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**DEMONSTRATION OF THE POTENTIAL FOR DESIGNING EXTRACTANTS WITH PRESELECTED
EXTRACTION PROPERTIES: POSSIBLE APPLICATION TO REACTOR FUEL REPROCESSING**

by

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Prepared for
American Chemical Society Meeting
Honolulu, Hawaii
April 2-5, 1979

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**Operated under Contract W-31-109-Eng-38 for the
U. S. DEPARTMENT OF ENERGY**

889
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Demonstration of the Potential for Designing Extractants with
Preselected Extraction Properties: Possible Application to
Reactor Fuel Reprocessing*

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From the knowledge of the extractant characteristics of both neutral and mono-acidic phosphorus-based organic compounds now available, it is possible to tailor-make extractants for a specifically desired separation of two metals. The present study is concerned with neutral mono-nuclear, phosphorus-based extractants for use in affecting the mutual separation of U(VI) and Th(IV).

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*Work performed under the auspices of the Office of Basic
Energy Sciences of the Department of Energy.

Liquid-liquid extraction (LLE) systems using neutral phosphorus-based organic compounds have been the subject of extensive study since Warf (1) first reported the use of tributyl phosphate, TBP, as a useful extractant for cerium(IV), uranyl and thorium nitrates. After more than twenty years, liquid-liquid extraction systems (such as the Purex and Thorex processes) employing TBP dissolved in a suitable diluent versus an aqueous HNO_3 phase remain the most widely accepted systems for reactor fuel reprocessing.

The use of extractants of the same general type as tributyl phosphate, i.e., neutral extractants containing the P=O coordinating group, but designed with specially selected extraction properties should have many advantages in the development of LLE systems which may be applicable to reactor fuel reprocessing.

The importance of the acidic and steric properties of mono-acidic phosphorus-based extractants in the extraction of metals has been well established. The work of Mason, Peppard, et al. (2,3) has shown that combined acidic and steric effects which result from altering the structure of the acidic extractants may be varied to give a wide range of extraction constants (K_s) for specific metals. $K_s = K[\text{H}^+]^a/F^b$, where K_s is a constant characteristic of the system, K is the distribution ratio,

H is the hydrogen ion concentration in the equilibrated aqueous phase, F is the concentration of extractant in the equilibrated organic phase, a and b are the respective hydrogen ion and extractant dependencies. Recent studies, to be published, involving the extraction of actinides (III), (IV) and (VI) and lanthanides (III) in which the steric properties of the extractants are varied, while keeping their acidities essentially constant, show that steric hindrance within the extractant molecule is the most important property effecting separation factors of metals in different oxidation states. The possibility of predicting the basicity of the P=O of neutral phosphorus-based compounds from the PK_A values of related monoacidic acids has been demonstrated by previous studies in this laboratory (4,5,6).

The above information plus the published work of researchers such as that of Siddall, Burger and Rosen (7,8,9,10) should allow one to state with confidence that liquid-liquid extraction systems may be designed for specific process applications. By varying the type and mode of bonding (i.e., COP or CP bonds) of organic groups in neutral phosphorus-based organic compounds, it is possible to exploit the changes in steric and inductive effects which result in the desired modification of extraction behavior. The purpose of this study is to

demonstrate the potential for such an approach.

Experimental

The symbols used to represent the phosphorus-based organic compounds are in accordance with previous usage (11,12) in which H represents a theoretically ionizable hydrogen; D and T the prefixes tri- and di-; G a generalized organic group and P the phosphorus atom. Thus, TGP, DG[GP] and G[DGP] represent the neutral phosphate, $(GO)_3PO$, phosphonate, $(GO)_2(G)PO$, and phosphinate esters, $(GO)(G)_2PO$, respectively; HDGP, HG[GP] and H[DGP] are the corresponding monoacidic acids. The enclosure of G, organic groups, in brackets indicates that the groups are attached to the phosphorus by CP bonds in contrast to COP bonds of G groups not enclosed by brackets. G groups represented by multiple characters are enclosed in parentheses.

Individual compounds used in this study are symbolized as TBP {tributyl phosphate, $(C_4H_9O)_3PO$ }, DB[BP] {dibutyl butyl phosphonate, $(C_4H_9O)_2(C_4H_9)PO$ }, B[DBP] {butyl dibutyl phosphinate, $(C_4H_9O)(C_4H_9)_2PO$ }, DA[AP] {diamyl amyl phosphonate, $(C_5H_{11}O)_2(C_5H_{11})PO$ }, DB[(CH)P] {dibutyl cyclohexyl phosphonate, $(C_4H_9O)_2(C_6H_{11})PO$ }, DB[(ClM)P] {dibutyl chloromethyl phosphonate, $(C_4H_9O)_2(ClCH_2)PO$ }, T(4-MPe-2)P {tri(4-methylpentyl-2) phosphate, $[(CH_3)_2CHCH_2CH(CH_3)O]_3PO$ }, D(4-MPe-2)[BP] {di(4-methylpentyl-2)

butyl phosphonate, $[(CH_3)_2CHCH_2CH(CH_3)O]_2(C_4H_9)PO$,
 D(4-MPe-2)[iBP] {di(4-methylpentyl-2 isobutyl phosphonate,
 $[(CH_3)_2CHCH_2CH(CH_3)O]_2[(CH_3)_2CHCH_2]PO$ }, D(4-MPe-2)[PP]
 {di(4-methylpentyl-2) propyl phosphonate, $[(CH_3)_2CHCH_2CH(CH_3)O]_2$
 $(C_3H_7)PO$ }, and D(EB)[(EB)P] {(di(2-ethylbutyl) 2-ethylbutyl
 phosphonate, $[(C_2H_5)_2CHCH_2O]_2[(C_2H_5)_2CHCH_2]PO$ }.

The concentration unit formality, $\underline{F}$, is defined as the number of formula weights of solute contained in 1 liter of solution.

The distribution ratio of a given nuclide is defined as the concentration of that nuclide in the organic phase divided by the concentration of nuclide in the aqueous phase of two mutually-equilibrated sensibly-immiscible liquid phases, the concentration of nuclide being on an atom basis as reflected in counting rates, alpha, beta or gamma.

The PK_A values (used in this paper) of phosphorus-based acids in 75% ethanol were determined in a comprehensive study, to be reported elsewhere, of the relationship of PK_A to structure and composition in $(X_1)(X_2)PO(OH)$ and $(X)PO(OH)_2$ compounds using a method described previously (5).

Source, Preparation and Purification of Materials.

The TBP, DB[BP] and DB[(ClM)P] were obtained from Commercial Solvents Corporation, Virginia-Carolina Chemical Corporation and Stouffer Chemical Company, respectively. The DA[AP] and

DB[(CH)P] were obtained from Hooker Chemical Corporation. The T(4-MPe-2), D(EB)[(EB)P], D(4-MPe-2)[BP], D(4-MPe-2)[(iB)P], D(4-MPe-2)[PP] and B[DBP] were prepared in this laboratory. The reagent-grade (99% minimum purity) dodecane used as a carrier diluent was obtained from Aldrich Chemical Company.

The commercially obtained extractants were purified by a modification of a method previously described (13) for the purification of TBP. The undiluted extractant was stirred with an equal volume 6 M HCl at room temperature for 1 hour and scrubbed with two equal volume portions of water. The aqueous phases were discarded, and the organic phase was stirred for 1 hour with 1 M NaOH at room temperature. The aqueous phase was discarded, and the organic (extractant) phase was diluted to 30 percent by volume with n-heptane. The n-heptane solution was scrubbed with 6 one-half volume portions of distilled water. The water phases were discarded, and the n-heptane was removed from the organic phase by evaporation in an open beaker at room temperature. The purified product was freed from traces of n-heptane, H₂O and alcohols (formed in the purification step) by pumping for eight hours at 10^{-2} mm pressure and at room temperature.

The neutral phosphonate esters, D(EB)[(EB)P], D(4-MPe-2)[BP], D(4-MPe-2)[(iB)P] and D(4-MPe-2)[PP] were prepared by the Michaelis-Arbuzov Reaction in which alkyl

halides were reacted with previously prepared trialkyl phosphites. The neutral phosphate, $T(4-MPe-2)P$, was prepared by a conventional esterification method in which 4-methyl-2-pentanol was reacted with $POCl_3$ in the presence of pyridine. The temperature during the reaction was kept below $15^\circ C$ to prevent disproportionation of the alkyl group. The neutral phosphinate ester, $B[DBP]$, was prepared by esterification of dibutyl phosphorus oxychloride, $(C_4H_9)_2POCl$, in the presence of pyridine.

The same general method as described for the purification of the commercially obtained extractants was used to purify the neutral phosphorus-based extractants prepared in this laboratory.

Alpha-active 1.6×10^5 -yr ^{233}U (^{238}U : ^{233}U mass ratio less than 0.03) and alpha-active 7.8×10^4 -yr ^{230}Th (^{232}Th : ^{230}Th mass ratio equals 10) were obtained from Argonne National Laboratory stocks. By methods described previously, the uranium (11) and thorium (14) tracers were purified from daughter activities just prior to use.

Determination of Distribution Ratios. The distribution ratio, K , was determined radiometrically as described previously (11) with the following exceptions. The aqueous and organic phases were mixed 4 minutes in culture tubes with teflon lined screw caps using a Thermodyne vortex mixer equipped with a specially designed tube holder. The

organic phases were pre-equilibrated before use by contacting each organic phase with two equal volume portions of barren aqueous phase (i.e., an aqueous phase containing all constituents except the radioactive tracer). Aliquots of the aqueous and organic phases were measured into a glass scintillation vial containing 10 ml of Beckman Ready-Solv GP scintillation cocktail and counted in a Beckman LS 100C scintillation counter. All distribution ratios were determined at $22 \pm 2^\circ\text{C}$.

Results and Conclusions

The wide range of separation factors, K_U/K_{Th} , for the extraction of U(VI) and Th(IV) from 2.00 M HNO_3 into eleven selected neutral phosphorus-based extractants shown in Table I, demonstrates the potential for designing extractant systems for specific metal separations. The separation factors range from 0.71 for B[DBP] to 162 for D(4-MPe-2)[iBP]: a K_U/K_{Th} ratio of 228.

The data of Figure 1 shows that, in the absence of steric effects, the extraction of both U(VI) and Th(IV) increases as the basicity of the coordinating P=O of the neutral extractant increases. The increase in the extraction of Th (3×10^3) which is an order of magnitude greater than the increase for U (3×10^2) leads to an inversion of their extraction for B[DBP], the most basic of the extractants

studied. (From the data of previous studies (4,5), the basicity of the $P=O$ is assumed to increase as the PK_A of the corresponding monoacidic acid increases. The corresponding monoacidic acid is a compound which contains an OH group in place of one of the ester groups. For example, HDBP is the corresponding acid for TBP.) Of the homologous series of neutral phosphate, phosphonate and phosphinate extractants, respectively, TBP, DB[BP] and B[DBP], the extractant that gives the best separation factor for U(VI) and Th(IV) is TBP. The TBP molecule also has the least basic $P=O$ of the series. It is apparent that changing only the basicity of the extractant has little useful advantage in the separation of U(VI) and Th(IV).

The distribution ratios of the extraction of U(VI) and Th(IV) into a highly hindered phosphate extractant, $T(4-MPe-2)P$, are low, 3.26 and 0.15 respectively, regardless of the relatively high basicity of the $P=O$. Therefore, the data for this extractant do not fit the curves of the plot of $\log K$ versus PK_A of Figure 1. The large effect of steric hindrance on the extraction of U(VI) and Th(IV) and on their separation factors is shown by these data and the data for the highly hindered phosphonate extractants, $D(4-MPe-2)[BP]$, $D(4-MPe-2)[PP]$, and $D(4-MPe-2)[iBP]$ given in Table I.

It should be noted that the linear curve for Th(IV) compared to the markedly concave curve for U(VI) (see the

plot of $\log K$ versus PK_A of Figure 1) indicate a difference in the mechanism of extraction for these two metals.

The extractant dependencies of the extraction of U(VI) and Th(IV) as shown in Figure 2 and Figure 3, are second power and third power, respectively, for DA[AP] and D(4-MPe-2)[BP] extractant phases versus low HNO_3 aqueous, i.e., 0.125 M HNO_3 and 0.50 M HNO_3 for the two systems, respectively. For the non-ideal solution range at concentrations of extractant greater than 0.50 F, the curves depart from integral slopes. The dependencies depart markedly from integral slopes when 2.00 M HNO_3 is used as the aqueous phase, the departure being greatest at high extractant concentrations. Since the portion of extractant tied up by HNO_3 remains constant at a specific HNO_3 concentration, the difference in dependency for the extraction from the aqueous 2.00 M HNO_3 phase is probably due to the change in the nature of the complexing environment caused by the high HNO_3 concentration in the organic phase.

The advantage from the improved separation factors at low extractant concentrations, shown in Figures 2 and 3, is greatest in processing systems in which the extraction of high concentrations of metal is not required.

The HNO_3 dependencies of the extraction of U(VI) and Th(IV), shown in Figure 4, should be considered of

operational significance only since several parameters vary simultaneously as the equilibrium aqueous HNO_3 concentration is varied. For example, NO_3^- activity and nitrate complexing of metals in the aqueous and the free extractant concentration in the organic phase may vary as the aqueous HNO_3 concentration is varied.

The difference in the HNO_3 dependency for the extraction of U(VI) and Th(IV) into D(4-MPe-2)[BP], curves A and D of Figure 4 and into DA[AP], curves B and C of Figure 4, results in a substantial difference in separation factor for these metals at low and high HNO_3 concentrations. The separation factors for their extraction range from 65 to 400 for D(4-MPe-2)[BP] and 4.5 to 32 for DA[AP]. The improvement in separation factors at low HNO_3 concentrations is a real advantage for processes in which hydrolysis of the metals at low acid concentration is not a problem.

Although the separation factors for the extraction of U(VI) and Th(IV) into DA[AP] and D(4-MPe-2)[BP] differ greatly (a factor of 28) due to the difference in steric properties of the extractants, the parameters of extractant dependencies, Figures 2 and 3, and HNO_3 dependencies, Figure 4, show a parallel relationship for the two extractants. The apparent independence of these parameters from the steric properties of the extractant greatly simplifies the selection of an extractant and the specific concentrations

of extractant and HNO_3 required for a desired separation.

Discussion

Some of the advantages of using neutral phosphorus-based organic extractants of the same general type as tributyl phosphate, TBP, designed with specially selected extraction properties in the development of LLE systems for use in reactor fuel reprocessing are:

- (1) The distribution ratios for the extraction of the elements to be recovered (uranium and thorium, for example) may be optimized such that both elements can be efficiently extracted then selectively stripped into HNO_3 . Optimizing the distribution ratios eliminates the necessity of adding complexing agents to the aqueous phase for selective stripping of the metals.
- (2) Since the extractants are of the same general type as TBP, systems based on their use would involve essentially the same well established technology as required for the use of TBP.
- (3) The high metal to extractant ratio for these extractants allows high metal loading of the extractant phase, thus reducing the required inventory of extractant.
- (4) The methods of production of neutral phosphorus-

based compounds is well known.

The widely different extraction of U(VI) and Th(IV), actinides (III) and lanthanides (III) as a function of the acidity and steric hindrance of monoacidic phosphorus-based extractants, shown in previous studies (2,3), led to the study of the effect of varying the structure of neutral phosphorus-based compounds on their behavior as extractants. The inverse relationship in the order of substituent base-increasing power and acid-increasing power of the same substituents in phosphorus-based organic compounds, established by previous studies (4,5,6), indicate the potential for predicting the basicity of the P=O in neutral phosphorus-based compounds from existing PK_A values for corresponding monoacidic compounds. Although the availability of basicity data for neutral phosphorus-based compounds is limited, the large volume of published PK_A data for phosphorus-based organic acids should make prediction of the basicity of a large number of such compounds possible.

There is no apparent correlation between the extraction of U(VI) and the PK_A or steric properties of monoacidic phosphorus-based acids, but the range of its K_s values is relatively small compared to the corresponding ranges for Th(IV), actinides (III) and lanthanides (III). The range of K_s values representing both acidity and steric effect is 2.7×10^5 ($< 2 \times 10^2$ for most extractants) for the

extraction of U(VI) compared to 3.3×10^{14} for Th(IV) and $>1.7 \times 10^{10}$ for Am(III) for the extractants reported (2,3).

In the extraction studies, to be reported elsewhere, involving the use of monoacidic phosphonate extractants of the $(GO)(ClCH_2)PO(OH)$ type (where G represents phenyl groups with various substituents) with essentially constant acidities but with varying amounts of steric hindrance within the extractant molecule, the range of K_s values was 2.6×10^7 for Th(IV) and 22 for U(VI). Thus, steric hindrance within the extractant molecule was established as a very important factor in LLE separations.

As might be expected from the relative stoichiometries involved,

compared to

(where S and HY represent one mole of neutral extractant and one monomeric unit of acidic extractant, respectively, and A and O represent the aqueous and organic phases, respectively),

the effect of steric hindrance on separation factors is much larger for U(VI) and Th(IV) for acidic extractants than for neutral extractants. A logical extension of this research would be a study in which the acidity and steric effects for neutral phosphorus-based extractants are correlated with these effects for their corresponding monoacidic acids.

Table I. Extraction of Uranium and Thorium into Several
Neutral Phosphorus-Based Organic Extractants from
2.00 M HNO_3 . Extractant Solutions are 1.00 F in Dodecane

Extractants	Distribution, K		Separation Factor, K_U/K_{Th}
	Uranium	Thorium	
TBP	17.5	1.74	10.1
T(4-MPe-2)P	3.26	0.15	21.7
DB[BP]	249	61	4.1
DA[AP]	295	70.5	4.2
DB[(CH)P]	245	23.8	10.3
DB[(ClM)P]	3.71	0.54	6.9
D(4-MPe-2)[BP]	362	3.12	116
D(4-MPe-2)[(iB)P]	56.8	0.35	162
D(EB)[(EB)P]	245	18.1	13.5
D(4-MPe-2)[PP]	374	2.89	129
B[DBP]	1175	1656	0.71

Figure Legends

Figure 1. Distribution ratio, K , of the extraction of U(VI), $\square$, and Th(IV), $\circ$, from 2.00 $\underline{\text{M}}$ HNO_3 into 1.00 $\underline{\text{F}}$ solutions of several phosphorus-based extractants in dodecane diluent versus the PK_A of their corresponding HDGP, HG[GP] or H[DGP] acids (Example: HDBP corresponds to TBP).

Figure 2. Extractant dependency of the extraction of U(VI) and Th(IV) into a dodecane solution of DA[AP] from: ($\square$, U; $\triangle$, Th) 0.125 $\underline{\text{M}}$ HNO_3 ; (∇ , U; $\circ$, Th) 2.00 $\underline{\text{M}}$ HNO_3 .

Figure 3. Extractant dependency of the extraction of U(VI) and Th(IV) into a dodecane solution of D(4-MPe-2)[BP] from: (∇ , U; $\triangle$, Th) 0.50 $\underline{\text{M}}$ HNO_3 ; ($\square$, U; $\circ$, Th) 2.00 $\underline{\text{M}}$ HNO_3 .

Figure 4. HNO_3 dependency of the extraction of U(VI) and Th(IV) into a dodecane solution of: (B, U; C, Th) 1.00 $\underline{\text{F}}$ DA[AP]; (A, U; D, Th) 1.00 $\underline{\text{F}}$ D(4-MPe-2)[BP].

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