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ALPHA RADIOLYSIS OF TRIBUTYL PHOSPHATE - EFFECT OF DILUENTS

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ABSTRACT

Alpha radiolysis of solutions of tributyl phosphate (TBP) in several different types of diluents was studied. Yields of dibutyl phosphoric acid (as measured by plutonium-IV retention) and chloride were measured up to a dose of ∿10 watt-hours per liter. Plutonium dissolved in the organic phase was the radiation source. The yields of dibutyl phosphoric acid (HDBP) and Cl^- *were the highest for carbon tetrachloride. The aromatic diluents give the best protection for TBP against radiolysis and also yield less* Cl^-*. The low yield of HDBP in aromatic diluents can be explained by assuming HDBP formation by dissociation of the parent ion* (TBP^+)*. Several radiation-resistant diluents are suggested as alternatives to* CCl_4 *and their Pu(IV) extraction properties are presented.*

ALPHA RADIOLYSIS OF TRIBUTYL PHOSPHATE - EFFECT OF DILUENTS

INTRODUCTION

Tributyl phosphate (TBP) extractants are commonly used to separate and purify plutonium and other alpha-emitting actinides by solvent extraction from aqueous solutions. At the Plutonium Reclamation Facility at Hanford, TBP is diluted with carbon tetrachloride to improve its extraction properties. Because plutonium is extracted into the organic phase, its high alpha activity causes radiolytic damage to the solvent. Two of the major radiolysis products, dibutyl phosphoric acid (HDBP) and chloride ion, cause problems with the solvent extraction process. Formation of HDBP causes loss of Pu in the stripping step, lowers decontamination factors for impurities, and results in poor phase separation. The presence of chloride ions causes corrosion of process vessels.

The objectives of this study were to determine the amount of degradation of the TBP-CCl_4 solvent as a function of dose (from alpha radiation) and to measure the effect on degradation of replacing the CCl_4 with other diluents or adding radiolysis inhibitors. Development of a heavier-than-water extractant with better resistance to radiolysis is the long-range goal.

Gamma radiolysis of the TBP-CCl_4 system has been studied previously by several workers.(1,2) However, no alpha radiolysis data are available for this solvent under conditions similar to those which exist in the solvent extraction process.

EXPERIMENTAL

MATERIALS

A Pu(IV) nitrate stock solution was prepared by loading an impure Pu solution (adjusted to 6$\underline{M}$ HNO_3) onto a column of 50-100 mesh nitrate-form Bio-Rex 9 anion exchange resin (Bio-Rad Laboratories). The column was washed with 6$\underline{M}$ HNO_3 and the Pu then eluted with 1$\underline{M}$ HNO_3. The stock solution was adjusted to 2.0$\underline{M}$ HNO_3.

The TBP was vacuum distilled. All other reagents were of reagent grade. The tetrachloroethylene was stabilized with 0.5 percent ethanol as antioxidant.

PROCEDURE

The TBP extractants were prepared by diluting 20 milliliters of TBP to a final volume of 100 ml with the diluent. This mixture was then pre-equilibrated with a 2.0$\underline{M}$ HNO_3 solution. The extractants were irradiated by stirring to emulsion equal volumes of the pre-equilibrated extractant and a Pu(IV) stock solution. The stirred mixtures were protected from light during the radiolysis experiments and were kept at room temperature (23 ± 5° C). The aqueous and organic phases were separated and sampled at various time intervals. These samples were analyzed for Pu and H^+ content.

The amount of Pu in the organic phase strongly complexed by radiolysis products (mainly HDBP) was measured by washing the organic phase five times with equal volumes of 0.2<u>M</u> HNO_3. The Pu in the organic phase after washing is the nonextractable Pu.

The total amount of chloride ion formed during radiolysis was measured (when using chlorinated diluents). The 0.2<u>M</u> HNO_3 wash solutions (containing chloride from the organic phase) were combined with a measured volume of aqueous phase from the stirred mixtures. This solution was analyzed for chloride ion.

The dose was calculated by assuming all the radiation from the Pu dissolved in the organic phase was adsorbed in the organic phase. The radioisotope decay energy was calculated from the isotopic distribution of the Pu used:

Isotope	Percent
^{239}Pu	85.160
^{240}Pu	12.201
^{241}Pu	2.373
^{242}Pu	0.200
^{238}Pu	0.066

The dose is the product of the decay energy (in watts per gram), the Pu concentration in the organic phase (in grams per liter), and the time of irradiation (hours).

ANALYSES

Plutonium concentration was determined by standard alpha counting techniques. Chloride was measured using a chloride specific ion electrode (Orion Model 96-17). The isotopic analysis of Pu was by mass spectrometry.

RESULTS AND DISCUSSION

DILUENT SELECTION

Tributyl phosphate diluents used in heavier-than-water solvent extraction systems must have the following properties.

- A density of > ∿1.4.
- A reasonably high flash point.
- Low water solubility.
- High solubility for Pu-TBP complexes.
- Innocuous degradation products from radiolysis and hydrolysis which can be removed with basic washes.
- Low cost.

Aromatic and unsaturated organic compounds are generally recognized to be more stable toward radiation (in the liquid state) than aliphatic compounds. Studies of various TBP-diluent systems have shown that these types of solvents actually protect the TBP molecule from degradation. Canva and Pagès(3) found that benzene, toluene, cyclohexene, and cyclooctatetraene protect TBP while saturated hydrocarbons such as hexane, cyclohexane, and dodecane sensitize TBP to degradation. Others have obtained similar results.(4,5) The aromatic and unsaturated compounds act as energy sinks which can absorb alpha radiation energy without damaging the TBP molecules.

In contrast to the aromatic and unsaturated compounds, carbon tetrachloride has been shown to sensitize TBP radiolysis.(1,2) Because of these results, it was decided to concentrate on aromatic and unsaturated compounds as substitutes for CCl_4. Due to the requirements of density, water solubility, nonflammability, and cost, the choice of diluents was narrowed to the following:

Aromatic Diluents	Unsaturated Diluents
1,2,4-Trichlorobenzene	Tetrachloroethylene
o-Dichlorobenzene	Trichloroethylene
Bromobenzene	
m-Dibromobenzene	
1-Bromo-4-fluorobenzene	

Some of the relevant chemical and physical properties of several of the most promising diluents are given in the appendix.

PLUTONIUM RETENTION

One of the principal radiolysis products of TBP is HDBP. The HDBP strongly complexes Pu(IV) in the organic phase to form one of the following species:(6-8)

$$PuR_4,\ Pu(NO_3)_2(HR_2)_2,\ \text{or}\ Pu(NO_3)R_3(HR)$$

where R represents $PO_2(OC_4H_9)_2^-$ and H_2R_2 is a dimer of HDBP. Since these complexes are more stable than the Pu(IV)-TBP complex, they cannot be stripped from the organic phase with dilute HNO_3. The amount of Pu retained in the organic phase after stripping with 0.2M HNO_2 is, therefore, a sensitive measure of TBP degradation.

Plutonium retention as a function of dose was measured for extractants composed of 20 percent (by volume) TBP-diluent. Each of the aromatic and unsaturated diluents listed above was tested in addition to CCl_4. The amount of Pu retained versus dose for the CCl_4 and bromobenzene diluents is shown in Figure 1. The plots show a linear relationship between the dose and the amount of Pu retained. The average amount of Pu retained for CCl_4 and bromobenzene was 56 milligrams Pu per watt-hour and 13 mg Pu/watt-hr, respectively. Table I gives the amount of Pu retained per watt-hour of dose for each of the diluents studied.

TABLE I

PLUTONIUM RETENTION FOR 20 PERCENT TBP-DILUENT

Diluent	Plutonium Retention mg Pu/watt-hr
Carbon tetrachloride	56
1,2,4-Trichlorobenzene	15
o-Dichlorobenzene	18
Bromobenzene	13
m-Dibromobenzene	14
1-Bromo-4-fluorobenzene	14
Tetrachloroethylene	32
Trichloroethylene	35
Dodecane	25(9)

The data show that TBP degradation is greatest when CCl_4 is used as the diluent. The aromatic compounds give the least amount of degradation when used as diluents. The range

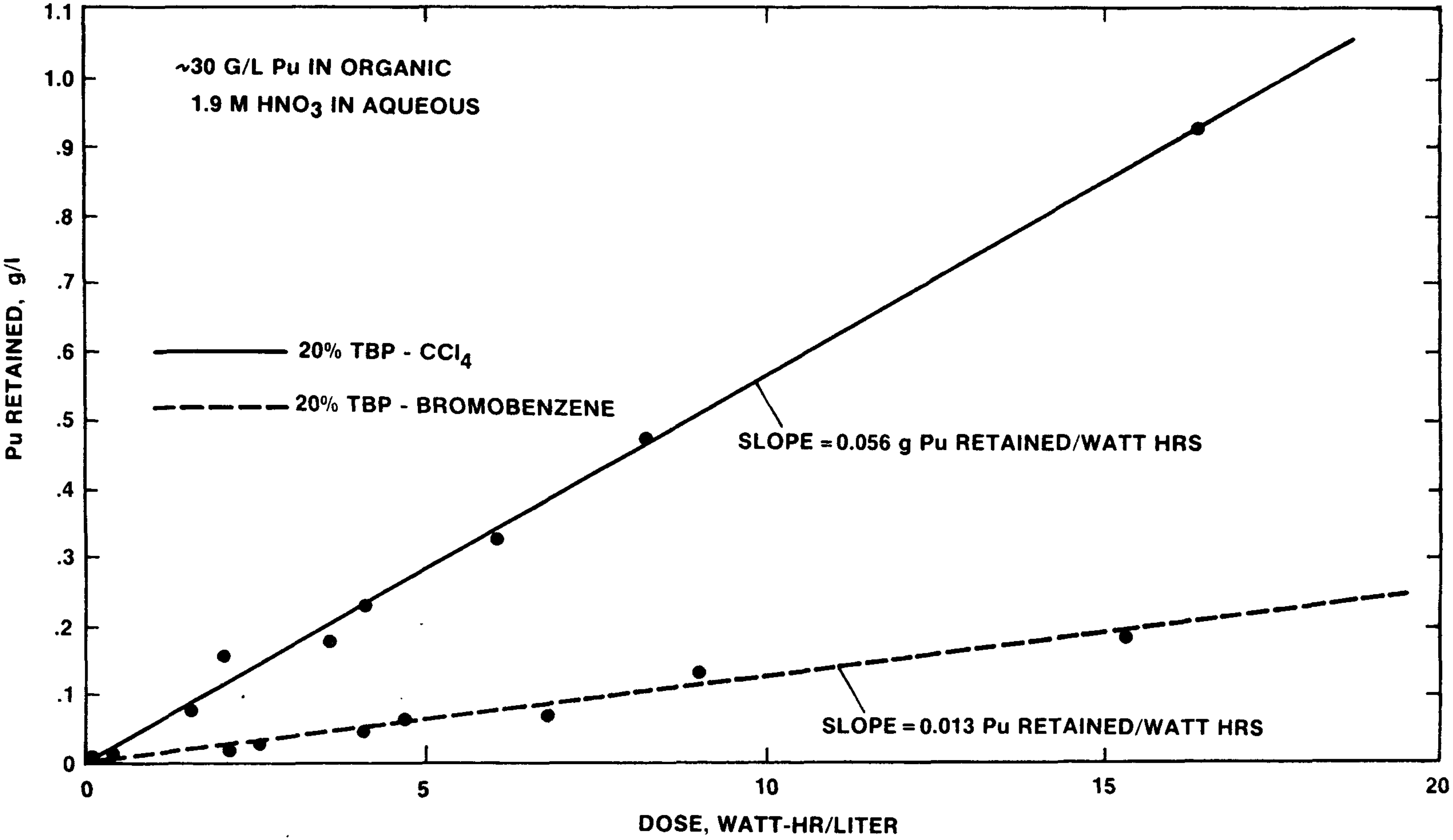

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FIGURE 1

Pu RETENTION IN ORGANIC PHASE

of values obtained for the aromatic solvents was very narrow (13-18 mg Pu retained/watt-hr). The ethylene compounds gave intermediate TBP degradation. The value for dodecane is given to compare Pu retention using nonhalogenated, aliphatic hydrocarbons as diluents.

The aromatic diluents provide significant protection against radiolysis of TBP and are much superior to CCl_4 in this respect. The stability of TBP in various diluents can be explained by the transfer of ionization from the diluent to TBP and subsequent dissociation of TBP^+.(3)

$$[\text{Diluent}] \rightsquigarrow [\text{Diluent}]^+ + e^- \tag{1}$$

$$[\text{Diluent}]^+ + \text{TBP} \rightarrow \text{TBP}^+ + [\text{Diluent}] \tag{2}$$

$$\text{TBP}^+ \rightarrow \text{H}_2\text{DBP}^+ + \text{C}_4\text{H}_7\cdot \tag{3}$$

$$\text{H}_2\text{DBP}^+ + e^- \rightarrow \text{HDBP} + \text{H}\cdot \tag{4}$$

If the diluent has a higher ionization potential than TBP, reaction 2 will occur and this will result in greater TBP degradation. Table II gives the ionization potentials for most of the diluents studied.

TABLE II

IONIZATION POTENTIALS OF DILUENTS

Diluent	Ionization Potential(10) Electron Volts
Carbon tetrachloride	11.47 ± 0.01
1,2,4-Trichlorobenzene	--
o-Dichlorobenzene	9.06
Bromobenzene	9.98 ± 0.02
m-Dibromobenzene	--
1-Bromo-4-fluorobenzene	8.99 ± 0.03
Tetrachloroethylene	9.32 ± 0.01
Trichloroethylene	9.45
Dodecane	10(3)
Indene	8.81

In general, the higher the ionization potential of the diluent, the greater the degradation of TBP (see Table I). The low ionization potential of the aromatic compounds (∿9 electron volts) allows these diluents to act as ionization sinks, thus protecting the TBP molecules.(3)

After long irradiation periods (dose >10 watt-hr/liter), the TBP diluted with aromatic solvents became yellow. This is probably due to polymer formation.(11) Most of the yellow color could be removed, however, by washing the organic phase with sodium carbonate solution.

The effect of chemical degradation of the extractants on Pu retention was measured. A mixture identical to that of the radiolysis experiments (except that no Pu was present) was exposed to 2.0M HNO_3 for time periods equal to those of the radiolysis experiments. No measurable Pu retention was observed. Therefore, chemical degradation was not significant in those experiments.

CHLORIDE FORMATION

Chloride ion is a major radiolysis product of chlorinated hydrocarbons. The rate of chloride formation was measured during alpha radiolysis for each of the chlorinated diluents studied. A plot of chloride concentration versus dose is shown in Figure 2 for the radiolysis of 20 percent TBP (by volume) - CCl_4. As expected, chloride formation is a linear function of dose with 5.2 millimoles of Cl^- produced per watt-hour. Results of measurements with other TBP-diluent solvents are given in Table III.

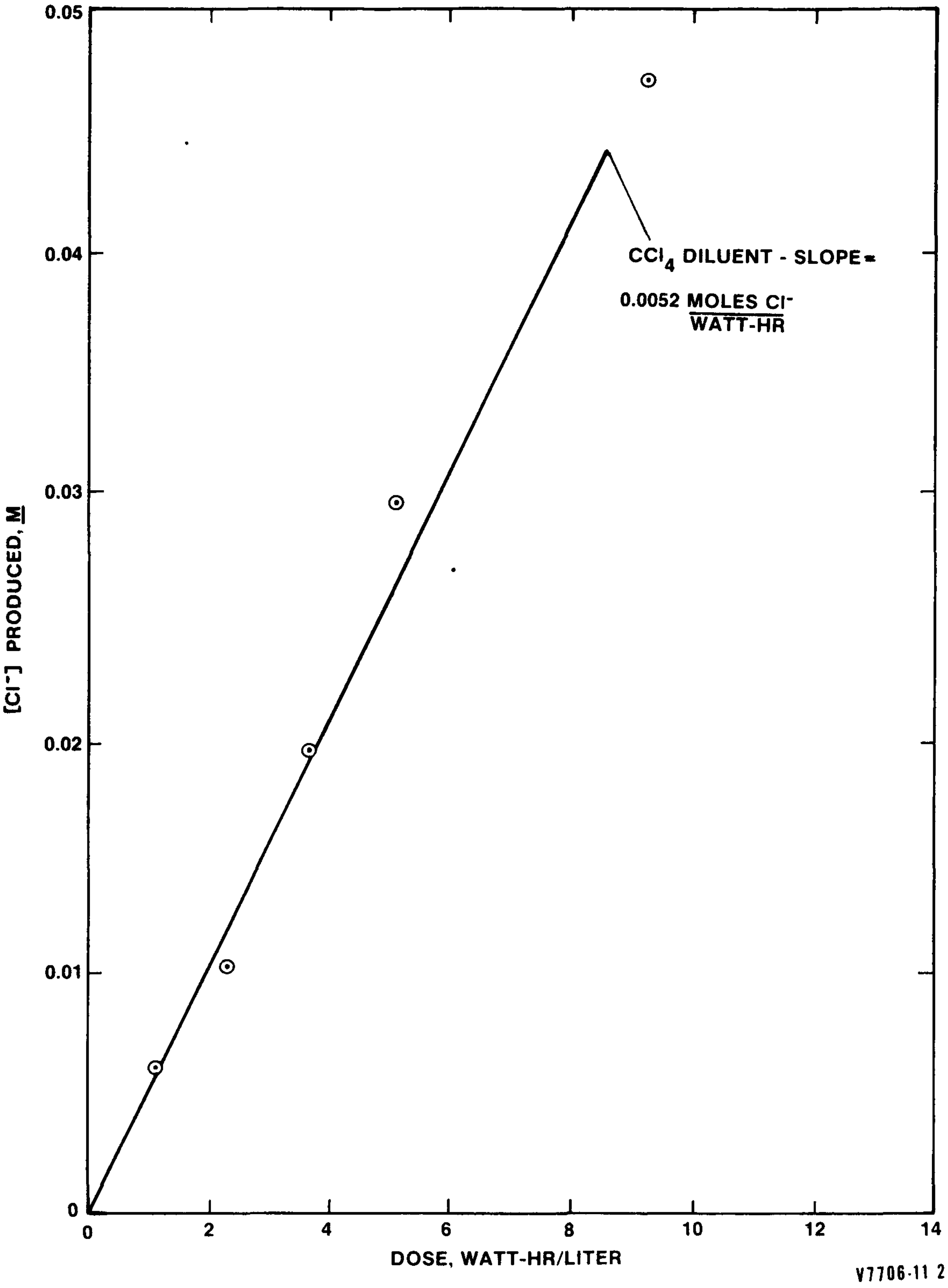

FIGURE 2

FORMATION OF CHLORIDE BY RADIOLYSIS OF SOLVENTS

TABLE III

CHLORIDE FORMATION FOR 20 PERCENT TBP-DILUENT

Diluent	Rate of Cl^- Formation mmole/watt-hr
Carbon tetrachloride	5.2
1,2,4-Trichlorobenzene	Nondetectable
o-Dichlorobenzene	Nondetectable
Tetrachloroethylene	2.5
Trichloroethylene	3.4

These data show that the unsaturated diluents are superior to CCl_4 with respect to chloride formation and that the aromatic chlorides produce very little chloride ion by radiolysis. This can be explained in terms of carbon-chlorine bond strengths for the three types of chlorinated hydrocarbons. The order of increasing bond strength is:

$$\text{aliphatic} < \text{olefinic} < \text{aromatic}.$$

Also, the percentage of carbon-chlorine bonds in the diluent molecules decreases according to the series:

$$CCl_4(100\%) > C_2Cl_4(80\%) > C_6H_4Cl_2(16.7\%).$$

Chloride ion produced by cleavage of a carbon-chlorine bond is, therefore, less likely for the aromatic and unsaturated solvents than for CCl_4.

RADIOLYSIS INHIBITOR

Wagner and Towle(12) found that the addition of indene to a 30 percent TBP-kerosine extractant significantly reduced radiolytic damage to TBP. It was, therefore, decided to measure the effect of indene addition to the 20 percent TBP-CCl_4 solvent.

Figure 3 shows no measurable difference in Pu retention when 10 percent (by volume) indene was added to the TBP-CCl_4 mixture. The indene appears to suffer severe damage after a dose of about 10 watt-hr/liter. The solution becomes dark brown and viscous after absorbing this dose. However, the rate of chloride formation was reduced from 5.2 mmoles/watt-hr to 2.4 mmoles/watt-hr by adding the indene.

EXTRACTION PROPERTIES OF TBP-DILUENTS

The extraction properties of TBP-diluent mixtures are very important in considering substitutes for the TBP-CCl_4 solvent. Diluents strongly influence the distribution coefficient for Pu(IV) extraction. Taube(13) has found that extraction of Pu(IV) with TBP is much greater using nonpolar diluents (CCl_4, benzene, cyclohexane, and n-heptane) than for polar diluents ($CHCl_3$, $CHBr_3$, and CH_2Br_2).

Distribution coefficients were measured for several of the most promising diluents using tracer amounts of Pu(IV). Plots of the distribution coefficient versus HNO_3 concentration are shown in Figure 4 for 20 percent TBP in CCl_4, tetrachloroethylene, 1,2,4-trichlorobenzene(14) and bromobenzene.(14) Below $\sim 2.5\underline{M}$ HNO_3, the ability of the TBP-diluent to extract Pu(IV) decreases according to the series: $C_2Cl_4 > C_6H_5Br > CCl_4 > C_6H_3Cl_3$.

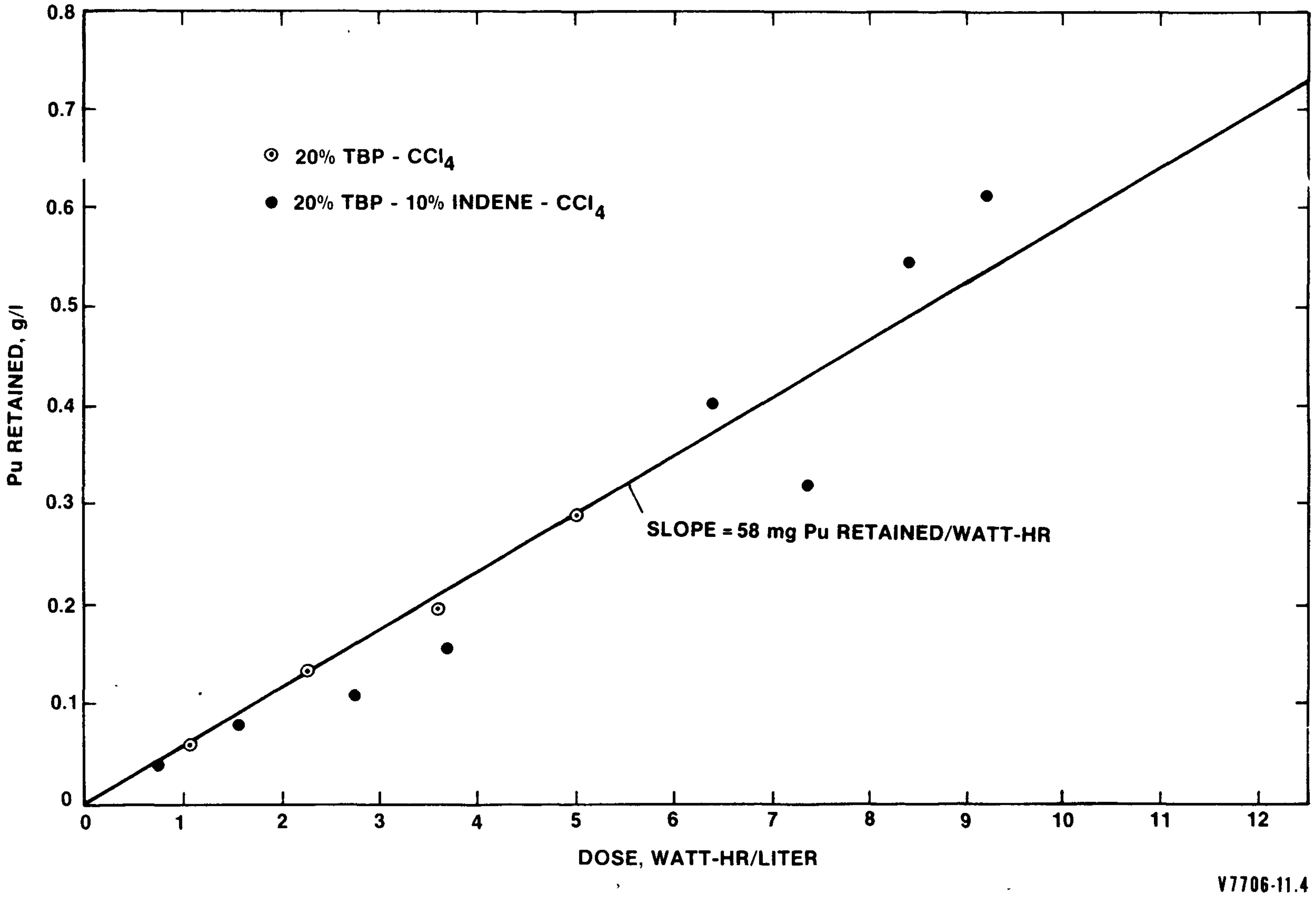

FIGURE 3

Pu RETENTION IN 20 PERCENT TBP-CCl_4-INDENE

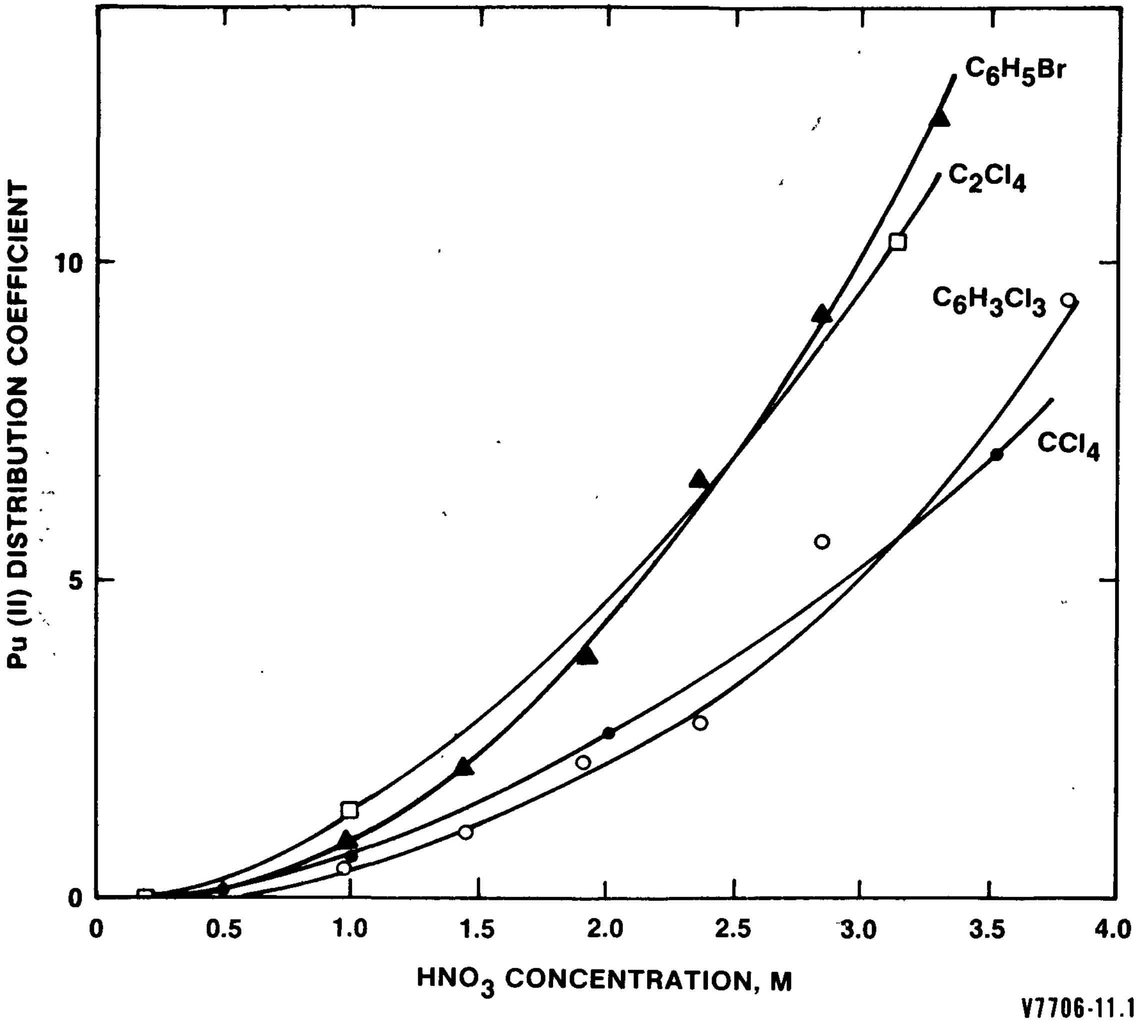

FIGURE 4

Pu(IV) DISTRIBUTION COEFFICIENTS
FOR 20 PERCENT TBP IN VARIOUS DILUENTS

ACKNOWLEDGMENTS

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REFERENCES

1. L. L. Burger and E. D. McClanahan, Jr., *Gamma Radiolysis of Tributyl Phosphate - Diluent Systems,* U.S. AEC Report HW-52943, General Electric Company, Hanford Atomic Products Operation, Richland, Washington, September 1, 1957.

2. M. M. Kurtepov, M. F. Pushlenkov, B. Ya. Zil'berman, A. S. Gryaznova, and T. I. Efremova, *Radiokhemiya,* 9, 32-7(1967).

3. J. Canva and M. Pagès, *Radiochemica Acta,* 4, 88-91(1967).

4. E. P. Bareko, I. P. Solyanina, and Z. I. Tsvetkova, *Atomnaya Energiya,* 21, 281-5(1966).

5. R. M. Wagner, E. M. Kinderman, and L. H. Towle, *Ind. and Eng. Chem.,* 51, 45-6(1959).

6. V. B. Shevchenko and V. S. Smelov, *Soviet J. At. Energy,* 6, 76(1959).

7. P. Dreze and G. Duyckaerts, *Euraton Report EUR-436F,* 1963.

8. L. Kuča, *Collection Czech. Commun.,* 32, 298(1967).

9. L. Stieglitz, W. Ochsenfeld, and H. Schnieder, *Gesellschaft Für Kemforschung M.B.H., Karlsruhe,* Report KFK-691, November 1968.

10. R. C. Weast, Editor, *Handbook of Chemistry and Physics,* 55th Edition, p. E74, CRC Press, Inc., Cleveland, Ohio, 1974.

11. J. Fajer and D. R. Mackenzie, *Adv. in Chem. Series*, 82, 469-74(1968).

12. R. M. Wagner and L. H. Towle, *Radiation Stability of Organic Liquids*, U.S. AEC Report AECU-4300, Stanford Research Institute, Menlo Park, California, June 1959.

13. M. Taube, *J. Inorg. and Nucl. Chem.*, 12, 174-80(1959).

14. R. A. Hamilton, *Physical and Chemical Studies of Radiolysis - Resistant Tributyl Phosphate Solvent Systems for the 880 Process*, U.S. AEC Report ARH-2785, Atlantic Richfield Hanford Company, Richland, Washington, May 1973.

APPENDIX

PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED DILUENTS

Properties	CCl_4	C_2Cl_4	$C_6H_3Cl_3$	C_6H_5Br
Density, g/ml at 20° C	1.5940	1.6227	1.4542	1.4950
Boiling Point, °C	76.54	121	213.5	156
Melting Point, °C	-22.99	-19	16.95	-30.82
Flash Point, °C	None	None	110	51
Solubility in Water, g/100 ml H_2O	0.08(20° C)	0.04(25° C)	0.22(25° C)	0.0446(30° C)
Viscosity, cp	0.969(20° C)	0.88(20° C)	1.97(25° C)	1.196(15° C)
Cost (relative units)	1.0	1.4	3.2	4

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