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Evaluation of Alternate Extractants to Tributyl Phosphate—Phase I

W. D. Arnold
D. J. Crouse

CONSOLIDATED FUEL REPROCESSING PROGRAM

ORNL

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Technical Information Center
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ORNL/TM-7536
Dist. Category UC-86
(Applied Technology)

Contract No. W-7405-eng-26

CONSOLIDATED FUEL REPROCESSING PROGRAM

EVALUATION OF ALTERNATE EXTRACTANTS TO TRIBUTYL PHOSPHATE – PHASE I

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Chemistry Division

and

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Fuel Recycle Division

Date Published: April 1981

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CONTENTS

HIGHLIGHTS

Preliminary evaluations have indicated that tri(*n*-hexyl) phosphate (THP) and tri(2-ethylhexyl) phosphate (TEHP) have some significant advantages over tri(*n*-butyl) phosphate (TBP) for fuel reprocessing although they also have some disadvantages. The longer alkyl chains in these new extractants decrease their aqueous phase solubility and increase the organic phase solubility of their metal complexes and the metal complexes of their degradation products.

Both THP and TEHP extract uranium and plutonium more strongly than TBP; thorium extraction is in the order THP>TBP>TEHP. Tritium extraction is highest with TBP because of slightly higher water extraction.

In extractions of thorium, a third liquid phase was formed using TBP at a solvent loading of about 40 g/L of thorium and above. Third-phase formation did not occur with THP or TEHP.

The dialkyl phosphoric acid degradation products of THP and TEHP showed a markedly lower tendency to precipitate with thorium than did dibutyl phosphoric acid (HDBP).

Chemical stability studies showed TEHP to have much greater stability to acid hydrolysis than TBP and THP, which were about equivalent. No differences were detected in the radiation stability of the three extractants.

The phase separation properties of THP and TEHP are inferior to those of TBP in both the nitric acid and sodium carbonate (solvent wash) systems. Phase separation was improved appreciably by using a lower extractant concentration than 1.09 *M* (equivalent to 30 vol % TBP). Difficulties were encountered with TEHP, however, owing to rapid degradation of its phase separation properties with time of contact with HNO_3; this problem requires additional study.

1. INTRODUCTION

Tributyl phosphate (TBP) is firmly entrenched as the extractant of choice for the solvent extraction processing of irradiated fuels. The versatile Purex process, which uses TBP as the extractant, has been employed successfully for more than two decades in the reprocessing of uranium-plutonium fuels (primarily low-burnup fuel) at plutonium production plants. Extraction with TBP has also been used for processing thorium-uranium fuels (Thorex process). The extensive production experience has been supplemented by large basic and applied research efforts to better understand and improve the process system.

Despite the overall success of TBP, there are some weaknesses that have become more apparent as the use of TBP extraction has been extended to the treatment of high-burnup power reactor fuels. Some of these weaknesses are:

1. Tributyl phosphate is subject to chemical and radiolytic degradation to form principally dibutyl phosphoric acid (HDBP) and monobutyl phosphoric acid (H_2MBP). These degradation products decrease the fission product decontamination efficiency and can prevent complete uranium and plutonium stripping, resulting in their losses to the solvent wash system. In addition, metal (Th, Zr, and Pu) complexes of these degradation products have low solubilities in the organic and aqueous phases and often precipitate and interfere with system operation.

2. The TBP complexes of thorium and plutonium have limited solubility in the organic phase and form a third phase at high solvent loadings. This can be avoided with plutonium by operating at 35 to 40°C; however, with thorium, solvent loading must be controlled at a relatively low level, or operation with three phases must be tolerated.

3. The solubility of TBP in the aqueous phase is relatively high (~0.2 g/L), which is a disadvantage since the dissolved TBP can hydrolyze to form primarily HDBP. This is always of concern in passing from one cycle to the next, particularly if an intercycle evaporator is used, since metal-HDBP precipitates can form and, in any case, the DBP can decrease the decontamination efficiency in the next cycle. Also, dissolved TBP in high-level wastes leads to early precipitation of solids in the waste concentration step.

Our evaluation of alternative extractants has been limited thus far to compounds of the same class, which are the trialkyl phosphates, but with longer alkyl chains. The two compounds examined thus far are trihexyl phosphate (THP) and tri(2-ethylhexyl) phosphate (TEHP). The process chemistry for these compounds is essentially identical to that for TBP, and much of the developed TBP technology would be applicable to them. Hence, there should be less resistance to the acceptance of such extractants than of those extractants with a different functional group and widely different extraction properties. Our objective is to retain the many advantages of TBP while mitigating or eliminating the disadvantages listed above.

Early studies by Siddall[1,2] showed that increasing the alkyl chain length slightly increased uranium extraction coefficients and avoided third-phase formation in thorium extractions. A recent Russian study[3] with tributyl phosphate isomers showed that appropriate branching of the alkyl chain increases the resistance to chemical degradation; this has enhanced our interest in TEHP.

The evaluation of THP and TEHP actually began in late 1969 as part of our LMFBR fuel reprocessing studies,[4–7] but was terminated soon after when the former Atomic Energy Commission (AEC) withdrew support of solvent extraction work. Studies made by J. G. Moore confirmed the higher uranium extraction powers of THP and TEHP compared to that of

TBP observed by Siddall. These studies further showed that the distribution of THP to the aqueous phase is negligible (<1 ppm).

This report summarizes the results of tests performed since the evaluation studies were reactivated in FY 1978. Both THP and TEHP have shown some important advantages over TBP, although they also have some disadvantages; further development of these extractants is indicated.

2. SOLUTION PREPARATION AND PROCEDURES

The TBP used in these studies is a sample of commercial material obtained from Fisher Scientific Company. The THP is not available commercially; the sample was obtained several years ago from Weston Chemical Company. Both the TBP and THP were purified by molecular distillation. Two batches of TEHP were tested. The first was an inexpensive, commercially available TEHP sample from Union Carbide Corporation having an advertised purity of greater than 99.5%. The second sample was obtained several years ago from Food Machinery and Chemicals Company. Neither sample was distilled before use.

The diluent used in essentially all tests was normal dodecane (NDD), which was greater than 99.5% pure and contained about 0.4% nonparaffinic impurities. In most tests, the concentration of trialkyl phosphate was 1.09 *M* which, in the case of TBP, corresponds to a 30% solution by volume. For THP and TEHP, this molar concentration corresponds to 41 and 52% solutions respectively.

The diluted extractants were scrubbed with dilute sodium carbonate solution and then with water to remove acidic impurities. In most tests, the scrubbed solvent was contacted with nitric acid prior to extraction to minimize change in the aqueous acid concentration in the extraction contact.

In extraction tests, the phases were contacted in separatory funnels mounted in a wrist-action shaker set for maximum agitation.

3. EXTRACTION BEHAVIOR

3.1 Uranium Extraction

The extraction of uranium as a function of HNO_3 concentration is shown in Fig. 3.1 for 1.09 *M* solutions of TBP, THP, and TEHP. In the acid concentration range of 2 to 3 *M*, which is typical of the extraction system, the uranium extraction coefficients for TEHP were about twice those for TBP, and for THP, about 1.6 times. At low acid concentrations, the data showed considerable scatter; however, the coefficients for TEHP and THP were always higher than for TBP. These compounds, therefore, would be somewhat more difficult to strip than TBP.

A study of the effect of extractant concentration on uranium extraction showed that, below 0.2 *M* concentration, the extraction coefficient is proportional to the square of the extractant concentration (log-log plot of extraction coefficient vs extraction concentration has a slope of 2.0, Fig. 3.2). In the concentration range of about 0.3 to 1 *M*, the coefficients are proportional to about the 1.4th power of the TBP or THP concentration and about the 1.6th power of the TEHP concentration. In these tests, the extraction phase ratio was varied so that the extractant loading (moles uranium per mole extractant) was low and about the same in all tests.

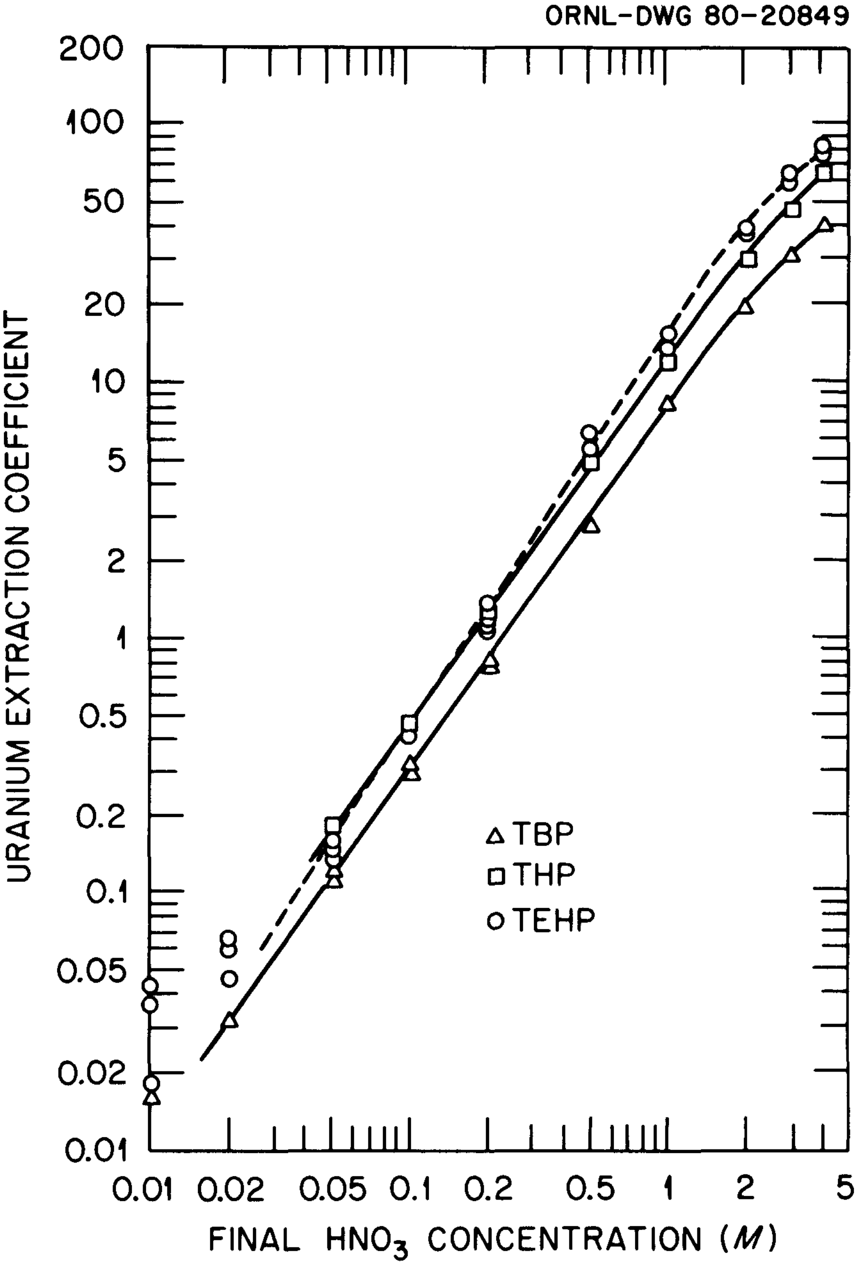

Fig. 3.1. Effect of HNO_3 concentration on uranium extraction with 1.09 *M* extractant at 23°C. Uranium loading of the solvent was 1 g/L or less

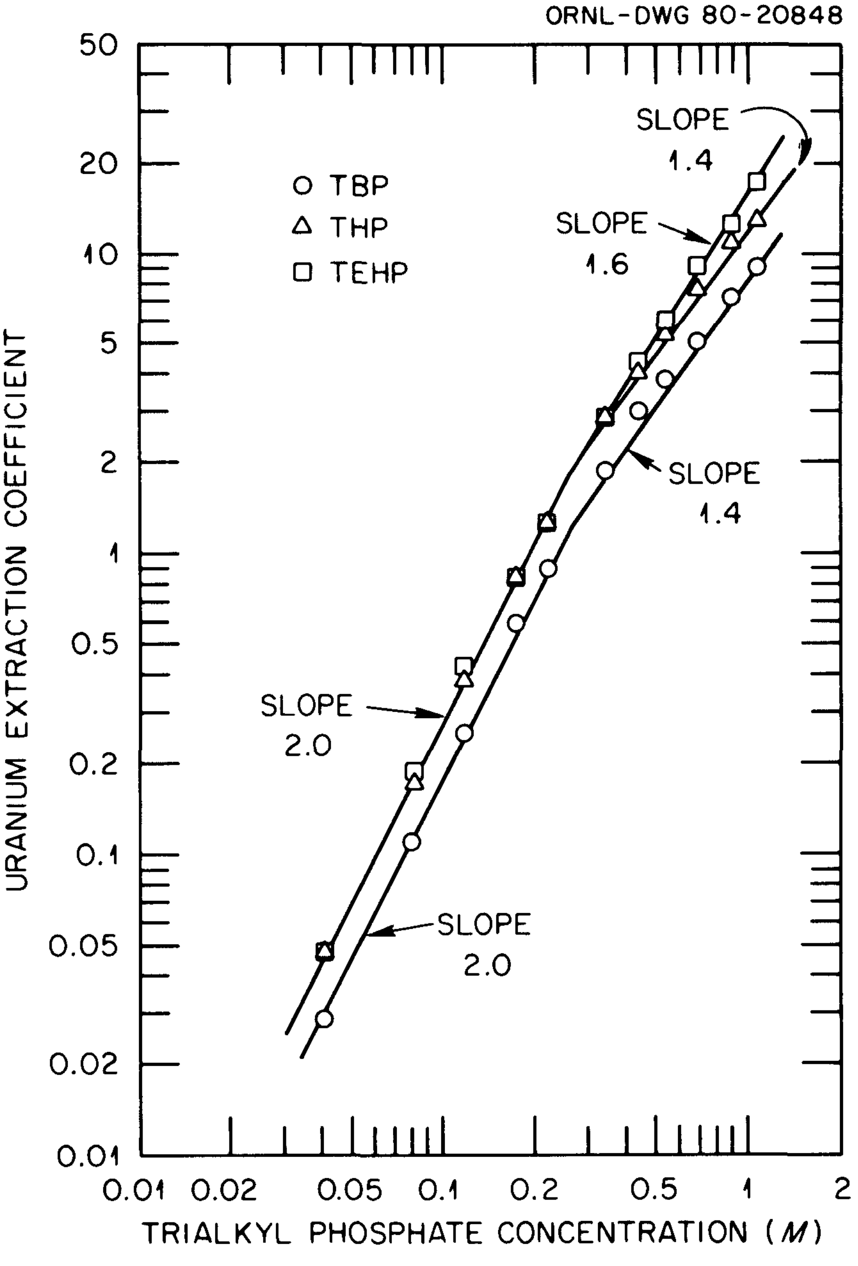

Fig. 3.2. Effect of extractant concentration on uranium extraction from 2 *M* HNO_3 at 23°C.

With all three extractants, increasing the temperature from 23 to 60°C lowered the uranium extraction coefficient by a factor of about 2 (Fig. 3.3).

Further comparison of the extraction power of TBP, THP, and TEHP is presented in the form of extraction isotherms (Fig. 3.4). The distribution coefficients up to near solvent saturation were in the order TEHP>THP>TBP. All three solvents reached a maximum uranium loading of 120 to 125 g/L, equivalent to about 0.5 mole of uranium per mole of extractant.

3.2 Plutonium Extraction

Comparative plutonium extraction tests showed that the plutonium extraction power is in the order TEHP>THP>TBP. The tests were made by M. H. Lloyd and S. E. North at the ORNL Transuranium Processing Facility.

The effect of acid concentration on plutonium extraction is shown in Fig. 3.5. The measured extraction coefficients for TEHP range from 20 to 80% higher than those for TBP over the acid concentration range of 0.3 to 3.5 *M*.

The efficiency of plutonium extraction with all three extractants increased as the temperature was increased from 30 to 50°C (Fig. 3.6). At all test temperatures, the extraction coefficients with TEHP were about 60% higher than those for TBP.

The effect of extractant concentration on plutonium extraction was studied with solutions of TBP and TEHP over the concentration range of 0.45 to 1.09 *M*. With both extractants, log-log plots of the plutonium extraction coefficients vs extractant concentration gave straight lines with a slope of about 1.4, indicating a 1.4th power dependence of the coefficient on extractant concentration (Fig. 3.7). This is the same power dependence observed for uranium extraction with TBP over this extractant concentration range (see Sect. 3.1), as well as for Pu(VI) extractions with TBP.[8] The indicated dependence for uranium extraction with TEHP was 1.6th power (Sect. 3.1).

Isotherms for the extraction of plutonium from 3 *M* HNO_3 with 1.09 *M* solutions of TBP, THP, and TEHP are shown in Fig. 3.8. The higher extraction power of TEHP compared to TBP would, of course, allow higher loading of the solvent in process operation. With 10 g/L plutonium in the aqueous phase, the indicated solvent plutonium loadings were about 73 g/L for TEHP and 64 g/L for TBP.

All tests except those shown in Fig. 3.8 and Table 3.1 were conducted so that the plutonium loading of the solvent was very low (<0.01 mole plutonium per mole of extractant).

3.2.1 Extraction from uranium-plutonium solutions

Data were obtained for the extraction of uranium and plutonium with 0.6 *M* solutions of TBP and TEHP from 3 *M* HNO_3 at 40°C and from 0.5 *M* HNO_3 at 25°C. These conditions of acid concentration and temperature approximate those that might exist in extraction and partitioning systems respectively. In these tests the U:Pu ratio was about 10, and the total heavy metal concentration of the initial aqueous solutions ranged from about 5 to 165 g/L.

As expected, both uranium and plutonium were extracted more effectively from both solutions with TEHP than with TBP (Table 3.1). The measured U:Pu separation factors were erratic in the 3 *M* HNO_3 tests. In the 0.5 *M* HNO_3 tests, the separation factors were consistently higher for TEHP than for TBP, but the differences were not large.

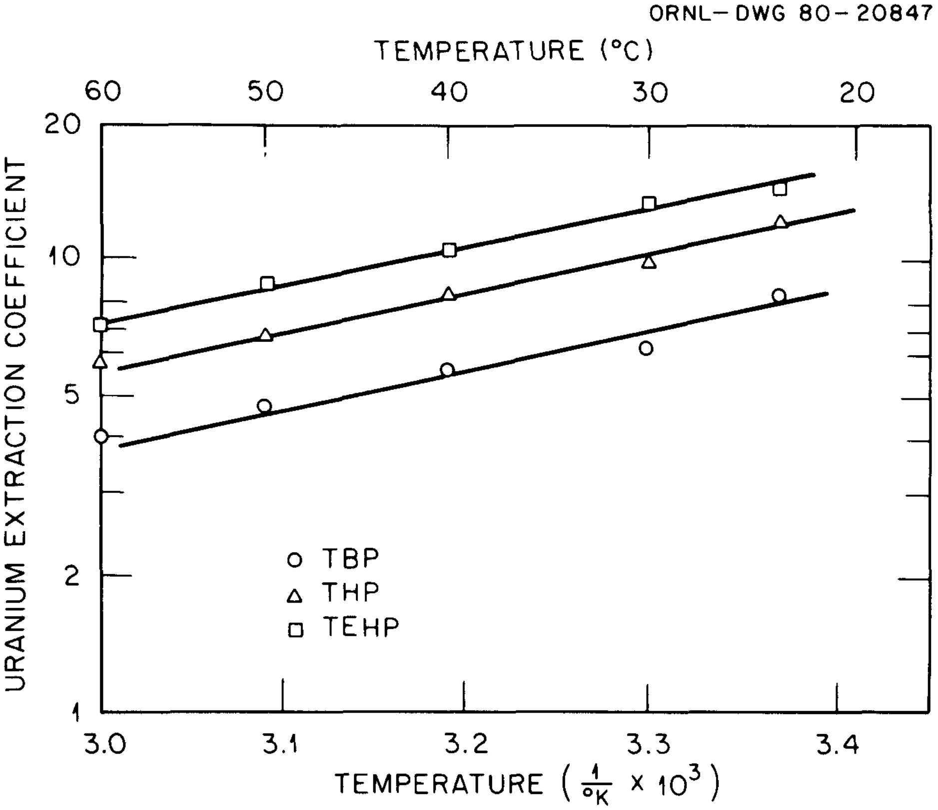

Fig. 3.3. Effect of temperature on uranium extraction from 2 *M* HNO_3 with 1.09 *M* extractants. Uranium loading of the solvent was 1 g/L or less.

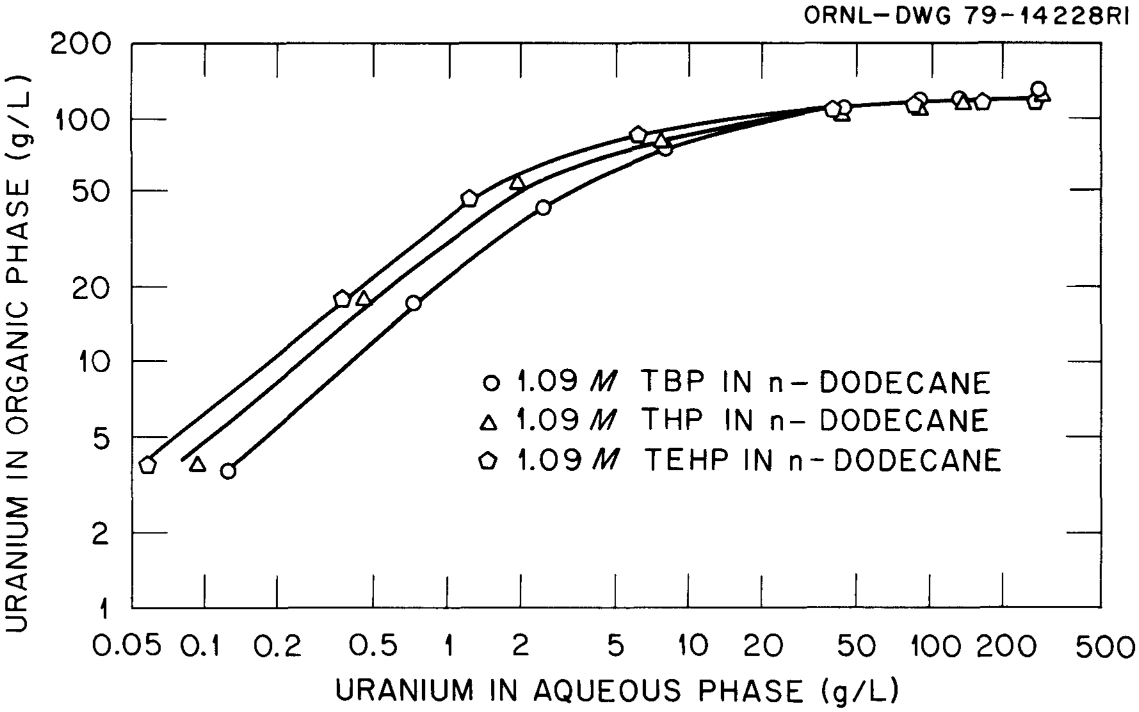

Fig. 3.4. Isotherms for extraction of uranium from 3 *M* HNO_3 (initial concentration) at 23°C.

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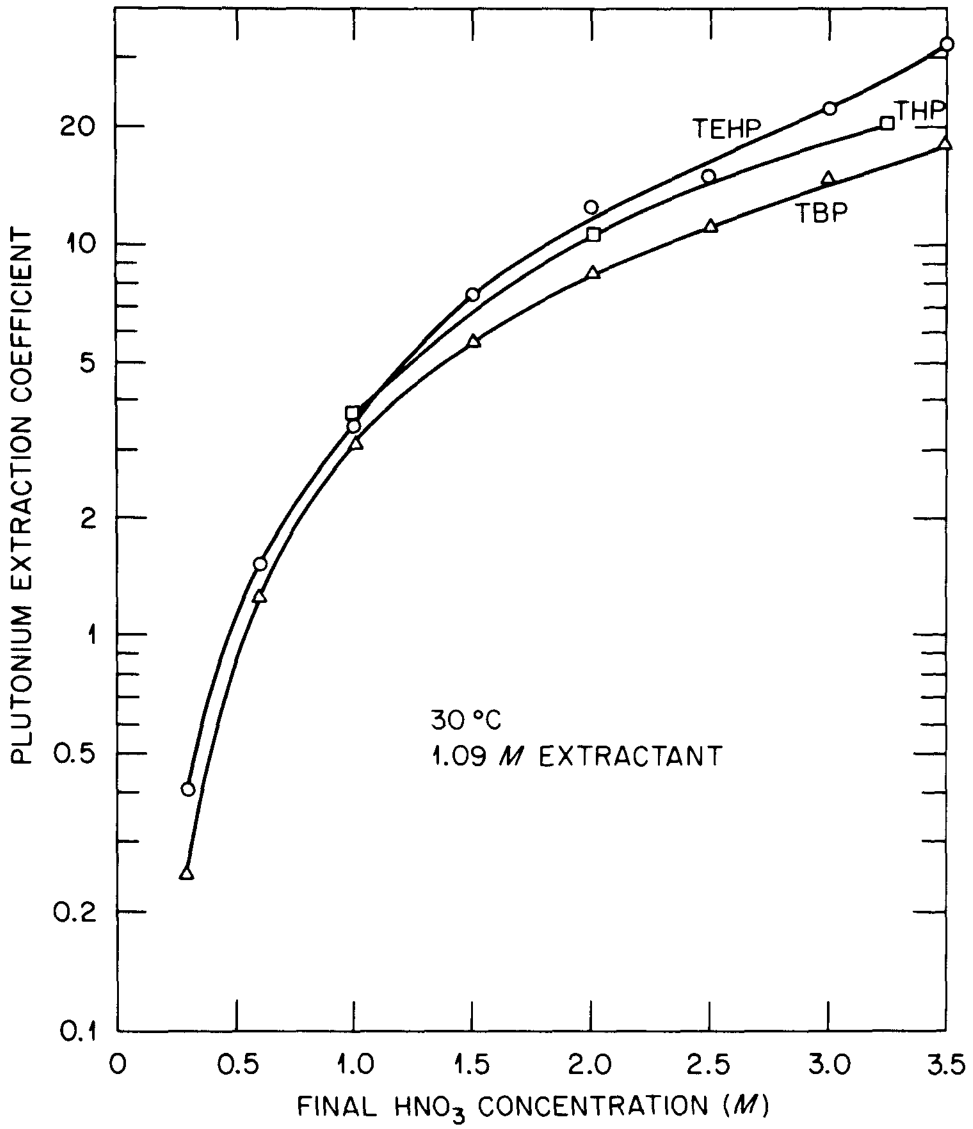

Fig. 3.5. Effect of HNO_3 concentration on plutonium extraction.

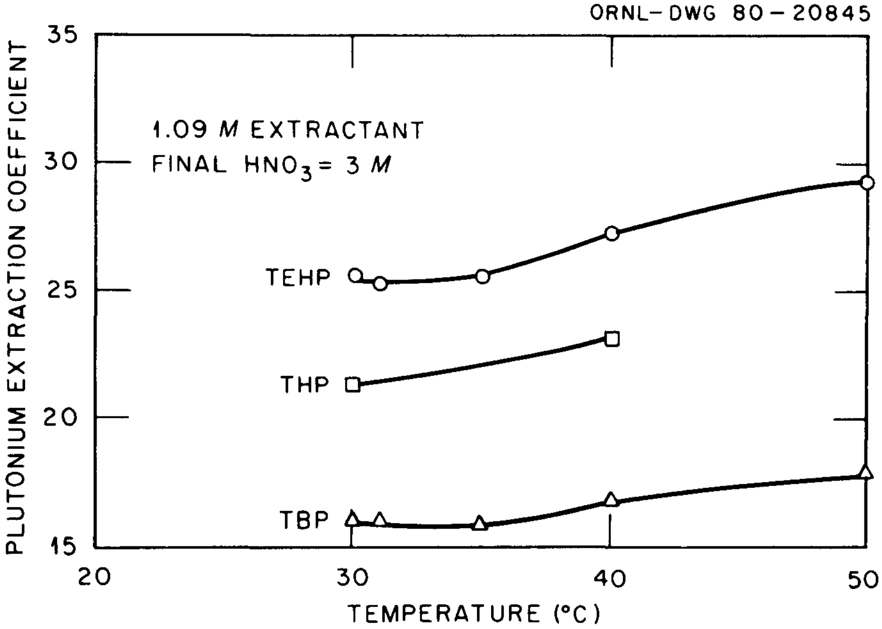

Fig. 3.6. Effect of temperature on plutonium extraction.

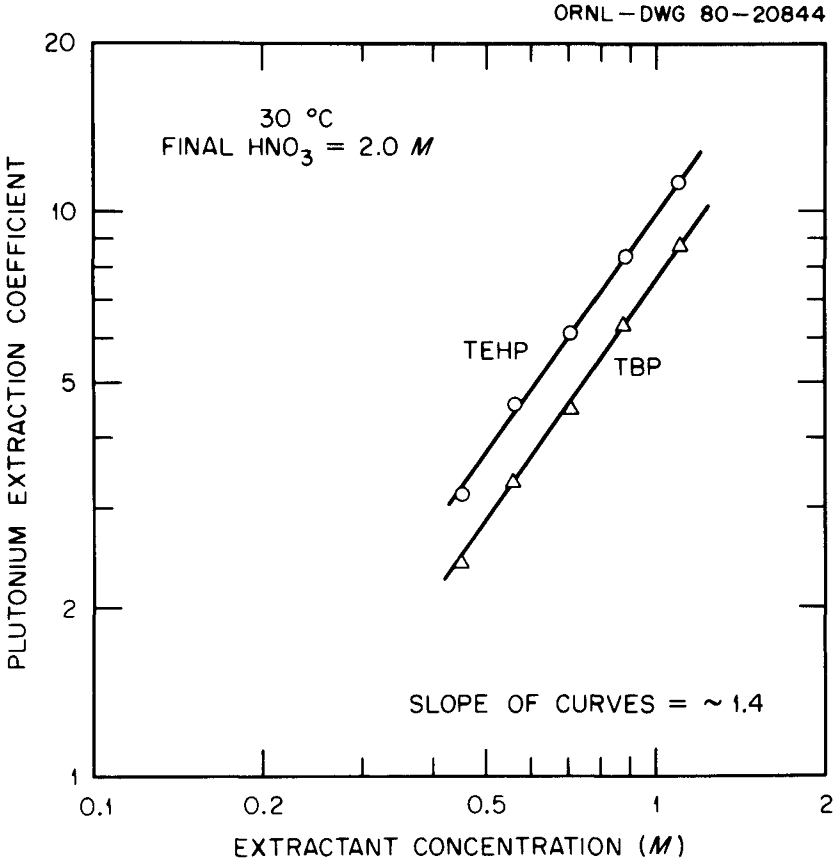

Fig. 3.7. Effect of extractant concentration on plutonium extraction.

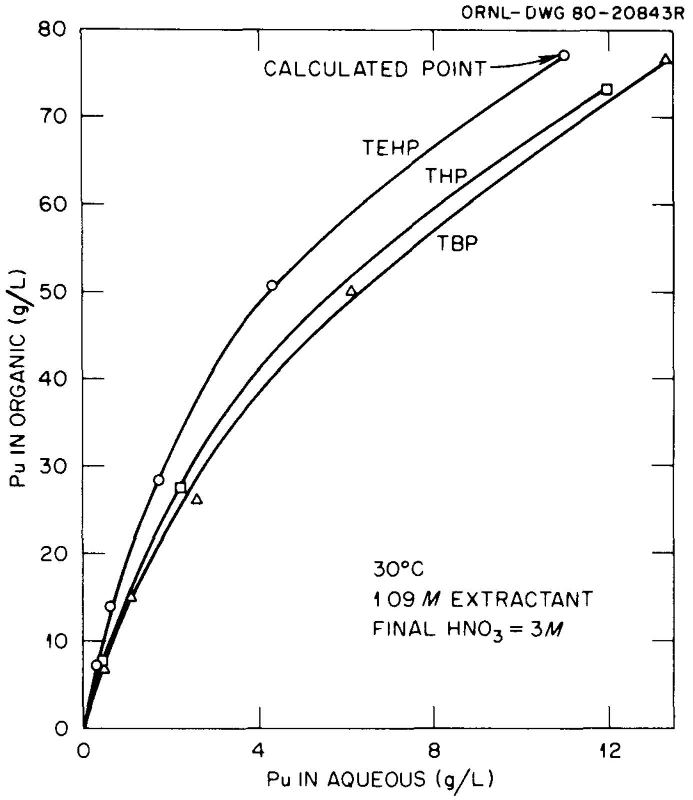

Fig. 3.8. Plutonium extraction isotherms. Test represented by top point on TEHP curve had very low material balance, organic phase plutonium concentration calculated on basis of initial and final aqueous phase concentrations

Table 3.1 Extraction of uranium and plutonium from 3 *M* and 0.5 *M* HNO_3 with 0.6 *M* solutions of TBP and TEHP in normal dodecane

Solvent	Temperature (°C)	Organic			Aqueous			Distribution coefficient		Separation factor, U Pu
		U (g/L)	Pu (g/L)	HNO_3 (M)	U (g/L)	Pu (g/L)	HNO_3 (M)	U	Pu	
0.6 *M* TBP	40	4.7	0.45	0.34	0.54	0.07	3.0	8.6	6.4	1.34
		8.0	0.99	0.32	1.24	0.16	3.0	6.5	6.2	1.05
		37.8	3.5	0.15	13.5	1.84	2.9	2.8	1.9	1.47
		56.2	4.6	0.11	97.8	11.5	2.9	0.57	0.40	1.42
0.6 *M* TEHP		5.4	0.50	0.32	0.44	0.05	3.0	12.3	10.0	1.23
		8.5	1.01	0.36	1.44	0.10	3.0	5.9	10.1	0.58
		39.6	3.8	0.16	9.8	1.49	3.0	4.0	2.5	1.60
		64.3	5.0	0.08	92.4	10.8	2.9	0.70	0.46	1.52
0.6 *M* TBP	25	3.3	0.12	0.05	2.6	0.39	0.51	1.27	0.31	4.1
		6.2	0.26	0.04	5.0	0.83	0.53	1.24	0.31	4.0
		25.4	0.96	0.02	27.7	4.2	0.55	0.92	0.23	4.0
		47.7	1.52	0.02	10.2	12.6	0.57	0.47	0.12	3.9
0.6 *M* TEHP		3.6	0.12	0.05	2.1	0.38	0.53	1.71	0.32	5.3
		7.0	0.26	0.04	4.2	0.81	0.54	1.67	0.32	5.2
		26.6	1.00	0.02	24.3	4.0	0.55	1.09	0.25	4.4
		51.3	1.55	0.05	96.8	12.2	0.56	0.53	0.13	4.1

3.3 Thorium Extraction and Third-Phase Formation

The order for the extraction of thorium with the three trialkyl phosphates is different than for uranium and plutonium. In the case of thorium, THP is a stronger extractant than TBP but TEHP is weaker. Figure 3.9 shows isotherms for thorium extraction from 3 *M* HNO_3 with 1.09 *M* solutions of TBP, THP, and samples of TEHP from two different suppliers. At low loadings, extraction coefficients with TBP were about 40% lower than with THP but about 40% higher than with TEHP. Only the lower part of the isotherm is shown for TBP since a third phase formed when thorium loading of the solvent was near 40 g/L. A third phase did not form with the alternate extractants, although loadings reached 65 to 70 g/L.

Isotherms comparing thorium extraction with TBP and THP at other nitric acid concentrations are shown in Fig. 3.10. Thorium extraction coefficients were about 40% higher with THP than with TBP at all of the acid concentrations tested. A third phase formed with TBP at thorium loadings in the neighborhood of 40 g/L, but none formed with THP.

3.4 Extraction of Nitric Acid, Water, and Tritium

Analyses of solvent samples from the thorium extraction isotherm tests (Fig. 3.9) showed no difference in the amount of nitric acid extracted by TBP, THP, and TEHP over a wide range of thorium loadings (Fig. 3.11).

The amount of water extracted was also determined for some of the organic phase samples. Water extraction was in the order TBP>THP>TEHP and decreased with an increase in thorium loadings (Fig. 3.12). For some unexplained reason, one of the TEHP samples extracted significantly less water than the other.

3.4.1 Tritium extraction

Tritium extraction would be of importance only if, instead of voloxidation, the water retention method (with confinement of tritium to the head-end, first-cycle extraction and high-level waste systems) were chosen as the method of tritium control. The tritium is

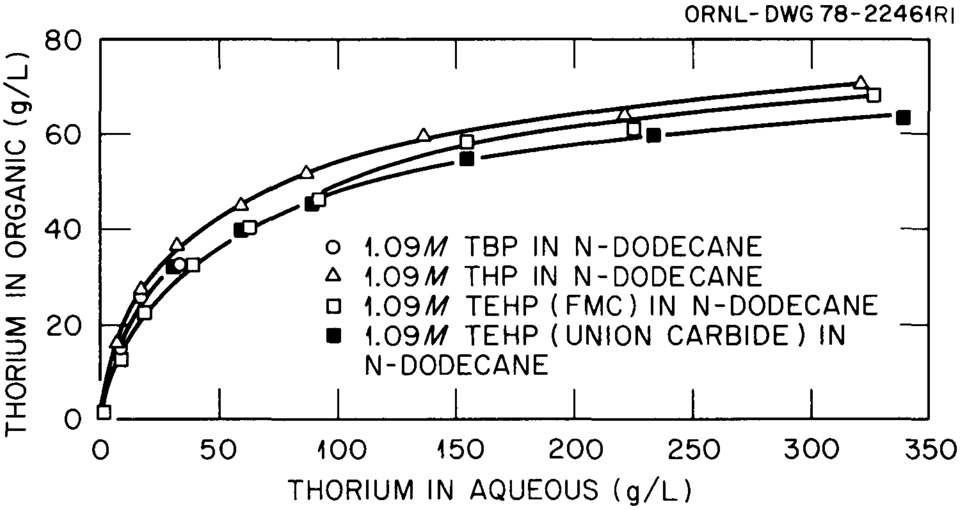

Fig. 3.9. Isotherms for extraction of thorium from 3 *M* HNO_3 (initial concentration) at 23°C.

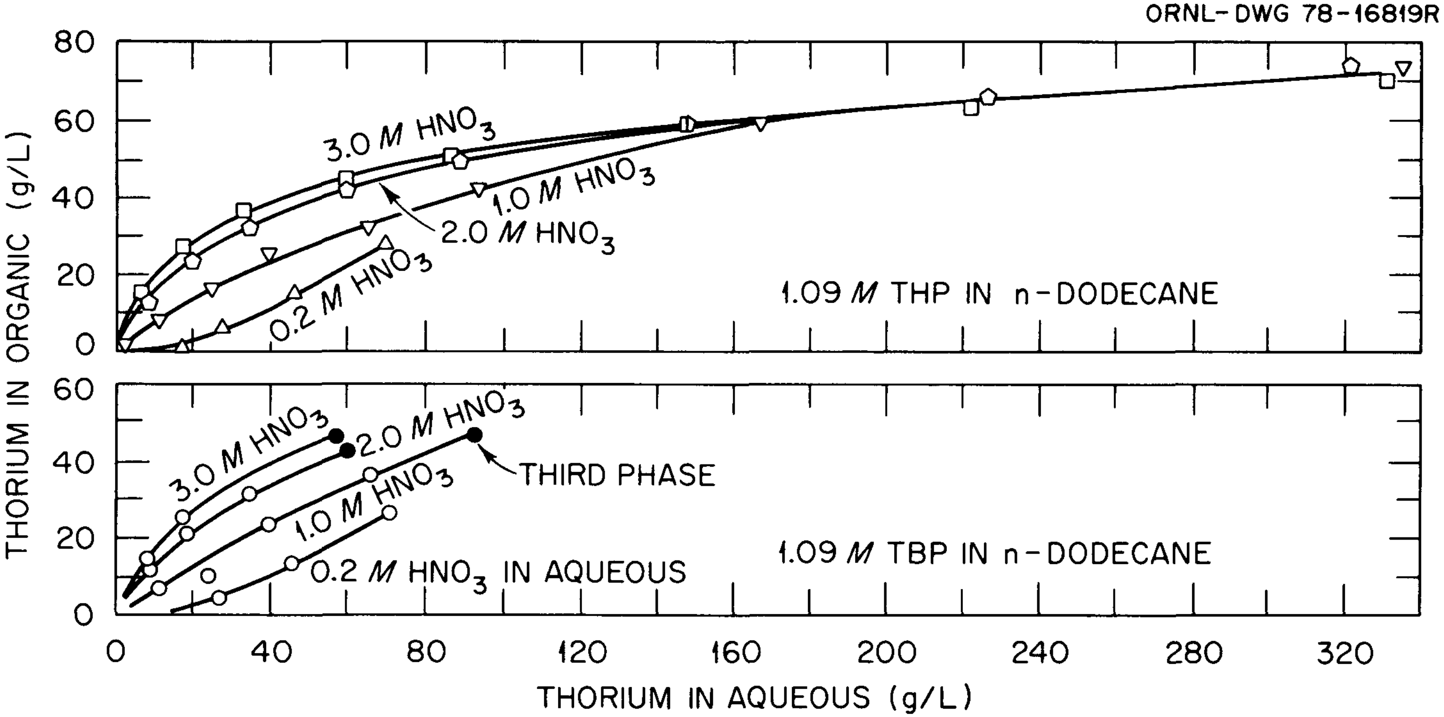

Fig. 3.10. Extraction of thorium with TBP and THP at about 23°C. Acid concentrations shown are initial values Organic phase thorium concentrations for the TBP tests, in which a third phase formed (darkened circles), were calculated on the basis of initial and final aqueous thorium concentrations

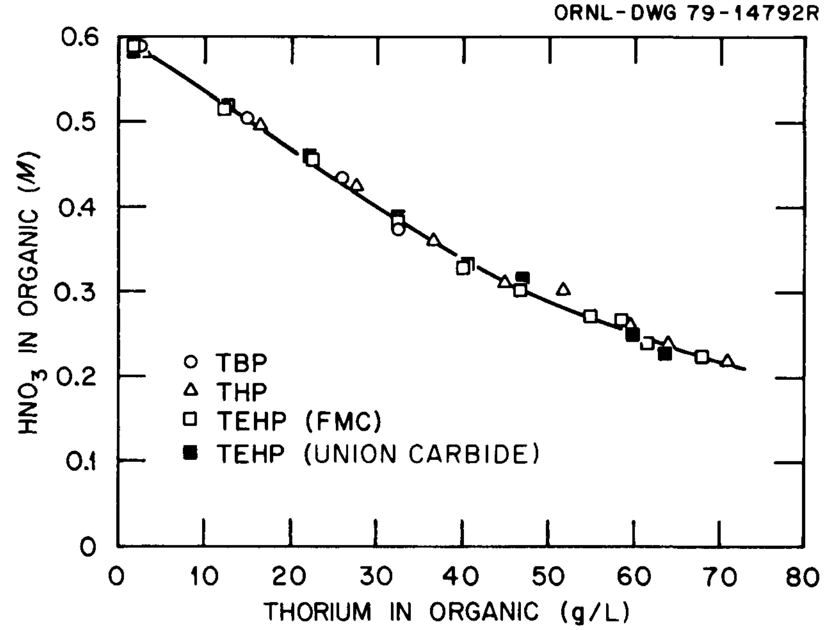

Fig. 3.11. Nitric acid extraction at 23°C with trialkyl phosphate solutions in normal dodecane as a function of organic phase thorium concentration. Initial aqueous phase acid concentration was 3.0 *M*

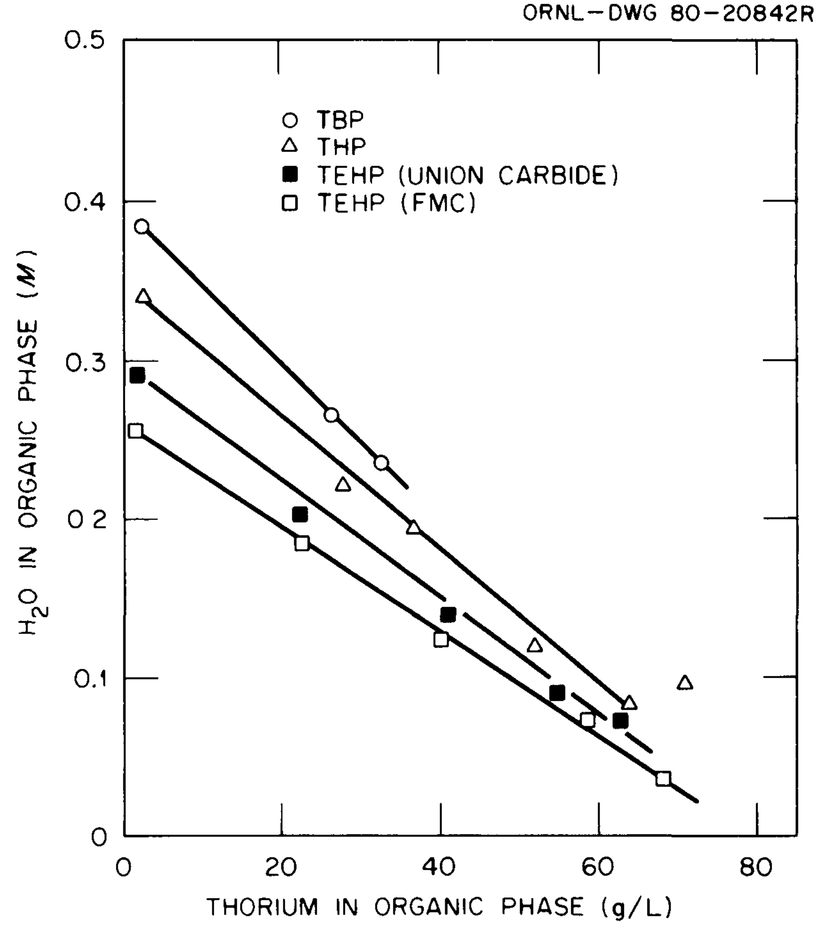

Fig. 3.12. Water extraction at 23°C with trialkyl phosphate solutions in normal dodecane as a function of organic phase thorium concentration. Initial aqueous phase acid concentration was 3 0 *M*

extracted as tritiated water and nitric acid and, therefore, the amount extracted is directly dependent on water and acid extraction.

Table 3.2 shows data for the extraction of water and HNO_3 with TBP and THP from nitric acid solutions containing tritium. The amounts of tritium extracted, based on radioactivity measurements, agreed well with the values that were calculated from the water and acid analyses and assuming complete H-T exchange. The extracted tritium in these tests (aqueous to organic phase ratio of 2:1) was 0.4 to 0.6% of the total tritium in the system. As in the thorium extraction tests, there was no significant difference in the amount of acid extracted by the two extractants; however, TBP extracted more water. Water extraction was the major contributor to tritium extraction even when the aqueous acid concentration was about 3 *M*.

Using the nitric acid and water extraction data (Figs. 3.11 and 3.12) from the thorium extraction isotherm tests, the tritium concentration in the organic phase was calculated as a function of the solvent thorium loading. It was arbitrarily assumed that the initial aqueous solution contained 1 μCi/mL. The calculated tritium concentrations in the organic phase at low thorium loadings were about 0.013, 0.011, and 0.010 μCi/mL for TBP, THP, and TEHP respectively. The values for THP and TEHP decreased to about 0.004 and 0.002 to 0.003 μCi/mL, respectively, as the thorium loading of the solvent was increased to 70 g/L (Fig. 3.13). The concentrations for TBP are shown only for low and moderate thorium loadings since a third phase formed at loadings of about 40 g/L.

These data indicate that the alternate extractants would have a small advantage over TBP if the water retention method were chosen for tritium control.

Table 3.2. Extraction of water, nitric acid, and tritium

(Organic phase: 1.09 *M* TBP or THP in normal dodecane; aqueous phase: H_2O or HNO_3 containing 0.15 μCi/L of ^3H; phase ratio: A:O, 2:1)

Extractant	HNO_3 in initial aqueous (*M*)	Concentration in organic (*M*)		Tritium in organic (μCi/mL)	
		HNO_3	H_2O	Calculated[a]	Measured
TBP	0		0.476	0.00133	0.00123
	0.5	0.066	0.467	0.00139	0.00129
	1.0	0.185	0.483	0.00155	0.00149
	2.0	0.407	0.491	0.00172	0.00168
	3.0	0.599	0.391	0.00200	0.00182
THP	0		0.391	0.00108	0.00106
	0.5	0.066	0.391	0.00118	0.00116
	1.0	0.179	0.384	0.00127	0.00134
	2.0	0.409	0.430	0.00157	0.00154
	3.0	0.600	0.353	0.00192	0.00170

[a] Calculated on basis of H_2O and HNO_3 analyses and assuming complete H-T exchange.

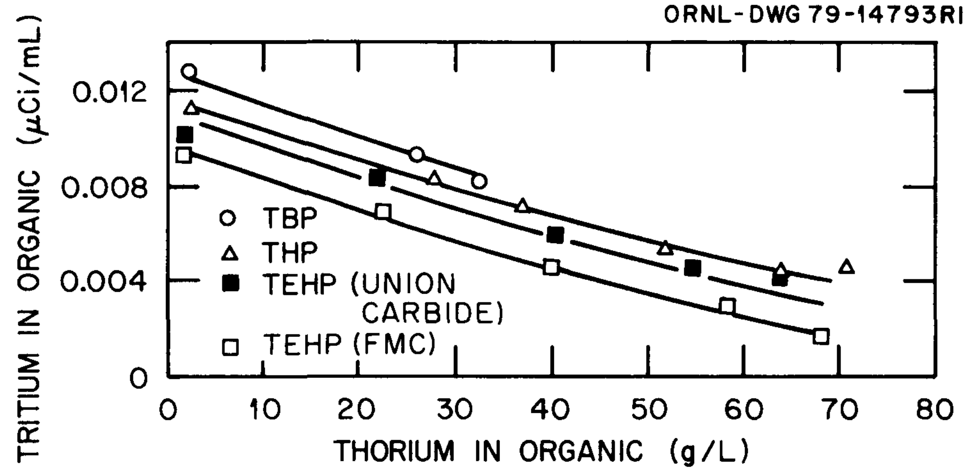

Fig. 3.13. Calculated tritium extraction (based on nitric acid and water analyses and assuming 1 μCi of tritium in the initial aqueous phase) from HNO_3-$Th(NO_3)_4$ solutions with 1.09 *M* solutions of TBP, THP, and TEHP. The initial acid concentration was 3 *M*.

3.5 Extraction of Fission Products

3.5.1 Zirconium extraction

The extraction of zirconium was studied with 0.001 *M* zirconium solutions traced with ^{95}Zr-^{95}Nb. Comparative tests showed the expected increase in ^{95}Zr-^{95}Nb extraction for all three extractants as the acid concentration was increased from 0.2 *M* to 4 *M* (Fig. 3.14). The extraction coefficients were roughly 50% higher for THP than for TEHP over the total range of acid concentrations, with the coefficients for TBP being intermediate in value. The extraction contact time in these tests was 2 min. A repeat of the tests, but using a contact time of 15 min, resulted in slightly higher coefficients.

3.5.2 Ruthenium extraction

Coefficients for the extraction of ruthenium with TBP were slightly higher than coefficients with THP, and several times higher than those with TEHP. The much weaker extractions with TEHP may be due to steric hindrance effects from the alkyl chain branching. The extraction coefficients reached a maximum at about 3 *M* HNO_3 in the TBP and THP tests and at 2 *M* HNO_3 in the TEHP tests (Fig. 3.15). Pruett[9] found maximum extraction of ruthenium with TBP from about 1 *M* HNO_3, indicating some variation in the ruthenium species present in the different experiments.

Our ruthenium solutions were prepared by dissolving ^{106}Ru-traced $RuNO(OH)_3 \cdot 2H_2O$ in 10 *M* HNO_3 to a ruthenium concentration of 0.1 *M*. After standing for two days, this solution was diluted to 10^{-3} *M* ruthenium and to the following nitric acid concentrations: 0.2, 0.5, 1.0, 2.0, 3.0, and 4.0 *M*. The diluted solutions were let stand for seven days prior to the ruthenium extraction tests.

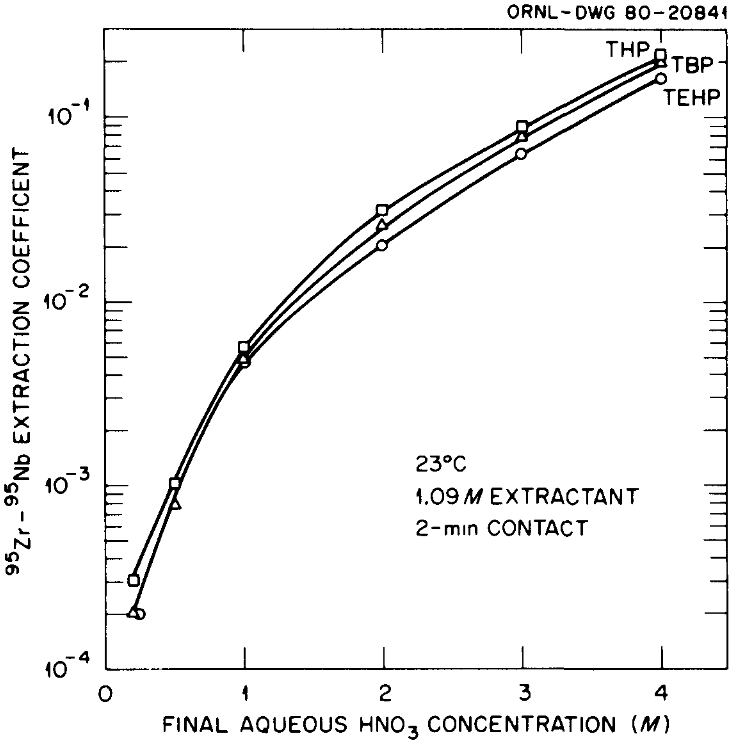

Fig. 3.14. Effect of nitric acid concentration on $^{95}Zr-^{95}Nb$ extraction.

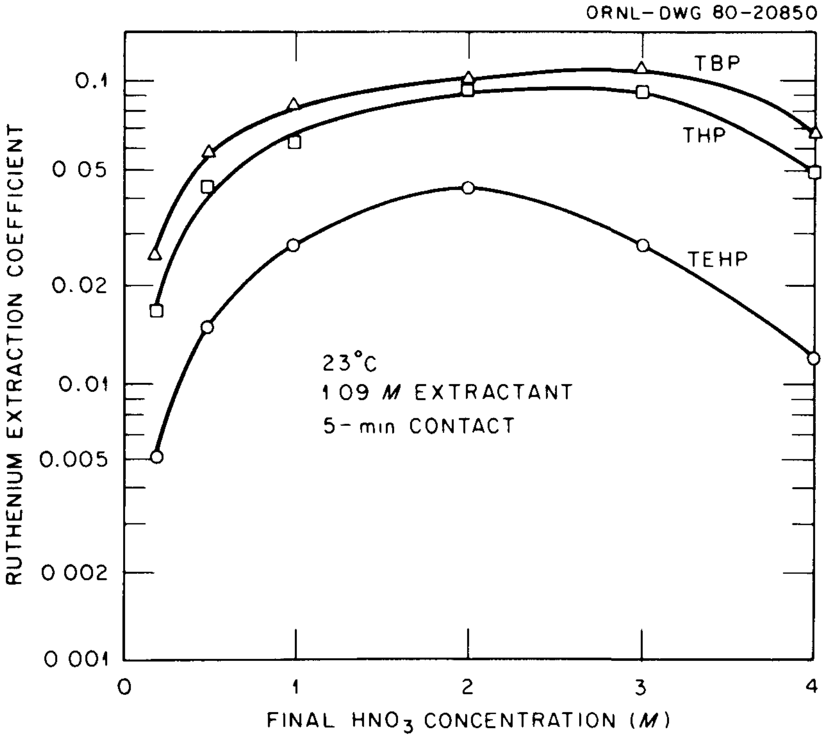

Fig. 3.15. Effect of nitric acid concentration on ruthenium extraction.

3.5.3 Behavior of zirconium and ruthenium in simulated process cycle

Tests were made with each of the three extractants to examine ^{95}Zr-^{95}Nb and ruthenium behavior in a series of batch extraction, scrub, and strip contacts that simulated a complete process cycle. The solvent was first contacted with 3 *M* HNO_3 to extract zirconium or ruthenium. The extract was then scrubbed with 1.5 *M* HNO_3 and stripped with 0.03 *M* HNO_3. Only the fission product (no uranium) was present.

The measured decontamination factors for ^{95}Zr-^{95}Nb were about 1200 for TBP and THP and 2600 for TEHP (Table 3.3). Less zirconium was extracted with TEHP, and a larger fraction of that extracted was removed by scrubbing. With all three extractants, essentially all of the decontamination achieved beyond the extraction contact was obtained in scrubbing. The extraction time was 5 min and the scrubbing and stripping contacts were 2 min each. In a duplicate test in which all contacts were for 15 min, the overall decontamination factors were 1180, 610, and 665, respectively, for TBP, THP, and TEHP. The lower decontamination efficiencies were primarily due to a decrease in scrubbing efficiency, particularly with TEHP.

In the ruthenium tests, little ruthenium was removed by the scrub contacts. (Table 3.3). With TBP and THP, decontamination in stripping was slightly higher than the total obtained in the extraction-scrubbing contacts; however, with TEHP, it was almost a factor of 10 lower. The measured overall DFs for TBP, THP, and TEHP were 215, 249, and 326 respectively.

3.5.4 Summary

Because of the complex chemistry of zirconium and ruthenium, tests of the type described in this section can provide only a rough indication of the comparative fission

Table 3.3. Zirconium and ruthenium decontamination efficiencies in simulated process cycle[a]

[Organic phase 1.09 *M* extractant in NDD (preequilibrated with 3 *M* HNO_3), aqueous phase 3 *M* HNO_3 with 10^{-3} *M* Zr traced with ^{95}Zr-^{95}Nb, or 10^{-3} Ru traced with ^{106}Ru]

Fission product	Extraction	Extraction coefficient	Decontamination factor			
			Extraction	Scrub	Strip	Overall[b]
Zr	TBP	0.074	15.0	80	1.05	1260
	THP	0.082	13.4	81	1.1	1190
	TEHP	0.052	20.4	98	1.3	2600
Ru	TBP	0.105	10.8	1.14	17.5	215
	THP	0.088	12.3	1.14	17.8	249
	TEHP	0.029	36.7	1.48	6.0	326

[a] Procedure solvent contacted with equal volume of aqueous to extract zirconium or ruthenium (5-min contact), extract scrubbed with three successive 0.2 volumes of 1.5 *M* HNO_3 (2 min) and stripped with three successive 0.5 volumes of 0.03 *M* HNO_3 (2 min), temperature was ~25°C.

[b] Ratio of the amount of ^{95}Zr-^{95}Nb (or ^{106}Ru) in the initial 3 *M* HNO_3 to the total amount in the strip solutions.

product decontamination efficiencies that can be expected for the three extractants in actual process operation. The results are influenced by the methods of preparing the feed solutions which affect the metal species that are present, by the contact times and temperature and by other variables. In particular, zirconium decontamination may be more strongly controlled by the degradation products of the extractant (and diluent) than by the extractant itself; therefore, the relative stabilities of the extractants are important (see Sect. 4). All of the accumulated data, however, indicate that decontamination from zirconium and ruthenium should probably be no worse when using THP or TEHP than when using TBP; in the case of TEHP, the decontamination efficiencies may be appreciably better. These indications need confirmation in countercurrent tests with actual reactor fuel solutions; plans for such tests are being made.

With respect to fission product decontamination, there is an advantage for THP and TEHP over TBP that is not obvious from the above tests. That is, both THP and TEHP extract uranium (and plutonium) more strongly than TBP; therefore, they can be loaded to a higher level with heavy metals in the extraction-scrubbing system. It is well known that increasing the solvent loading has a strong beneficial effect on decontamination efficiencies.

3.6 Extraction Kinetics

Studies of U(VI) transfer rates for various trialkyl phosphates in a Lewis cell by J. C. Mailen, D. E. Horner, and J. K. Storey of ORNL showed that the uranium transfer rates in both the extraction and stripping modes decreased as the alkyl chain length and branching increased.[10] The decrease was in the order TBP>TIBP*>THP>TEHP. Although uranium transfer was a factor of 5 to 10 slower with TEHP than with TBP, transfer was still very rapid. The significance of these lower transfer rates for THP and TEHP solvents needs to be evaluated in typical solvent extraction contactors.

4. SOLVENT STABILITY

When TBP solutions are contacted with nitric acid solutions, the TBP slowly hydrolyzes to form primarily dibutyl phosphoric acid (HDBP) and monobutyl phosphoric acid (H_2MBP). The yield of HDBP is about a factor of 10 greater than that of H_2MBP. The hydrolysis is accelerated in a radiation field. The degradation products increase the extraction of fission products and lower the decontamination efficiency. They also prevent complete stripping of uranium, plutonium, and thorium and contribute to their losses to solvent-wash waste streams. In addition, the organic and aqueous phase solubilities of the zirconium and thorium complexes with HDBP (and with H_2MBP) are low, and they can precipitate and cause operational problems. Davis and Kibbey[11] measured the hydrolysis rate of TBP dissolved in the aqueous phase as a function of nitric acid concentration and temperature. A recent study with tributyl phosphate isomers showed that branching of the alkyl chain affects the hydrolysis rate.[3] It has also been shown that TBP hydrolysis is catalyzed by the presence of uranium, thorium, and zirconium, particularly zirconium.[12]

Tests of the chemical stability of TBP, THP, and TEHP, which are described below, showed that TBP and THP degrade at about the same rates on extended contact with dilute HNO_3 and that TEHP is more stable by at least a factor of 5. On the other hand, the three trialkyl phosphates showed essentially equivalent radiation stabilities. The presence of

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*TIBP = tri(isobutyl) phosphate.

uranium appreciably accelerated the rate of acid hydrolysis but had no significant effect on the radiolysis rates.

4.1 Analytical Methods

Measurement of the low concentrations (10^{-5} to 10^{-3} *M*) of dialkyl phosphoric acids in the solvents was a problem in these studies. Gas chromatographic and ion chromatographic methods were not suitable for dihexyl phosphoric acid (HDHP) or di(2-ethylhexyl) phosphoric acid (HDEHP) in tests made in ORNL's Analytical Chemistry Division. Consequently, zirconium extraction, measured in standard tests, was used to indicate the dialkyl phosphoric acid concentrations. The zirconium extraction coefficients for the three solvents as a function of added dialkyl phosphoric acid concentration are shown in Fig. 4.1. The aqueous phase was 1 *M* HNO_3 that contained 3 X 10^{-5} *M* Zr and ^{95}Zr tracer (>90% of the ^{95}Nb daughter activity was separated from the ^{95}Zr prior to the extraction tests). The slope of the linear portion of the extraction curves is approximately 2, indicating a second power dependence of the extraction coefficient on dialkyl phosphoric acid concentration. This dependence has been observed by others.[13] The zirconium extraction coefficients for THP-HDHP and TEHP-HDEHP solvents were about the same and were about a factor of 2 higher than those for the TBP-HDBP combination.

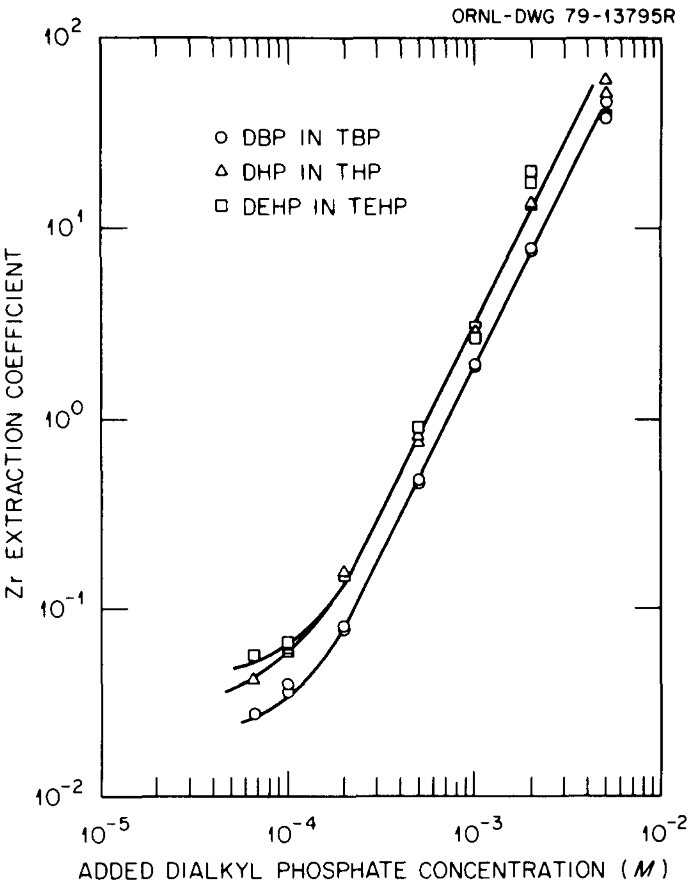

Fig. 4.1. Effect of dialkyl phosphate concentration on zirconium extraction from 1 *M* HNO_3 with 1.09 *M* trialkyl phosphate solutions in NDD.

4.2 Chemical Stability

In chemical stability tests, 1.09 *M* solutions of TBP, THP, and TEHP in NDD were equilibrated for 73 days with an equal volume of 1 *M* HNO_3 at 23°C. Light was excluded from the test solutions. Samples were removed periodically for analysis, and the degradation rates of the trialkyl phosphates were estimated from the formation rates of the corresponding dialkyl phosphoric acids. The latter were determined by measuring the zirconium extraction coefficients from 1 *M* HNO_3 and comparing them with those of the standard extraction curves of Fig. 4.1. The hydrolysis rates of TBP and THP were essentially the same, but the rate of TEHP was at least a factor of 5 lower (Fig. 4.2). The indicated organic phase dialkyl phosphoric acid concentrations after 73 days were 5.1×10^{-4} *M* HDBP in the TBP, 4.7×10^{-4} *M* HDHP in the THP, and less than 1×10^{-4} *M* HDEHP in the TEHP. The degradation rates indicated by these concentrations are about 3×10^{-4} millimoles L^{-1} h^{-1} for TBP and THP, and less than 0.6×10^{-4} millimoles L^{-1} h^{-1} for TEHP. The low HDEHP formation rate in TEHP solutions was confirmed by radioactive scandium extraction tests and comparison with a standard curve for scandium extraction. This was not possible with the TBP and THP solutions because the scandium complexes of HDBP and HDHP precipitated at the low acidities necessary for effective scandium extraction.

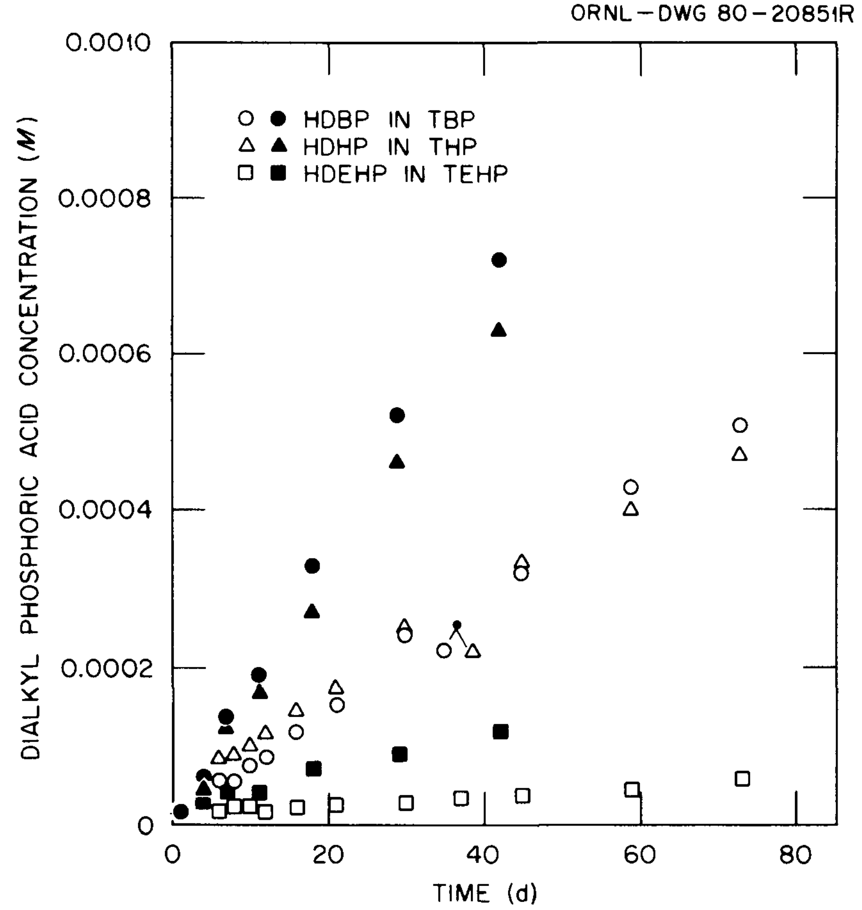

Fig. 4.2. Hydrolytic degradation of 1.09 *M* trialkyl phosphate solutions in contact with 1 *M* HNO_3 at 23°C. The darkened points are for tests with uranium present.

The degradation rates of all three trialkyl phosphates increased when uranium was added to the system to provide an organic phase loading of 20 g/L (Fig. 4.2). The degradation rates of TBP and THP were again about the same and substantially higher than the degradation rate for TEHP. The degradation rates indicated by the dialkyl phosphoric acid concentrations measured with uranium present were about 6.9 millimoles L^{-1} h^{-1} for TBP and THP and about 1.1 millimoles L^{-1} h^{-1} for TEHP. These rates for TBP and THP are about a factor of 2.5 higher than in the uranium-barren system, and the rate for TEHP is about a factor of 4 higher.

The results of these chemical stability tests are in agreement with those of the Russian study[3] with tributyl phosphate isomers, which showed that compounds with branching on the second carbon are more resistant to hydrolytic degradation than those with straight hydrocarbon chains or with branching on the first carbon.

4.3 Radiolytic Stability

Comparative radiolytic stability tests were made to a total dose of 4 W·h/L in a ^{60}Co source with 1.09 *M* solutions of trialkyl phosphates in contact with 1 *M* HNO_3. The strength of the radiation field was 3.5 W/L, and the temperature of the solutions was maintained at 23°C by cooling. Following irradiation, dialkyl phosphoric acid concentrations in the organic phase samples were determined by measuring the ^{95}Zr extraction coefficient as described above.

The results (Fig. 4.3) indicate no differences in the radiolysis rates for the three trialkyl phosphates. The organic phase samples contained about 3 × 10^{-4} *M* dialkyl phosphoric acid

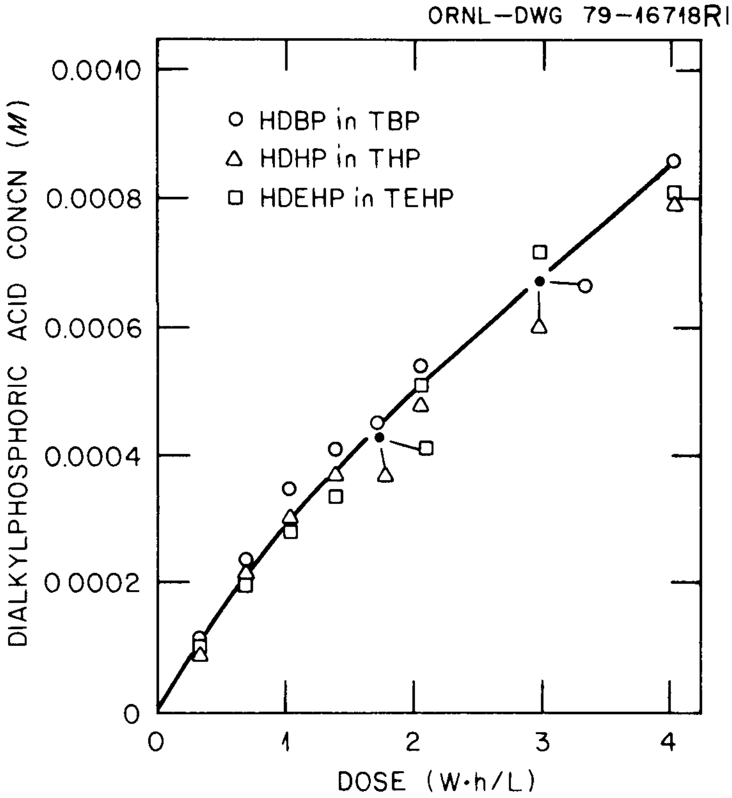

Fig. 4.3. Radiolytic degradation of 1.09 *M* trialkyl phosphate solutions in contact with 1 *M* HNO_3 at 23°C.

after a dose of 1 W·h/L. The formation rate per unit of exposure then decreased slowly as the dose was increased. In process operation, the radiation dose for each cycle is expected to be well below 1 W·h/L.

Some of the irradiation tests were repeated with uranium present in the 1 *M* HNO_3 so that the uranium concentration in the solvent was about 20 g/L. The data were somewhat scattered, but most data points were approximately the same as were obtained with uranium absent. We conclude, therefore, that uranium does not have a significant effect on the radiolytic degradation rate.

5. PRECIPITATION OF METAL-DIALKYL PHOSPHATE COMPLEXES

Problems have been encountered in past TBP processing experience from the precipitation of thorium and zirconium complexes of TBP degradation products, primarily HDBP. These precipitates collected at the interfaces and on the surfaces of processing equipment. In the more extreme cases, particularly in the processing of thorium fuels, shutdown and cleanout of the contactor was necessary. The results of our preliminary thorium extraction and stripping tests indicate that the degradation products of THP and TEHP, dihexyl phosphoric acid (HDHP), and di(2-ethylhexyl) phosphoric acid (HDEHP), are less likely to precipitate with thorium than HDBP. Precipitation occurs at a much lower thorium concentration in the stripping system than in the extraction system, probably because the low acid concentrations used in the former encourage thorium hydrolysis.

In these tests, thorium was extracted from 2 *M* HNO_3 containing 50 g/L thorium with 1.09 *M* solutions of the trialkyl phosphates that had the corresponding dialkyl phosphoric acids added to concentrations of 0.0025, 0.0050, 0.0075, and 0.0100 *M*. Precipitation was not observed with any of the solvents in the extraction tests (Table 5.1). The extracts were then contacted three times with equal volumes of 0.1 *M* HNO_3 to strip the thorium. Precipitation did not occur with any of the solvent samples until the third stripping contact; then precipitates formed with all four TBP-HDBP solutions, with the amount of precipitate being roughly proportional to the HDBP concentration. Precipitates also formed at this point with the THP solutions that contained 0.0075 and 0.0100 *M* HDHP; however, the amounts were less than in the corresponding tests with TBP-HDBP. Precipitates did not form with the TEHP-HDEHP solvents in the contacts with 0.1 *M* HNO_3. However, precipitation did occur at all four HDEHP concentrations in the third equal volume contact with 0.01 *M* HNO_3 made after the 0.1 *M* HNO_3 contacts.

These preliminary experiments indicate that increasing the chain length of the trialkyl phosphate extractants significantly increases the organic phase solubility of the complexes of their principal degradation product (dialkyl phosphoric acids) with thorium. Presumably, the same would apply to the zirconium complexes and the complexes of these metals with monoalkyl phosphoric acid degradation products. Therefore, the precipitation problems encountered with TBP may be greatly decreased or avoided by using these higher molecular weight extractants. The solubilities of the thorium and zirconium complexes of these degradation products will be measured in future studies for a range of process conditions.

Table 5.1. **Precipitation of thorium dialkyl phosphates at 23°C**[a]

Trialkyl phosphate	Dialkyl phosphoric acid concentration (*M*)	Extraction	Strip with 0.1 *M* HNO_3 contact			Strip with 0.01 *M* HNO_3 contact		
			1	2	3	1	2	3
TBP	0.0025	NP[b]	NP	NP	TP[c]			
	0.0050	NP	NP	NP	P[d]			
	0.0075	NP	NP	NP	P			
	0.0100	NP	NP	NP	P			
THP	0.0025	NP	NP	NP	NP			
	0.0050	NP	NP	NP	NP			
	0.0075	NP	NP	NP	P			
	0.0100	NP	NP	NP	P			
TEHP	0.0025	NP	NP	NP	NP	NP	NP	P
	0.0050	NP	NP	NP	NP	NP	NP	P
	0.0075	NP	NP	NP	NP	NP	NP	P
	0.0100	NP	NP	NP	NP	NP	NP	P

[a] Procedure: 1.09 *M* solutions of TBP, THP, and TEHP in NDD contacted with 3 *M* HNO_3 containing 50 g/L thorium at an aqueous-to-organic phase ratio of 2:1. Extracts were stripped of thorium by three successive contacts with an equal volume of 0.1 *M* HNO_3; TEHP stripping was continued with 0.01 *M* HNO_3.

[b] No precipitate.

[c] Trace precipitate.

[d] Precipitate.

6. PHYSICAL PROPERTIES

The three extractants were measured to determine their density, viscosity, and interfacial tension as functions of their concentration in NDD. When compared on a molar concentration basis, the magnitude of all three properties of the solvent was in the order TEHP> THP>TBP.

The density (Table 6.1) and viscosity (Fig. 6.1) of the solvents increased with an increase in extractant concentration. The interfacial tension, which was measured against 1 *M* HNO_3 at 25°C by the drop volume method,[14] did not change significantly over the extractant concentration range of 0.5 to 1.09 *M*, but was substantially lower for these solutions than for the NDD diluent (Fig. 6.2).

6.1 Aqueous Phase Solubility

Comparative data for distributions of TBP and THP to water and dilute HNO_3 for 0.5 *M* solutions of the extractants in NDD are listed in Table 6.2. These data were obtained in early studies by J. G. Moore.[5,7] The concentration of TBP in the aqueous phase ranged from 0.17 to 0.24 g/L when the solvent was contacted with 0 to 3 *M* HNO_3 solutions, with the maximum value being observed at 1.0 *M* HNO_3 concentration. The concentration of THP in the aqueous phase was less than 1 ppm in all tests, or at least a factor of 200 lower than the TBP values. Although the aqueous solubility of TEHP was not measured, it is also expected to be less than 1 ppm.

Table 6.1. Density of trialkyl phosphate solutions in NDD[a]

Trialkyl phosphate	Molarity	Density at 25°C, g/cm^3
TBP	0.5	0.775
	0.75	0.790
	1.09	0.813
	undiluted	0.973
THP	0.5	0.779
	0.75	0.797
	1.09	0.823
	undiluted	0.937
TEHP	0.5	0.785
	0.75	0.806
	1.09	0.835
	undiluted	0.921

[a] NDD density is 0.747 g/cm^3.

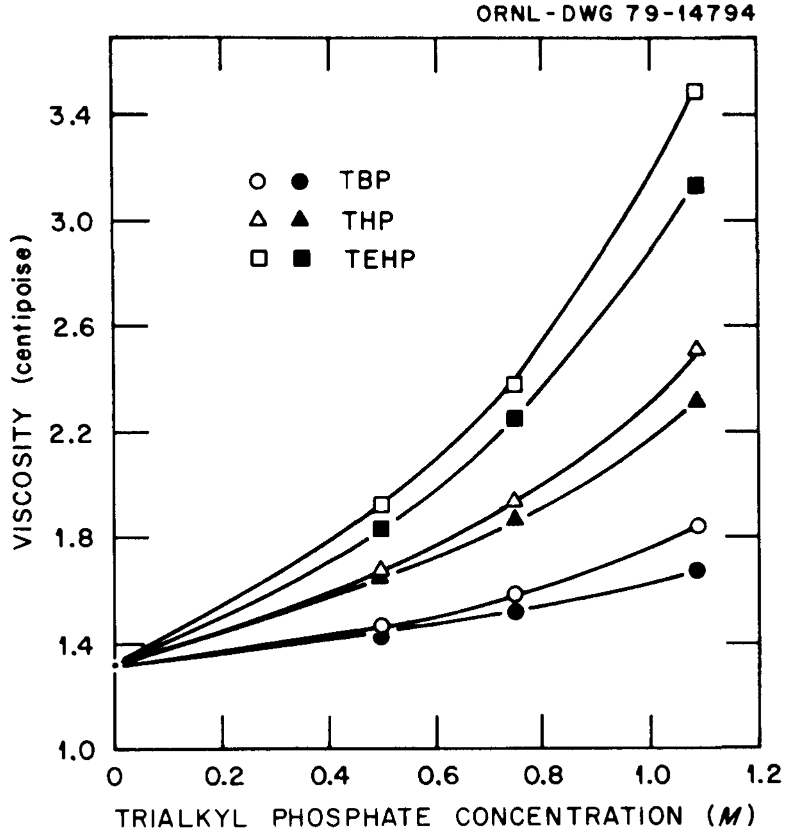

Fig. 6.1. Viscosity of trialkyl phosphate-NDD solutions. Darkened points before equilibration with 1 *M* HNO_3, open points after equilibration with 1 *M* HNO_3. Viscosity of the undiluted extractants was TBP, 32.9 cP; THP, 6.66 cP, and TEHP, 11.7 cP.

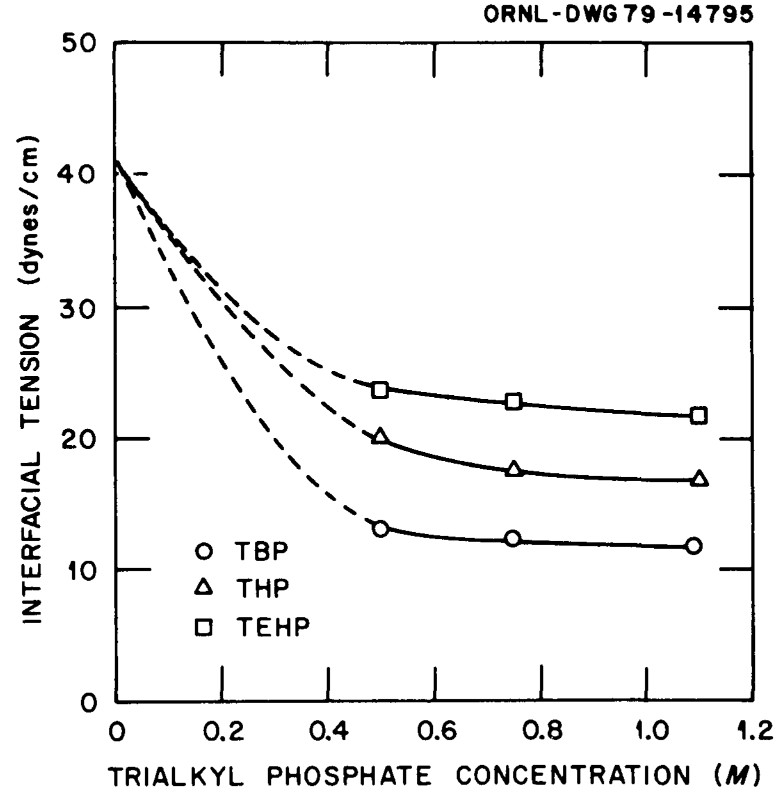

Fig. 6.2. Interfacial tension of trialkyl phosphate-NDD solutions against 1 *M* HNO_3 at 25°C.

Table 6.2. Distribution of TBP and THP to the aqueous phase[a]

Nitric acid concentration (*M*)	Aqueous phase concentration, g/L	
	TBP	THP
0	0.20	<0.001
0.1	0.21	<0.001
0.5	0.22	<0.001
1	0.24	<0.001
2	0.20	<0.001
3	0.17	<0.001

[a] In contact with 0.5 *M* solutions of TBP or THP in NDD at 25°C.

7. PHASE SEPARATION TESTS

Preliminary batch and continuous phase separation tests were made to compare the phase separation characteristics of TBP and TEHP under some standard test conditions.

7.1 Batch Tests

A series of tests was made in which organic solvent was mixed vigorously with an equal volume of 3.0, 0.3, or 0.01 *M* HNO_3 in a baffled mixer agitated with a two-blade paddle stirrer. Mixing was then ceased and the phases allowed to separate. Both aqueous-continuous and organic-continuous mixing conditions were compared. Table 7.1 summarizes the results.

For comparable test conditions, phase separation with TBP solvent was more rapid than with TEHP solvent. Also, the separated TBP solvent was usually somewhat less turbid than the separated TEHP solvent. In general, phase separation was accelerated by increasing the temperature from 23 to 50°C and decreasing the extractant concentration from 1.09 to 0.6 *M*. Also, separations were faster from 3 *M* than from 0.01 *M* HNO_3 and with the aqueous rather than the organic as the continuous phase.

Similar tests were run using 3 *M* HNO_3 that initially contained 0.5 *M* $UO_2(NO_3)_2$ as the aqueous phase. Comparative performance of the two extractants was about the same as in the tests with 3 *M* HNO_3 alone, but phase separation times were somewhat longer (Table 7.2).

Table 7.1. Phase separation times after mixing of TBP or TEHP in NDD with an equal volume of nitric acid

Extractant	Continuous phase	Phase separation times,[a] min		
		3 *M* HNO_3	0.3 *M* HNO_3	0.01 *M* HNO_3
1.09 *M* TBP	Organic	0.6, 0.5, 0.4, 0.4	1.1, 1.0, 0.9, 0.8	1.3, 1.3, 1.0, 0.9
	Aqueous	0.5, 0.5, 0.4, 0.4	0.4, 0.4, 0.3, 0.3	0.5, 0.5, 0.5, 0.5
1.09 *M* TEHP	Organic	0.9, 0.6, 0.5, 0.4	1.0, 0.9, 0.8, 0.7	*b*
	Aqueous	0.8, 0.7, 0.6, 0.5	0.5, 0.5, 0.5, 0.5	1.3, 1.2, 1.0, 0.9
0.6 *M* TBP	Organic	0.6, 0.5, 0.4, 0.4	1.1, 1.0, 0.8, 0.8	1.0, 0.9, 0.8, 0.7
	Aqueous	0.6, 0.5, 0.5, 0.4	0.5, 0.5, 0.5, 0.5	0.6, 0.6, 0.6, 0.4
0.6 *M* TEHP	Organic	0.6, 0.4, 0.4, 0.3	*b*	*b*
	Aqueous	0.8, 0.7, 0.6, 0.5	0.8, 0.8, 0.7, 0.7	1.0, 0.9, 0.6, 0.6
0.6 *M* TEHP[c]	Organic	0.7, 0.6, 0.5, 0.5	*b*	
	Aqueous	0.7, 0.6, 0.5, 0.5	1.1, 0.8, 0.7, 0.6	

[a] Times shown in each case are for tests at 23, 30, 40, and 50°C respectively.

[b] Organic phase continuous mixing could not be maintained at the test phase ratio (1:1); reverted to aqueous continuous.

[c] Diluent was normal paraffin hydrocarbon (NPH) rather than NDD.

Table 7.2. Phase separation times after mixing TBP or TEHP in NDD with an equal volume of 3 *M* HNO_3 – 0.5 *M* $UO_2(NO_3)_2$ solution

Extractant	Continuous phase	Phase separation times,[a] min	Organic phase appearance
1.09 *M* TBP	Organic	1.0, 0.9. 0.8, 0.7	Turbid
	Aqueous	1.1, 0.9, 0.8, 0.7	Clear
1.09 *M* TEHP	Organic	1.4, 1.3, 1.0, 0.9	Turbid
	Aqueous	1.2, 1.3, 1.2, 1.1	Somewhat turbid
0.6 *M* TEHP	Organic	0.8, 0.6, 0.6, 0.6	Turbid
	Aqueous	0.9, 0.9, 1.0, 0.8	Clear

[a] Times shown in each case are for tests at 23, 30, 40, and 50°C respectively.

Tests were also run using 0.3 *M* Na_2CO_3 solution as the aqueous phase to simulate the solvent wash system. Again, phase separation was more rapid with TBP than with TEHP, and the differences in the rate of phase separation and solvent clarity were more dramatic than in the acid system (Table 7.3). Increasing the temperature from 23 to 50°C had a large beneficial effect on separation times.

7.2 Continuous Tests

Phase separation characteristics of the solvents were compared on a continuous basis in a closed system which included a baffled mixer, a settler, and a pump and surge tank for both the aqueous and organic solutions. The solutions were pumped to the mixer and the separated phases returned from the settler to the surge tanks. The thickness of the dispersion band in the settler was determined as a function of the total solution flow while maintaining the flow ratio of the organic and aqueous solutions constant at 1:1.

As in the batch tests, phase separation with both solvents was faster for aqueous-continuous than for organic-continuous mixing. In tests with TBP (Fig. 7.1), the dispersion band was about twice as thick for organic-continuous than for aqueous-continuous mixing at the lowest flow tested, and 3.5 times as thick at the highest flow. Doubling the flow rate increased the dispersion band thickness by a factor of 3 with aqueous-continuous conditions and a factor of ~3.6 with organic-continuous conditions.

In similar tests with TEHP, phase separation was slower and difficulties were encountered owing to deterioration of the phase separation characteristics of the solvent with time. The same aqueous and organic solutions were left in the system for the eight-day period of the tests (Fig. 7.2). The thickness of the dispersion band for a given flow increased by a factor of 3 to 4 over this period. An increase in the band thickness with aging was also observed with TBP; however, the increase was minor (20 to 30% over a period of about two weeks).

Tests were also made with 0.6 *M* TEHP in NDD. The thickness of the dispersion band again increased considerably with time. The band thickness for a given flow was smaller than in the tests with 1.09 *M* TEHP, but the difference was not large.

Table 7.3. Phase separation times after mixing of TBP or TEHP in NDD with an equal volume of 0.3 *M* Na_2CO_3 solution

Extractant	Continuous phase	Phase separation times,[a] min	Organic phase appearance
1.09 *M* TBP	Organic	1.0, 0.8, 0.6, 0.6	Turbid
	Aqueous	0.9, 0.7, 0.5, 0.5	Clear
1.09 *M* TEHP	Organic	2.3, 1.2, 1.1, 0.8	Very turbid
	Aqueous	1.2, 1.1, 1.3, 1.4	Very turbid
0.6 *M* TBP	Organic	0.8, 0.6, 0.4, 0.4	Turbid
	Aqueous	1.3, 0.9, 0.7, 0.6	Clear
0.6 *M* TEHP	Organic	3.0, 2.2, 1.7, 1.2	Turbid
	Aqueous	2.8, 1.8, 1.4, 1.2	Turbid
0.6 *M* TEHP[b]	Organic	2.2, 1.5, 1.2, 1.1	Very turbid
	Aqueous	1.4, 0.9, 0.9, 0.8	Very turbid

[a] Times shown in each case are for tests at 23, 30, 40, and 50°C respectively.

[b] Diluent was normal paraffin hydrocarbon (NPH) rather than NDD.

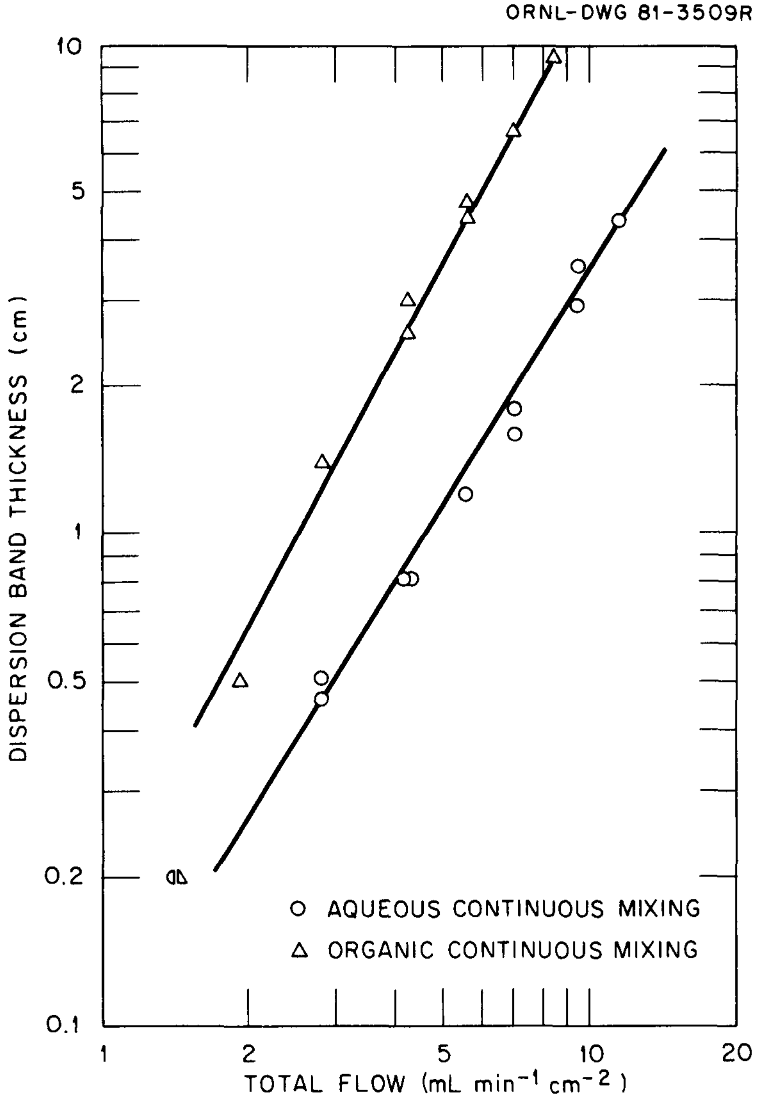

Fig. 7.1. Continuous phase separation tests with 1.09 *M* TBP in NDD and 3 *M* HNO_3 at ~23°C; flow ratio of 1:1.

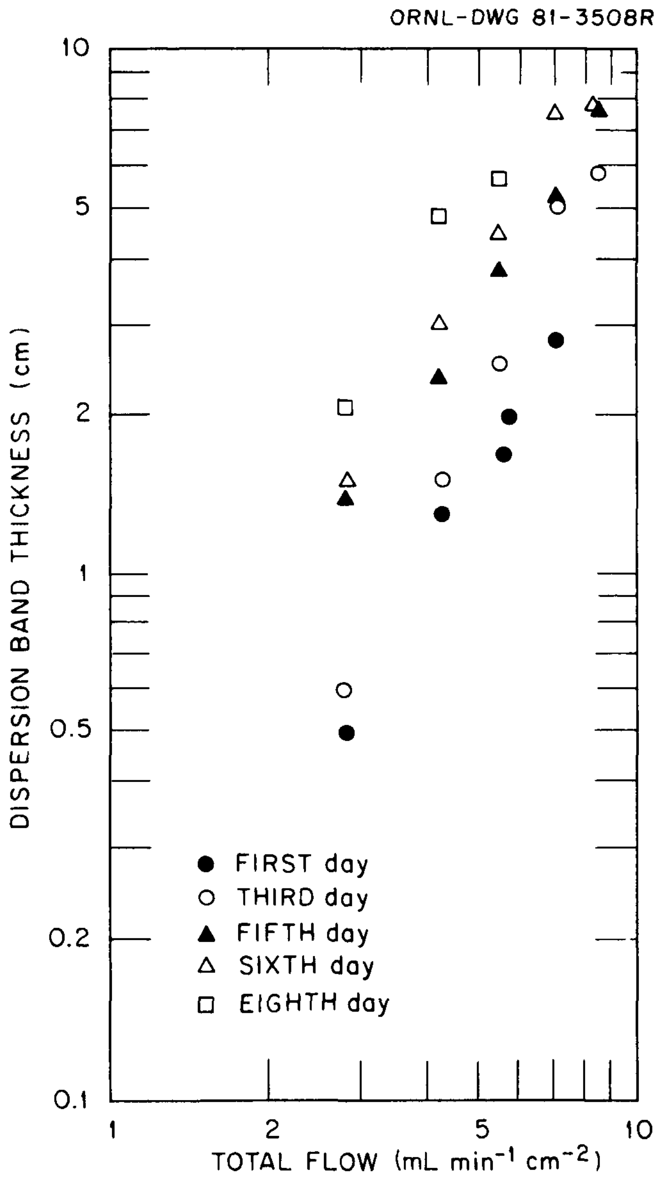

Fig. 7.2. Continuous phase separation tests with 1.09 *M* TEHP in NDD and 3 *M* HNO_3 at ~23°C; aqueous-continuous mixing, flow ratio of 1:1. Tests of the effect of temperature on phase separation (see Fig. 7.4) were made on the seventh day.

The reason for the severe degradation of TEHP phase separation characteristics is not understood, since other studies (Sect. 4.1) have shown that TEHP is much less subject to chemical degradation than TBP. It may be that TEHP degradation products are much more efficient emulsion formers than the degradation products of TBP. Further study is needed to obtain a better understanding of the observed effects and their process importance.

The effect of temperature on the phase separation of TBP and TEHP is shown in Figs. 7.3 and 7.4. As expected, increasing the temperature appreciably improved the phase separation. For a given temperature, the dispersion band thickness in the TEHP tests was larger than in the TBP tests, even though solution flow in the latter was a factor of 2 higher. The TEHP and 3 *M* HNO_3 used in these tests had been in the system for seven days.

ACKNOWLEDGMENTS

We gratefully acknowledge the excellent technical assistance of Faith I. Case, who performed most of the experiments. The plutonium data were obtained at the ORNL Transuranium Processing Facility by S. E. North under the supervision of M. H. Lloyd. Uranium and thorium analyses were made by personnel in the ORNL Analytical Chemistry Division under the direction of L. L. Brady and R. R. Rickard.

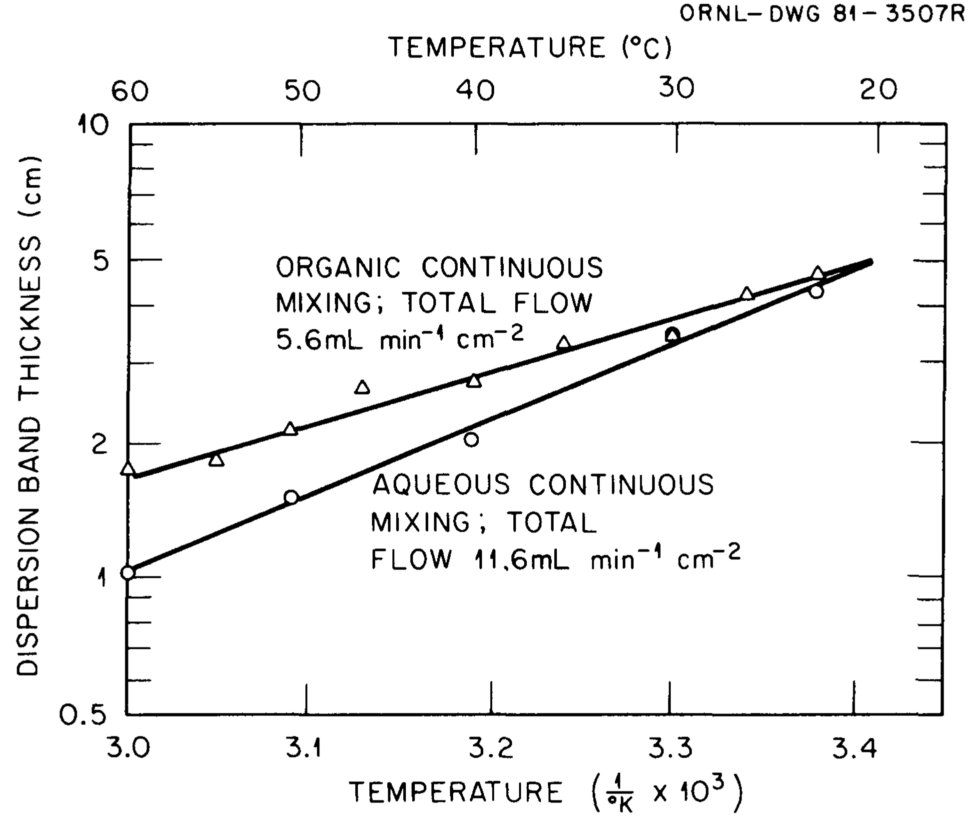

Fig. 7.3. Effect of temperature on phase separation of 1.09 *M* TBP in NDD and 3 *M* HNO_3; flow ratio of 1:1.

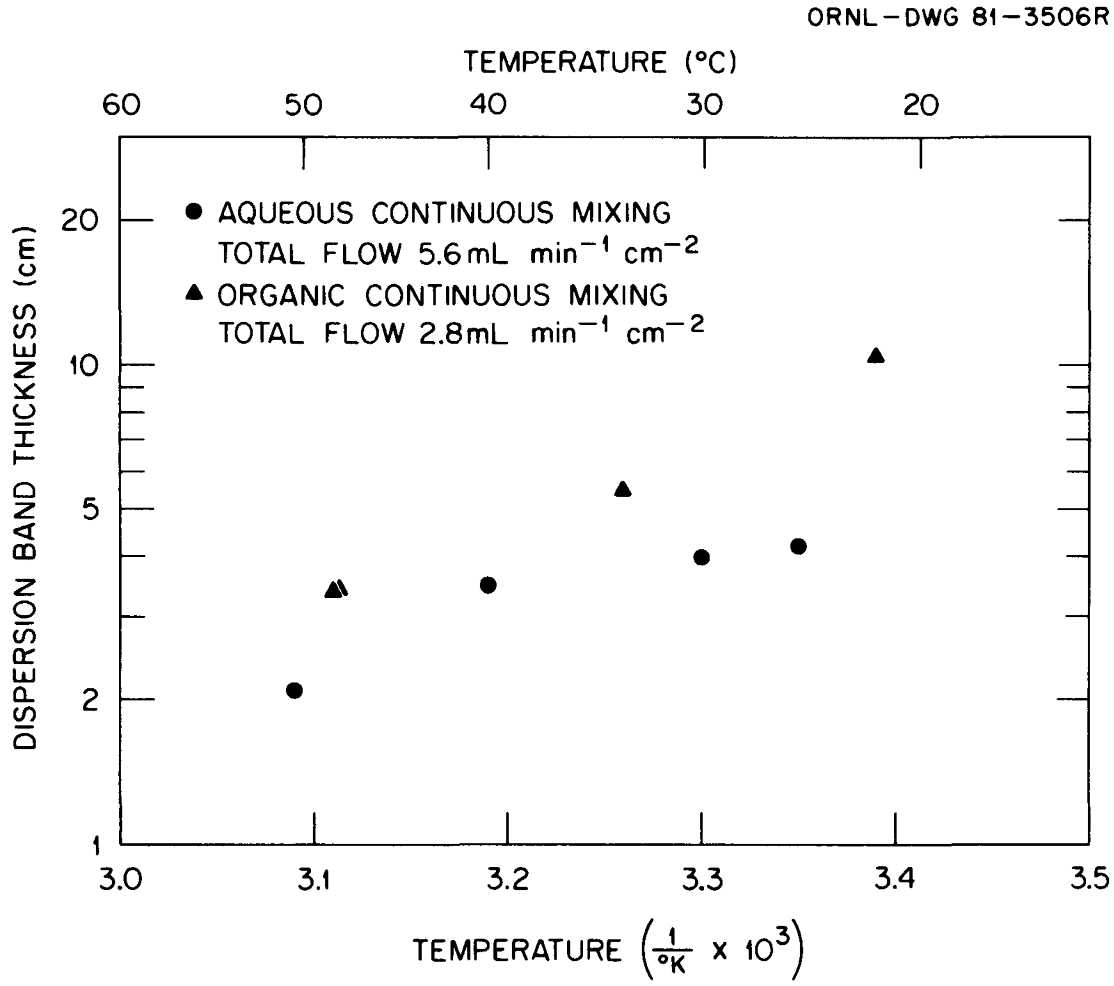

Fig. 7.4. **Effect of temperature on phase separation of 1.09 *M* TEHP in NDD and 3 *M* HNO_3; flow ratio of 1:1.** These tests were run after the solutions were in the system for seven days.

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