modification of the kerosene diluent either with one of the synergistic additives or with a long-chain alcohol. The alkaline stripping is effective in the presence of either. The minimum concentration required for miscibility differs with different additives, and also varies as a linear function of D2EHPA concentration over the range 0.1 to 0.4 M (Table 3.6). A method for determining the modifier concentration present is included in the Appendix.

Alternatively, if special circumstances bar alkaline stripping, stripping can be accomplished by concentrated acids in direct reversal of the extraction reaction.[2] As expected, amenability to acid stripping decreases in direct proportion to increased extraction power, so that acid stripping of the synergistic extractants is feasible only if the effect of hydrogen ion is reinforced by strong aqueous complexing, as with hydrofluoric or phosphoric acid (Table 3.7).

3.7 Distribution of Synergistic Reagents to Aqueous Phases

Some compounds meeting process requirements of low loss to aqueous solutions are commercially available for use in synergistic reagent combinations. Loss of D2EHPA from a 0.1 M solution in kerosene to several acidic uranium liquors of about 0.5 M $SO_4^=$, pH 1 was <1 ppm, to 10 M HCl the loss was <2 ppm, and to 1 M Na_2CO_3 the loss increased only to 40-50 ppm (27). Neutral reagents can have low loss rates also, depending to some degree on their molecular weight. While DBBP and TBP have distributions of ~25 to acidic and alkaline liquors from 0.1 M solutions, DHHP and DAAP have even lower losses to the acidic liquor (<5 ppm). In extraction from a liquor containing, e.g., 1 g U_3O_8 per liter, this level would correspond to a loss of but 0.005 lb of reagent per lb of uranium recovered. Losses to alkaline solutions, not measured, would presumably be less than the 25 ppm shown by DBBP and TBP.

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[1] Reference (2), p. 32.

[2] Reference (2), p. 47.

Table 3.6 Concentrations of Modifiers Required For Preventing Third Phase Formation with 10% Na_2CO_3

Minimum* modifier concentration
w/v % = A + B M, moles/liter = A' + B' M

where M = molarity of D2EHPA, between 0.1 and 0.4 (except didecyl decylphosphonate, 0.1-0.3 only) in kerosene, and A and B are the tabulated parameters.

Modifier	Temp. (°C)	Minimum Modifier Concentration (w/v %) A	B	(moles/liter) A'	B'
Tributylphosphate	28	1.7	5.3	0.063	0.20
Dibutyl butylphosphonate	28	0.8	5.2	0.034	0.21
Diamyl amylphosphonate	30	1.3	4.6	0.045	0.16
Dihexyl hexylphosphonate	29	1.6	3.7	0.048	0.11
Didecyl decylphosphonate	30	5.2	5.8	0.104	0.12
Dibutyl chloromethylphosphonate	29	0.9	5.1	0.037	0.21
Di(2-ethylhexyl) chloromethyl-phosphonate	28	3.3	4.2	0.093	0.12
Butyl dibutylphosphinate	28	0.3	6.2	0.011	0.26
Butyl dihexylphosphinate	27	0.5	3.1	0.016	0.11
Tributylphosphine oxide	31	0.2	9.0	0.007	0.41

*It should be noted that the modifier requirement as listed in Table 3.6 is the measured critical concentration for miscibility of NaR_2PO_4 at the temperature specified and in the absence of any other solute. The minimum operating requirement in a process will be this critical concentration plus a reasonable margin to cover variations. Besides being affected by variations in concentrations, temperature, etc., miscibility will also be affected by the amount of uranium still in the organic phase when stripping is partially completed. For example, in stripping 0.1 M di(2-ethylhexyl)phosphoric acid/kerosene, loaded to 6 g U per liter, with 10% Na_2CO_3, the critical concentration of TBP required was found to increase as follows:

g U per liter organic:	0	0.03	0.09	0.17	0.19	0.28
w/v % TBP required:	2.2	2.2	2.3	2.4	2.5	2.7

4.0 TESTING OTHER SYNERGISTIC URANIUM EXTRACTION REAGENT COMBINATIONS

4.1 Other Combinations of Neutral Organophosphorus Compounds with D2EHPA

As the data of Table 4.1 show, D2EHPA, TBP, DBBP and TBPO are not the only organophosphorus compounds which can be used to achieve

Table 3.7 Effect of Synergism on Stripping D2EHPA with Acids

Organic phase: D2EHPA in kerosene, modified as indicated, containing 2.6 g U(VI) per liter
Temperature: 25-29°C
Aqueous/organic phase ratio: 1
Contact time: 10 min (wrist-action shaker)

	Uranium Stripping Coefficient (S_a^o)			
	0.1 M D2EHPA		0.2 M D2EHPA	
Stripping Agent	No Additive	0.1 M TBP	No Additive	0.1 M TBP
9 M HCl	35	0.4	11	0.3
12 M HCl	25	1	11	0.9
3 M H_2SO_4	3	0.4	0.6	0.1
6 M H_2SO_4	14	2	4	0.6
3.3 M H_3PO_4	15	4	-	1
5.3 M H_3PO_4	100	20	20	6
0.5 M HF	1	0.3	-	-
1.0 M HF	3	1	-	-
3.0 M HF	30	10	-	-
6.0 M HF	90	70	-	-

such a synergistic enhancement. All the neutral organophosphorus compounds tested, with the exception of the aromatic phosphates, trichlorooctyl- and tri(2-ethylhexyl)phosphate, enhanced the extraction coefficient at least by a factor of 2. The degree of the effect varied both with the type of the reagent and its structure. For example, in the series of phosphonates, the straight-chain compounds, dibutyl butyl, diamyl amyl, dihexyl hexyl, didecyl decyl, and dibutyl chloromethyl, all had coefficients higher than those shown by the compounds having the branched 2-ethylhexyl, hydroxy-2-ethylhexyl, cyclohexyl or aromatic side chains. Similar effects of branching were apparent in tests with phosphites, phosphates and phosphine oxides. The tetraalkyl diphosphonates showed no branching effects and gave about the same enhancement as the straight-chain dialkyl alkylphosphonates.

The tests described above were performed at only one concentration-level of neutral reagent, and the synergistic advantages observed were not optimum for all of the reagent combinations in Table 4.1. (It will be recalled that the data of Fig. 3.1 obtained with TBP and DBBP showed that the concentration of neutral additive was critical in determining the maximum synergistic effect, the critical concentration differing with the different additives.) Accordingly, several of these reagents were examined in more detail with respect to effect of reagent concentration and the data are plotted on Fig. 4.1. The curves for TBP and DBBP from Fig. 3.1 are repeated for comparison. Apparently, the shape of the curve and the concentration of

Table 4.1 Testing Other Neutral Reagents with D2EHPA for Synergistic Uranium Extraction Ability

Aqueous phase: as indicated with 0.004 M U(VI)
Organic phase: 0.1 M D2EHPA, 0.1 M additive, kerosene diluent
Agitation: 10 min (wrist-action shaker)
Aqueous/organic phase ratio = 1

Neutral Compound	Batch No.	Source[a]	U Extraction Coefficient (E_a^o) 0.5 M SO_4, pH 1 27°C	1.5 M H_2SO_4 25-27°C	1.5 M H_2SO_4 50°C
None			110	3	~1.5
Phosphites					
Tri-n-butyl (83%)	OP-85	VC		12	4.5
Tri(2-ethylhexyl) (92%)	OP-83	VC	330	7	3.0
Di-n-hexyl[b]	OP-325	L		25	
Phosphates					
Tri-n-butyl (TBP)	OP-338	CS	470	10	3.8
Tri-iso-butyl	OP-342	E, V	450	9	
Tri(2-methylbutyl)	OP-397	E	400	10	
Tri(2-ethylhexyl)	OP-210	C	270	5	2.0
Tri-n-amyl	OP-378	ORNL[c]		10	3.7
Tricresyl	OP-333	ORNL[c]		2	1.5
Triphenyl	OP-322	ORNL[c]		5	3.1
Tri(terbutylphenyl)	OP-328	L		4	
Triallyl	OP-351	S	600	12	
Trioctylchloro	OP-369	V	110	3	
Phosphonates					
Di-n-butyl n-butyl (DBBP)	OP-306	VC	1700	30	12
Diamyl amyl (DAAP)	OP-	S	2000	50	
Di-n-hexyl n-hexyl (DHHP)	OP-383	S	2200	45	
Di-n-decyl n-decyl	OP-	S	600	40	
Di-2-ethylhexyl 2-ethylhexyl	OP-162	VC	900	17	5
Di-n-butyl chloromethyl	OP-319	V		30	9
Di-n-butyl cyclohexyl	OP-347	S		9	
Di(2-ethylhexyl) chloromethyl	OP-318	V		20	6
Di-n-butyl benzene	OP-101	V		14	5
Diethyl 2-ethyl-1-hydroxyhexyl	OP-171	VC		11	
Phosphinates					
n-Butyl di-n-butyl (BDBP)	OP-93	ORNL[c]	3500	80	25
n-Butyl di-n-hexyl	OP-313	W	3500	75	25
Phosphine oxides					
Tri-n-butyl (TBPO)	OP-300-C	ORNL		120	
Tri(2-ethylhexyl)	OP-299	ORNL	650	12	4
Tri-n-octyl (TOPO)	OP-289	ORNL, DPI	3500	70	30
Tri-n-decyl	OP-292	ORNL		75	25

Neutral Compound	Batch No.	Source[a]	U Extraction Coefficient (E_a^o) 0.5 M SO_4, pH 1 27°C	1.5 M H_2SO_4 25-27°C	1.5 M H_2SO_4 50°C
Phosphine oxides (cont'd)					
2-Phenylvinyl dioctyl	OP-398	K	4000	80	
Diphosphonates					
Tetra(2-ethylhexyl) trimethylene-diphosphonate	OP-25	VC	1350	30	
Tetra(2-ethylhexyl) ethylenedi-phosphonate	OP-168	VC	1000	20	
Tetrabutyl trimethylene-diphosphonate	OP-272	K	1000	20	
Tetrabutyl ethylene-diphosphonate	OP-273	K	1200	30	
Other compounds					
n-Octylbis(dimethylamido)-phosphate	OP-336	P		30	
Tridecylbis(dimethyl-amido)-phosphate	OP-337	P		30	
Tri(2-ethylhexyl)-phosphonoacetate	OP-312	W		12	5

[a] C = Carbide and Carbon Chemicals Co., New York.
CS = Commercial Solvents Corporation, Terre Haute, Ind.
L = Lubrizol Corp., Cleveland, Ohio.
P = Pennsylvania Salt Manufacturing Co., Philadelphia.
S = Shea Chemical Corporation, New York.
V = Victor Chemical Works, Chicago.
VC = Virginia-Carolina Chemical Corp., Richmond, Virginia.
W = Westvaco Mineral Products Division, Carteret, New Jersey.
E = Eastman Chemical Products, Inc., Kingsport, Tenn.
K = Prepared by Dr. G. M. Kosolapoff, Auburn Univ.
DPI = Distillation Products Industries, Rochester, New York.

[b] Di-n-hexylphosphite, $(RO)_2POH$. The hydrogen is not ionized sufficiently to be titrated satisfactorily with 0.1 M NaOH in 70% aqueous ethanol.

[c] Supplied by W. H. Baldwin, Chemistry Division, ORNL.

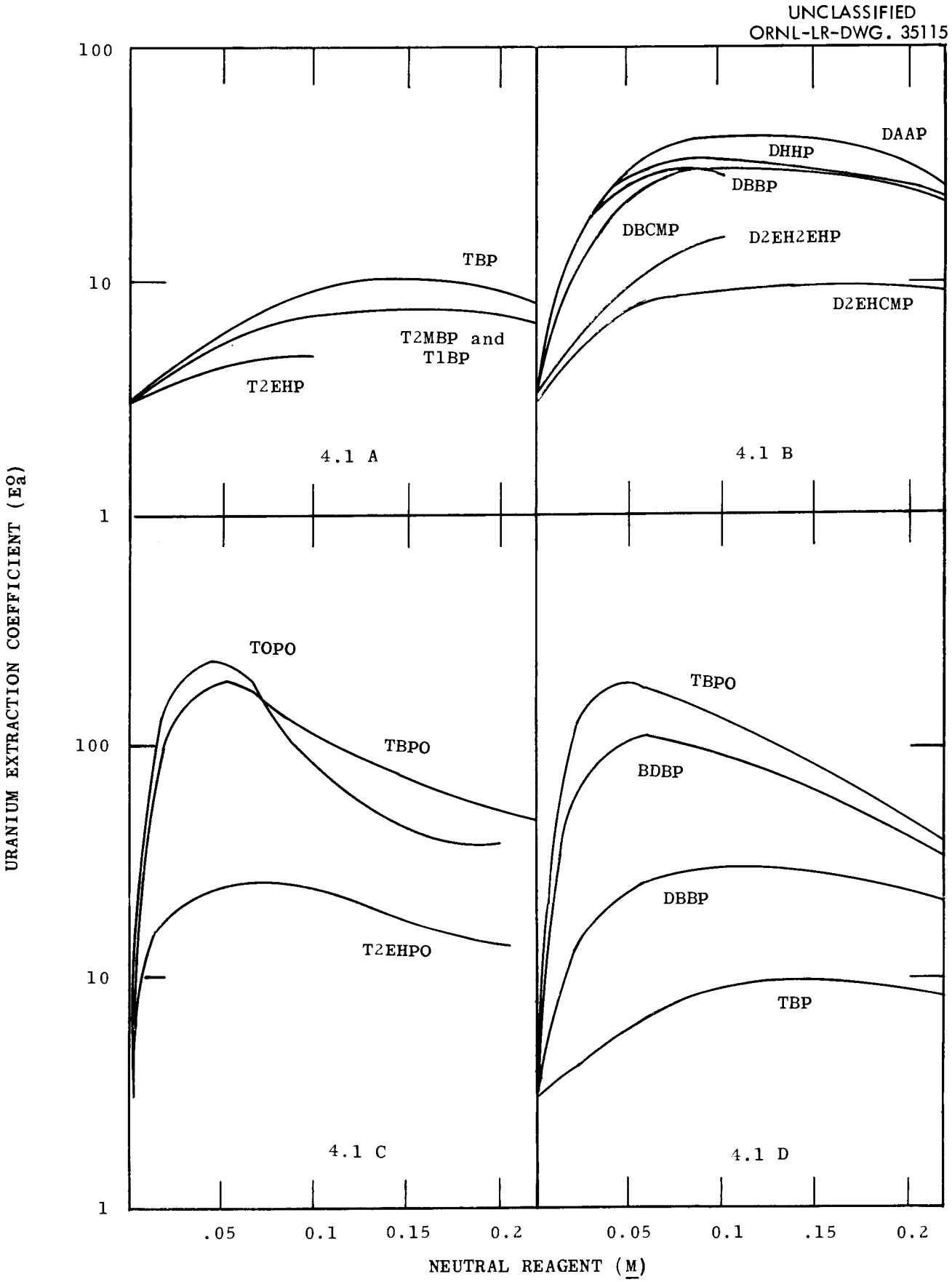

Fig. 4.1 Effect of Neutral Reagent Concentration on Synergistic Uranium Extraction. A - trialkylphosphates; B - dialkyl alkylphosphonates; C - trialkylphosphine oxide; D - various butyl derivatives; all with 0.1 M D2EHPA in kerosene. Aqueous phase: 1.5 M H_2SO_4, 0.004 M U(VI) initially. Aqueous/organic phase ratio = 1, 10-min agitation, 30°C.

additive giving the maximum extraction coefficient were dependent upon the type of compound rather than on its constituent side chains. Thus, the phosphine oxides had their peak extractions at ~0.05 M (Fig. 4.1c) even though the magnitude of the synergistic effect achieved differed. Similarly, ~0.1 M phosphonate or 0.1-0.2 M trialkylphosphate was required to give maximum extraction (Fig. 4.1b, 4.1a).

The results with butyl dibutylphosphinate were intermediate between those with tributylphosphine oxide and dibutyl butylphosphonate and thus complete the pattern established by these reagents and tributylphosphate (Fig. 4.1d).

4.2 Synergistic Reagent Combinations of Neutral Organophosphorus Compounds with Dialkylphosphoric Acids Other than D2EHPA

In addition to D2EHPA, the other dialkylphosphoric acids tested, di-n-octyl, di(3,5,5-trimethylhexyl)-, and bis(diisobutylmethyl)-, showed synergistic enhancement of uranium extraction coefficient when used in combination with neutral organophosphorus reagents (Table 4.2). The uranium extraction abilities of the

Table 4.2 Synergistic Extractions with Various Dialkylphosphoric Acids

Aqueous phase: 1.5 M H_2SO_4, 0.004 M U(VI)
Organic phase: 0.1 M Dialkylphosphoric acid, 0.1 M neutral additive, kerosene diluent
Aqueous/organic phase ratio: 1
Agitation: 10 min (wrist-action shaker)
Temperature: 25-28°C

	Extraction Coefficient (E_a^o)				
	Acid	Neutral Additive			
Dialkylphosphoric Acid	Alone	TBP	DBBP	BDBP	TBPO
n-Octyl	9	30	75	120	170
3,5,5-Trimethylhexyl	5	16	55	90	130
2-Ethylhexyl	3	10	30	80	120
Diisobutylmethyl	0.2	0.4	1.3	3.5	7
E_a^o with 0.1 M neutral reagent alone	-	<0.0001	<0.0001	0.0002	*

*3rd phase, 48% extraction of uranium.

acid reagents when used alone increase with reagent acid strength and with decreased branching of the alkyl groups. (1,2) The same trends were preserved when the neutral additives were used, i.e., combinations with di-n-octylphosphoric acid were up to two times more effective uranium extractants than similar combinations with di(3,5,5-trimethylhexyl)phosphoric acid, etc. Again, as in D2EHPA combinations, the synergistic enhancement imparted to extractions with an individual acid reagent increased as TBP, DBBP, BDBP and finally TBPO were used in sequence.

4.3 Simultaneous Use of More Than One Neutral Additive

If an operator decides for reasons of cost, supply or usability to change from one synergistic additive to another, it would be undesirable to discard the total initial mixed solvent inventory. Replenishing inevitable losses of the original additive (distribution spillage) with the newer additive would accomplish an eventual conversion to the new reagent mixture. It is also possible to use a combination of a synergistic additive with a cheaper alcohol, the first in amounts large enough to offset the decrease in extraction ability caused by the alcohol (1) or to provide some net enhancement of the coefficient, and the latter to provide most of the reagent necessary for modification of the organic phase to insure alkaline stripping compatibility. Use of such mixtures would require that new methods be developed for the analytical determination of their concentrations. Tests were made to characterize briefly the extraction behavior of these two mixture types.

Fig. 4.2 shows results in tests where mixtures of DBBP and TBP were used in 0.1 M D2EHPA. The top and bottom curves represent extractions with DBBP and TBP, respectively, at the indicated concentration level. The intermediate curves show extractions with 25-75, 50-50, and 75-25% mixtures of these two reagents, the sum of their concentration being as indicated.

By interpolation it should be possible to estimate uranium extraction ability for any reagent combination for which such a series of curves has been determined in the desired aqueous phase.

A few tests have been made with tridecyl alcohol--DBBP mixtures and these are summarized in Table 4.3. The presence of a small amount of alcohol had a larger depressive effect upon the extraction ability of the mixture than anticipated from previous tests in which alcohol alone was used. In the latter case, it has been found possible to predict the alcohol effect with an equation such as the following

$$\log E_p = \log E_o - 0.2\ P \qquad (6)$$

where E_p is coefficient at alcohol concentration P, E_o is coefficient without alcohol, and P is w/v % alcohol. This equation has been used to calculate the coefficients listed in the last column of Table 4.3, and as pointed out above, the observed effect was larger than the calculated one where DBBP was present. No further work has been done with alcohol-synergistic additive mixtures, but these few tests show that the effect is not one of simple additivity.

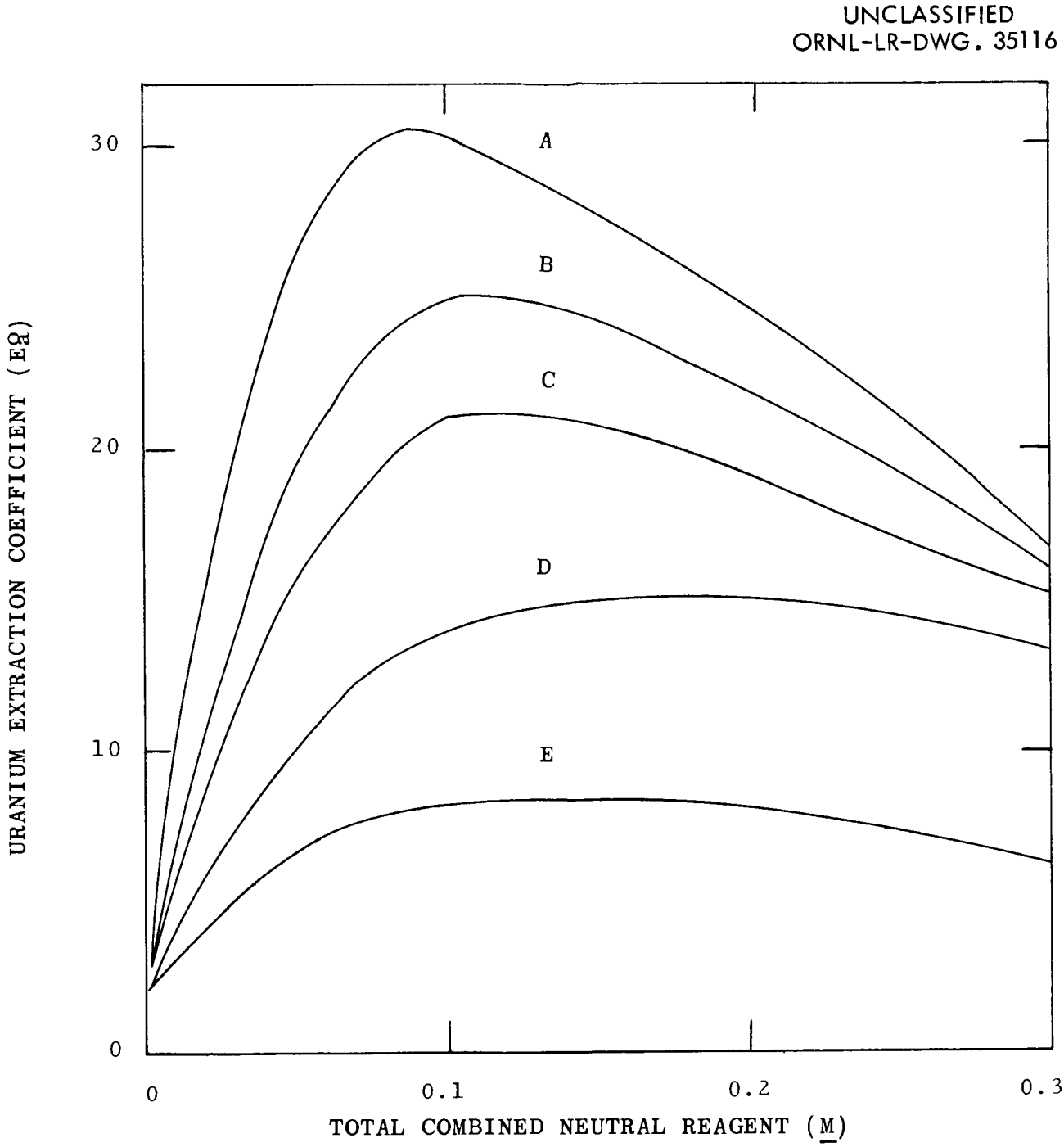

Fig. 4.2 Synergistic Extractions With More Than One Neutral Reagent. Organic Phase - 0.1 M D2EHPA in kerosene with: A, DBBP; E, TBP; and B, C, D, mixtures of DBBP and TBP, 75-25, 50-50, and 25-75 mole percent, respectively. Aqueous Phase - 1.5 M H_2SO_4, 0.004 M U(VI) initially. Aqueous/organic phase ratio = 1, 10-min agitation, 32-34°C.

Table 4.3 Extraction of Uranium with D2EHPA and Tridecyl Alcohol--DBBP Mixtures

0.1 M D2EHPA-Kerosene
0.5 M SO_4, pH 1.3, 0.005 M U(VI)
15-min agitation

DBBP (M)	Uranium Extraction Coefficient (E_a^Q) Tridecyl Alcohol None	1 w/v %	Calculated from log E_p = log E_o-0.2P*
0	220	140	140
0.01	870	330	550
0.03	2600	920	1640

*E_p = coefficient at alcohol concentration P
E_o = coefficient without alcohol
P = w/v % alcohol

4.4 Combinations of Alkylamines and Organophosphorus Acids

Combinations of long chain alkylamines and D2EHPA have been tested in uranium extractions to check the possibility of formation of an amine-uranylorganophosphate salt, perhaps with a synergistic enhancement of extraction coefficient. Tri-n-octylamine, bis(2,6,8-trimethylnonyl-4)amine (Amine S-24), dilaurylamine, and 3,9-diethyltridecyl-6amine were tested. A possible synergistic enhancement was noted only with the last amine and here the coefficient of the amine-D2EHPA mixture was only twice the sum of those of the individual reagents (Table 4.4). It was necessary to add 2-ethylhexanol to avoid precipitation of the trioctylamine sulfate. (8-12)

The mixture of tri-n-octylamine and D2EHPA showed extraction power which was only a little better in the alcohol-kerosene diluent than the coefficients of the individual components and poorer than their sum. The extraction ability of the branched didodecyl amine S-24--D2EHPA mixture was poorer than those of either the amine or D2EHPA. Such comparisons cannot be made with experiments using di-n-dodecylamine since precipitation of uranium occurred during its testing. The data are recorded in terms of per cent uranium removal from the aqueous phase, which from the 0.5 M SO_4 solution was about the same for the mixture of amine and D2EHPA as for that observed when the amine alone was used.

The absence of synergistic enhancement with either a straight or a branched chain (secondary) didodecylamine is in contrast with results reported by Dow Chemical Co. (28), which showed an enhancement in extractions with mixtures of didodecylamine and D2EHPA. In addition, while the present data show possible synergism with the branched chain primary amine, the Dow data indicated none when a (primary) n-heptylamine--D2EHPA combination was used. Dow tests with mono(2,6,8-trimethylnonyl-4)phosphoric acid (DDPA)--didodecylamine showed extractions no better than those achieved with the secondary amine alone.

Table 4.4 Uranium Extractions with Combinations of Amines and Di(2-ethylhexyl)phosphoric Acid

All component reagents at 0.1 M
Aqueous uranium concentration: 0.004 M U(VI)
Agitation: 10 min (wrist-action shaker)
Temperature: 26°C

Amine	Diluent	Extraction Coefficient (E_a^o) D2EHPA Alone	Amine Alone	D2EHPA-Amine Combination
	0.5 M SO_4, pH 1			
Tri-n-octyl	Kerosene + 5 w/v % 2-Ethylhexanol	17	19	26
Di(2,6,8-trimethylnonyl-4)	Kerosene	110	360	52
Di-n-dodecyl	Kerosene	110	a	b
3,9-Diethyltridecyl-6	Kerosene	110	100	480
	1.5 M H_2SO_4			
Tri-n-octyl	Kerosene + 5 w/v % 2-Ethylhexanol	0.5	5.2	4.9
Di(2,6,8-trimethylnonyl-4)	Kerosene	3	5.2	4.7
3,9-Diethyltridecyl-6	Kerosene	3	1.0	9.0

[a]Precipitate in organic phase, 99.1% uranium removal from aqueous phase.

[b]Precipitate in organic phase, 99.0% uranium removal from aqueous phase.

The Bureau of Mines at Salt Lake City has proposed (29) use of a mixed reagent containing DDPA and "Trifatty Amine," presumably a mixture of tertiary amines containing n-octyl, n-decyl, and n-dodecyl groups. While there was no synergistic enhancement of uranium coefficient they report one for vanadium. In addition, iron extraction was reportedly suppressed. No phase separation difficulty was noted with this reagent combination.

4.5 Basis for Selection of Reagent Combination

Criteria which affect the choice of reagents for a synergistic extraction combination include availability of reagents, the complexing strength desired, and physical performance.

4.5.1 Availability

D2EHPA is available in quantity from Virginia-Carolina Chemical Corp., Richmond, Virginia and from Union Carbide Chemicals Co., South Charleston, West Virginia. Two dialkylphosphoric acids which perform similarly to D2EHPA, i.e., di(2-ethyl-4-methylpentyl)- and di(2-propyl-4-methylpentyl)phosphoric acids, are reported by Eastman Chemical Products, Inc., Kingsport, Tennessee to be potentially available. These three chemicals are in the dollar-per-pound range. TBP, DBBP, DHHP, and DAAP are all available in quantity from sources listed in Table 4.1, TBP at 50-60 cents per pound, the others at 70-90 cents per pound. (TOPO is being marketed as a specialty chemical at 40-50 cents per gram by Distillation Products Industries, Rochester, N. Y. Others of the reagents in Table 4.1 are available, notably the trialkylphosphites and phosphates and the chloromethylphosphonates.)

At these prices the cost per gallon of extractant solution is about 55 cents for 0.1 M D2EHPA--0.1 M TBP-kerosene or about 65 cents for 0.1 M D2EHPA--0.1 M DHHP-kerosene. Assuming loss by entrainment amounting to 0.05% of the aqueous raffinate (i.e., 0.5 gal per 1000 gal of raffinate), together with the losses by solubility of <5 mg D2EHPA and 25 mg TBP or 5 mg DHHP per liter of raffinate (Sec. 3.7), this indicates a makeup cost with either extractant of about 40 cents per 1000 gal of liquor treated. At a typical assay of 1 g of U/liter, this amounts to about 5 cents per pound of uranium produced. The lower solubility loss of DHHP compensates for its higher initial cost, so that it has a slight cost advantage over TBP when entrainment losses are 0.05% or less.

4.5.2 Complexing Strength

As described in Sec. 3.2, the composition of the aqueous phase determines the strength of the reagent needed to achieve efficient extraction. Stronger reagents or higher concentrations are needed to extract uranium from 0.5 M phosphate solution than from 0.5 M sulfate solution, for example. The available reagents provide a wide range of extraction power, e.g., a factor of about 300 between 0.05 M D2EHPA--0.1 M TBP and 0.4 M D2EHPA--0.1 M DHHP.

4.5.3 Physical Performance

When the process cycle includes alkaline stripping or scrubbing of the extract, the choice of type and concentration of neutral reagent is influenced by the requirement to maintain miscibility of the alkali dialkylphosphate salt (Sec. 3.6). Considered together with the extraction power required, this may lead to choice of a synergistic additive, a non-synergistic additive (e.g., an alcohol), or a mixture (Sec. 4.3). Miscibility of the alkali salt in kerosene also requires choice of a branched dialkylphosphoric acid; no modifier has been found which will solubilize, e.g., sodium di-n-octylphosphate in kerosene. (2)

The dependence of extraction selectivity on reagent structure also affects physical performance, in that iron and aluminum are precipitated by straight-chain acids and by those with branching only at a distance from the phosphorus atom (e.g., iso-octyl and 3,5,5-trimethylhexyl). (2)

5.0 USE OF ACID COMPONENTS OTHER THAN DIALKYLPHOSPHORIC ACIDS

Although a synergistic effect has been found with all of the dialkylphosphoric acid-neutral organophosphorus compound combinations tested, no such effect has been observed with any of the other types of organophosphorus acids (Table 5.1). In fact, combinations of other types of acid and neutral extractants may lead to an effect which is opposite to that desired, e.g., addition of 0.1 M tributylphosphate to 0.1 M mono(2,6,8-trimethylnonyl-4)-phosphoric acid, DDPA, decreases the uranium extraction by 85%. Combinations with other monoalkylphosphoric acids and 2-ethylhexylphosphonic acid show a similar decrease, but little or no effect was noted with phosphinic acids. Other phosphonic acids and the only available sulfonic acids happened to be water soluble and showed no effect when tested.

Table 5.1 Use of Acid Components Other Than Dialkylphosphoric Acids

Aqueous phase: 1.5 M H_2SO_4, 0.004 M U(VI)
Organic phase: 0.1 M TBP, 0.1 M indicated acid, kerosene diluent
Phase ratio, aqueous/organic: 1
Agitation: 10 min (wrist-action shaker)
Room temperature

Acid Reagent[a]	Uranium Extraction Coefficient (E_a^o)	
	Acid Alone	TBP-Acid Combination
Monoalkylphosphoric Acids		
n-Octyl	27	11
3,5,5-Trimethylhexyl	28	8
Diisobutylmethyl	13	1.4
4-Ethyl-1-isobutyloctyl	7	1.0
2,6,8-Trimethylnonyl-4	7	0.9
3,9-Diethyltridecyl-6	8	1.0
Phosphinic Acids		
n-Hexyl	2.8	2.6
2-Ethylhexyl	1.5	1.3
Phosphonic Acid[b]		
2-Ethylhexyl	29	3

[a] Isoamylsulfonic, benzene sulfonic, and naphthalene-3,6-disulfonic acids (water soluble) tested without effect.

[b] n-Butyl and benzene phosphonic, and hexamethylenediphosphonic acids (water soluble) tested without effect.

The negative results with the dialkylphosphinic acids were surprising in view of their similarity in structure to the dialkylphosphoric acids. It is possible that the ester oxygen present in the phosphoric acids contributes to the effect. Comparison of extraction with acids which incorporate an ether oxygen or with the acid esters of alkylphosphonic acids may help define the structures essential for synergistic extraction. On the possibility that the lack of enhancement with the di(2-ethylhexyl)phosphinic acid was perhaps due to use of an unfavorable concentration of neutral reagent, a series of tests were made in which tributylphosphine oxide was added in increasing amounts to 0.1 M di(2-ethylhexyl)phosphinic acid. No increase was found in extraction which could be attributed to a synergistic enhancement. (At about 0.2 M the phosphine oxide becomes an effective extractant in its own right (30).) These reagents were tested only for uranium extraction. Possible effects with other metals could exist.

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7.0 APPENDIX

7.1 Determination of Minimum Modifier Requirement

The modifier requirement discussed below is the measured critical concentration for miscibility of NaR_2PO_4 at the temperature specified and in the absence of any other solute. The method of determination was originally presented in ORNL-2172 (2). Since modifier requirements increase slightly with increasing temperature, the curve should be established for the temperature at which the extractant is to be used.

1. Prepare solutions of dialkylphosphoric acid in diluent to be used, the concentrations covering the range of interest (e.g., 0.05 to 0.5 M D2EHPA in kerosene).

2. Contact a sample (e.g., 5 ml) of each reagent solution with an equal volume of sodium carbonate solution (e.g., 10%).

3. Centrifuge the mixture and observe for the presence of a third phase.

4. When a third phase is present, add from a calibrated dropper a kerosene solution (e.g., 10%) of the modifier being tested, shaking and centrifuging after each addition until the third phase just disappears.

5. From the volumes* added and the known original dialkylphosphoric acid concentration and volume, calculate the final reagent and modifier concentrations.

6. Plot modifier vs final reagent concentration, or fit the results with an empirical equation, e.g., w/v % modifier = A + B ($\underline{M}$ R_2HPO_4).

7.2 Determination of Modifier Concentration in Organic Phase by Titration to Critical Miscibility Point

When the minimum modifier requirements are known, it is possible to determine the concentration of modifier in unknown solutions by the following method. (2)

1. Contact the reagent-modifier-diluent sample (e.g., 5 ml) with an equal volume of 10% sodium carbonate.

2. Centrifuge the mixture and observe for the presence of a third phase.

3a. When third phase is present, add from a calibrated dropper a standard solution (e.g., 10 w/v %) of the modifier in the same diluent, shaking and centrifuging after each addition until the third phase just disappears.

3b. If no third phase is present, add a measured amount of modifier-free diluent solution containing the reagent at a known concentration higher than that in the original solution, mix, centrifuge and observe for third phase. Repeat until a third phase is observed, then backtitrate as described in 3a.

4. Determine by pH titration the concentration of dialkylphosphoric acid in the original unknown test solution.

5. From volumes added and the known original reagent (dialkylphosphoric acid) concentration and volume calculate the final reagent concentration.

6. Determine from the miscibility curve (step 6, above) the critical quantity of modifier required to maintain miscibility in the final organic volume, and from this subtract the amount of modifier added in step 3a or 3b. The difference is the amount of modifier in the original sample.

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*All volumes should be measured with the reagent in acid form, and not when the reagent is in the NaR_2PO_4 form. There is a volume increase when the acid reagent solution contacts alkaline solutions. (2)

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