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DI n-OCTYL PHOSPHINIC ACID AS A SELECTIVE EXTRACTANT FOR METALLIC CATIONS

SELECTED M(III) AND M(VI) TRACER STUDIES*

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Abstract —Hydrogen ion dependencies and extractant dependencies of M(III) elements represented by Ce³⁺, Eu³⁺, Tm³⁺, Yb³⁺, Y³⁺, Am³⁺ and Cm³⁺ and of an M(VI) element, UO₂²⁺, into a benzene solution of di n-octyl phosphinic acid, (*n*-C₈H₁₇)₂PO(OH), H[DOP], from an aqueous acidic chloride medium have been determined radiometrically. The observed stoichiometries are represented as:

$$M_{A}^{+3} + 2 \cdot 5(HY)_{2_{0}} \rightleftharpoons MY(HY_{2})_{2_{0}} + 3H_{A}^{+}$$
$$UO_{2_{A}}^{+2} + 2(HY)_{2_{0}} \rightleftharpoons UO_{2}(HY_{2})_{2_{0}} + 2H_{A}^{+}$$

where the subscripts A and O refer, respectively, to the mutually equilibrated aqueous and organic phases and (HY)₂ represents the dimeric form of H[DOP].

Values of K_s , defined by the expressions:

$$K_s = K[H^+]^3/F^{2.5}$$
 , for M(III)
 $K_s = K[H^+]^2/F^2$, for U(VI)

where $[H^+]$ is the molar hydrogen ion concentration in the aqueous phase, F is the formal concentration of extractant in the organic phase and K is the observed distribution ratio of the metal are reported for the above elements from an aqueous phase 1.0 M in (NaCl + HCl).

Comparison of the K_s values of Pm(III), Cm(III) and U(VI) in systems involving di n-octyl phosphinic acid, (n-octyl)₂PO(OH), H[DOP]; 2-ethyl hexyl 2 ethyl hexyl hydrogen phosphonate, (2-ethyl hexyl 0) (2-ethyl hexyl)PO(OH), HEH[EHP]; and di 2-ethyl hexyl phosphoric acid, (2-ethyl hexyl 0)₂PO(OH), HDEHP, have been made.

A plot of log K vs. Z, in a study involving all of the lanthanides (III) except Gd, shows a slight odd-even effect, the even Z elements lying above a straight line which acceptably represents the the odd-Z elements.

It is tentatively concluded that in the series: $(GO)_2PO(OH)$, (GO)(G)PO(OH), $(G)_2PO(OH)$ if G remains fixed the extraction of U(VI) increases slightly to the right while that of the M(III) elements considered decreases markedly.

FROM A comparative study of $(GO)_2PO(OH)^{(1-3)}$ and $(GO)(G)PO(OH)^{(3.4)}$ where G is the 2-ethyl hexyl group (in toluene as carrier diluent) as extractants of lanthanides (III), actinides (III) and U(VI) from a given aqueous mineral acid phase, the following points seem important: (1) The direct extractant dependency and the inverse hydrogen

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ion dependency are numerically equal to the charge on the cation for both the M(III) elements and U(VI);⁽¹⁻⁴⁾ (2) Under comparable conditions, the K in the phosphate system is greater than that in the phosphonate system for the M(III) elements, the ratio of the respective K values being approximately 100 and 50 for Pm(III) and Cm-(III),⁽⁴⁾ respectively; (3) Under comparable conditions, the K in the phosphate system is less than that in the phosphonate system for U(VI), the ratio of the respective K values being approximately 0.5.⁽³⁾

It seemed logical to extend the study to include $(G)_2PO(OH)$ in order to determine the effect of eliminating the one remaining P—O—C linkage. However, isolation of this compound, in which G is 2-ethyl hexyl, in a state of purity warranting its use in tracer studies has proved difficult. Therefore, the more readily purified compound containing the n-octyl group was chosen. Further, in order that future studies may be correlated more readily with respect to the nature of the carrier diluent, aromatic hydrocarbon, aliphatic hydrocarbon, carbon tetrachloride, etc., benzene (pure aromatic), rather than toluene (mixed aromatic-aliphatic), has been employed in the study presently reported.

EXPERIMENTAL

Nomenclature

In an extension of previous usage⁽³⁾ in which H represents a theoretically ionizable hydrogen, D the prefix di-, and G a generalized organic group, a phosphinic acid containing two like G groups, $(G)_2 PO(OH)$, is represented as H[DGP]. The bracket serves to distinguish it from $(GO)_2 PO(OH)$ a phosphoric acid, which is represented as HDGP. The compound of intermediate structure, (GO)(G) PO(OH), a G ester of a G phosphonic acid, is represented as HG[GP]. In this system, the brackets indicate that a G within the brackets is attached to P through a C—P bond. The absence of brackets indicates that each G is attached to P through an O atom.

The extractants to be compared are di 2-ethyl hexyl phosphoric acid, (EHO)₂ PO(OH), HDEHP;^(5a) 2-ethyl hexyl hydrogen 2-ethyl hexyl phosphonate, (EHO)(EH)PO(OH), HEH[EHP];^(5b) and di n-octyl phosphinic acid, (n-Oct)₂PO(OH), H[DOP] where O represents the n-octyl group. Di 2-ethyl hexyl phosphinic acid, (EH)₂PO(OH), is represented as H[DEHP].

Since each of these mono-acidic extractants is dimeric in the aromatic carrier diluent,⁽⁵⁾ it is represented in the interest of brevity in the discussion of extraction stoichiometry, as HY in the hypothetical monomeric state, Y representing the aggregate excepting the ionizable H atom, and as $(HY)_{2}$ in the dimeric state.

The distribution ratio, K, is defined as the concentration of nuclide in the upper divided by the concentration of nuclide in the lower of two mutually equilibrated sensibly-immiscible liquid phases, the concentrations of nuclide being on an atomic basis as reflected in alpha or beta counting rates.

The term carrier diluent is used so that no implication of "inertness" may result. (Work now in progress shows a system otherwise identical with that presently reported but employing n-heptane, rather than benzene, as carrier diluent to differ widely in several important respects from the system now under discussion.) The concentration unit, formality, F, is defined as the number of formula weights per liter of solution.

Sources of materials

The beta-active nuclides 285-day ¹⁴⁴Ce, (13, 16) year^{183,184}Eu and 58-day⁹¹Y were obtained from the Isotopes Division of the Oak Ridge National Laboratory. The cerium nuclide was further purified by extraction as Ce(IV) by HDEHP;⁽⁶⁾ and traces of ¹⁴⁷Pm were removed from the ⁹¹Y by use of the HDEHP vs. mineral acid system in which Y is preferentially extracted into the HDEHP

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phase.^(6,7) The beta-active nuclides 129-day ¹⁷⁰Tm and (32, 4·2) day ^{169,175}Yb were prepared by neutron bombardment of gross Tm and Yb oxides, respectively, obtained in "99·9% purity" with respect to contamination by other rare earths from Research Chemicals, Inc.

Of the other beta-active nuclides employed in the Z study, Fig. 7: 40h ¹⁴⁰La (in equilibrium with parent 12·8 day ¹⁴⁰Ba), 13·7 day ¹⁴³Pr, 11·3 day ¹⁴⁷Nd, 2·6 year ¹⁴⁷Pm and 47 h ¹⁵³Sm were obtained from the Isotopes Division of the Oak Ridge National Laboratory, and 72 day ¹⁶⁰Tb, 82 h ¹⁶⁶Dy, 9·4 day ¹⁶⁹Er and 6·8 day ¹⁷⁷Lu were prepared by neutron irradiation of rare earths of normal isotopic composition in the form of oxides obtained in 99·9 + % purity from Research Chemicals, Inc. (In the preparation of Dy tracer, secondary neutron capture led to the formation of 82 hr ¹⁶⁶Dy which has a 27·2 hr ¹⁶⁶Ho daughter. By means of differential counting, both Dy and Ho data were obtained in a single experiment.) The ¹⁴⁰La was isolated from parent ¹⁴⁰Ba and purified with respect to beta active Ce and Y contaminants, and ¹⁴³Pr was purified with respect to contaminant beta active Ce as described previously.⁽⁶⁾

The alpha-active nuclides, 470-year ²⁴¹Am, 18-year ²⁴⁴Cm and 1.6×10^5 year ²³³U (²³⁸U:²³³U mass ratio less than 0.03) were obtained from Argonne National Laboratory stocks. Each was purified by means of liquid–liquid extraction techniques: the Am and Cm to remove traces of Pu by extraction into an HDEHP (in n-heptane) phase from dilute HNO₃ and re-extraction into a 10 M HNO₃ \pm 0.2 M KBrO₃ phase, the Pu remaining as Pu(IV) in the organic phase, the procedure being a modification of that reported for Bk(IV);⁽⁸⁾ and U to remove daughter activities by use of the tri n-butyl phosphate vs. HCl system.⁽⁹⁾

The reagent grade benzene used as carrier diluent was obtained from the General Chemical Division, Allied Chemical Co. The sources of compounds used in the synthesis of H[DOP] were: n-octene-1, n-C₆H₁₂CH=CH₂, "pure" grade (99+%), Phillips Petroleum Company; hypophosphorus acid, H₃PO₂, as a "50%" aqueous solution from J. T. Baker Chemical Co.; benzoyl peroxide, (C₆H₅CO₂)₂, Distillation Products Industries, Eastman Organic Chemicals Department; and 95% ethanol, C₂H₅OH, U.S. Industrial Chemicals Co.

Preparation of di n-octyl phosphinic acid, H[DOP]

A modification of the procedure described by WILLIAMS and HAMILTON⁽¹⁰⁾ using 95% ethanol, rather than 1,4-dioxane, as solvent was employed. A mixture of 471 g (4·2 moles) of octene-1, 254 g of "50%" aqueous hypophosphorous acid (2·0 moles of H₂PO₂H), 132 g of water, 700 ml of 95% ethanol and 24·2 g (0·10 mole) of benzoyl peroxide was refluxed for 24 hr.

To the cooled mixture (approximately 20 °C) was added 0.5 1. of benzene and 2.0 1. of 1.0 M HCl. The lower phase was removed, and the upper (benzene) phase containing the product was scrubbed with two 0.5-1. portions of 1.0 M HCl. Following removal of the benzene by evaporation, the product was converted to its sodium salt by dissolution in 1.5 1. of 2.0 M NaOH. The cooled solution (approximately 10 °C) was added to 2.0 1. of diethyl ether in a 5–1, separatory funnel. Following thorough agitation and subsequent phase disengagement, the lower phase was discarded. The ether solution of the sodium salt of the product was scrubbed with six 1.0-1. portions of 1.0 M NaOH. (The purpose of this step is to remove (n-octyl) (H)PO(OH) which is preferentially re-extracted into into the aqueous NaOH.)

The ether phase was then contacted with 1.01. of 3.0 M HCl. Following removal of the lower (aqueous) phase, the ether phase containing the product as free acid was scrubbed with two 1.0-1. portions of 1.0 M HCl. The ether was then removed by evaporation. The yield of essentially pure product was 540 g (93.0% based upon H₂PO₂H).

Since a benzene solution of the product did not give extraction data for the extraction of Eu tracer in the presence of gross Eu consistent with those for tracer Eu, the tracer Eu extracting by far the better, it was presumed that the product might contain a trace of 2-hexyldecyl phosphinic acid, $(C_{16}H_{33})$ (H)PO(OH),⁽¹¹⁾ the $C_{16}H_{33}$ resulting from telomerization of the octene-1.⁽¹¹⁾ (This point will be elaborated in the Discussion Section.)

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Following four recrystallizations from n-heptane the product gave self-consistent extraction data for Eu tracer in the presence and absence of gross Eu and for Yb tracer in the presence and absence of gross Yb. It was, therefore, presumed free from interfering contaminants.

Potentiometric titration in 75% ethanol showed the product to be a monobasic acid (less than 0.5% dibasic) with an equivalent weight of 289.6 ± 0.5 g (theoretical equivalent weight for (C₈H₁₇)₂ PO(OH), C₁₈H₃₅PO₂, 290.4 g.) The respective percentage contents of C, H, and P presented as found, followed by theoretical values in parentheses, are: 66.33(66.17), 12.51 (12.15) and 10.72 (10.67). The melting point was 84.0 ± 0.2 °C, to be compared with 85°C as reported by WILLIAMS and HAMILTON.^(10,12)

In a measurement in which $(n-C_8H_{17})_2$ PO(OH) and $(n-C_8H_{17})_2$ (H)PO, prepared by WILLIAMS and HAMILTON procedure,⁽¹⁰⁾ were melted side by side in the Capillary Melting Point Apparatus the respective melting points, without correction, were 84.0 and 86.0°C. WILLIAMS and HAMILTON^(10,12) report 85°C as the melting point of each.

Analytical and Physical data

The C, H and P analyses were performed by the Schwarzkopf Microanalytical Laboratory. Melting points were determined in a Thomas Hoover Capillary Melting Point Apparatus obtained from the Arthur H. Thomas Co.

Potentiometric titrations in 75% and 95% ethanol media (i.e. solutions prepared, respectively, by using absolute ethanol and water in the ratios of 75:25 and 95:5 by volume) were made with a modified Precision-Dow Recordomatic Titrator using a standard solution, approximately 0.10 F, of NaOH in 75% or 95% ethanol as titrant. From these data the purity of the sample was established and the pK_A values calculated as described previously.^(13a) The resultant pK_A values of 5.3 (75% ethanol) and 5.8 (95% ethanol) may be compared with the value of 5.2 (70% ethanol) reported by Blake, et al.^(13b) (Blake et al^(13b,c) report 5.6 (70% ethanol) as the pK_A for H[DEHP].)

The state of aggregation of H[DOP] was determined cryoscopically in benzene by a technique to be described in detail in a later paper. In solutions approximately 0.075 F and 0.050 F the freezing point depressions corresponded respectively to $(HY)_{2\cdot18}$ and $(HY)_{2\cdot09}$. It is, therefore, concluded that H[DOP] is dimeric in "dry" benzene.

Determination of distribution ratios

The distribution ratio, K, of a specific nuclide was determined as described previously.^(4a) Alphaactive Cm and beta-active Ce were simultaneously present as were alpha-active Am and beta-active Eu, the alpha-counting and beta-counting ratios being determined in the manner previously reported.⁽⁴⁾

In obtaining the Dy-Ho data, an aliquot of each phase was evaporated on a platinum disc immediately following phase disengagement after equilibration. These samples were then assayed at once by beta counting through an aluminum absorber (100 mg), the absorber serving to screen out essentially all of the Dy activity. Approximately seven days later, the plates were assayed by beta counting without absorber at which time the 82 hr ¹⁶⁶Dy parent and 27·2 hr ¹⁶⁶Ho daughter were essentially at secular equilibrium. From these two sets of data, both Ho and Dy K values were calculated.

RESULTS AND CONCLUSIONS

From Figs. 1–3 it is seen that the K for the actinide (III) and lanthanide (III) elements investigated is inversely third-power dependent upon the concentration of hydrogen ion in the aqueous phase and that the K for U(VI), i.e. UO_2^{2+} , is correspondingly inversely second-power hydrogen ion dependent. These dependencies, numerically equal to the presumed charge of the metallic cation, indicate that no chloride is

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FIG. 1.—Hydrogen ion dependency of the extraction from 1.00 F (NaCl + HCl) aqueous solution of: (A) Y(III) into 0.300 F H[DOP] and (B) Cm(III) and Ce(III) into 0.424 F H[DOP]. Benzene diluent.



FIG. 2.—Hydrogen ion dependency of the extraction from 1.00 F (NaCl + HCl) aqueous solution of: (A) Yb(III) into 0.150 F H[DOP] and (B) Eu(III) and Am(III) into 0.424 F H[DOP]. Benzene diluent.



FIG. 3.—Hydrogen ion dependency of the extraction from 1.00 F (NaCl + HCl) aqueous solution of: (A) U(VI) into 0.0265 F H[DOP] and (B) Tm(III) into 0.212 F H[DOP], and from aqueous HCl of (C) Tm(III) into 0.212 F H[DOP]. Benzene diluent.

contained in the extracted entity. This conclusion is strengthened by the observation that the hydrogen ion dependency curve for Tm(III), Fig. 3, is considerably steeper from a varying HCl medium than from a constant ionic strength chloride solution.

The extractant dependency of the K for each of the M(III) nuclides of Figs. 4-6 is 2.5 power. That of the K for U(VI), Fig. 6, is 2.0 power.



FIG. 4.—Extractant dependency of the extraction into H[DOP], benzene diluent, of: (A) Y(III) from 0.05 F HCl and (B) Cm(III) and Ce(III) from 0.010 F HCl.



These data, in conjunction with the assumed dimeric formula for H[DOP] in the "wet" equilibrated organic phase indicate extraction stoichiometries:

$$M_{A}^{3+} + 2.5(HY)_{2_{0}} \rightleftharpoons M(Y)(HY_{2})_{2_{0}} + 3H_{A}^{+}$$
 (1)

$$\mathrm{UO}_{2_{A}}^{2+} + 2(\mathrm{HY})_{2_{0}} \rightleftharpoons \mathrm{UO}_{2}(\mathrm{HY}_{2})_{2_{0}} + 2\mathrm{H}_{A}^{+}$$
(2)

the subscripts A and O referring, respectively, to the mutually equilibrated aqueous and organic phases.

The stoichiometries of Expressions (1) and (2) were respectively deduced from the following expressions relating K to the concentrations (in formality units) of H[DOP] in the organic phase and the concentration of hydrogen ion in the aqueous phase.

For
$$M^{3+}$$
: $K = K_s F_{H(DOP)}^{2.5} / [H^+]_A^3$ (3)

For
$$UO_2^{2+}$$
: $K = K_8 F_{H(DOP)}^2 / [H^+]_A^2$ (4)

Values of K_s for each of the M(III) elements and for U(VI), calculated using Expressions (3) and (4) and values read from the lines as drawn of Figs. 1–6, are presented in Table 1.



FIG. 6.-Extractant dependency of the extraction into H[DOP], benzene diluent of: (A) U(VI) from 1.0 F HCl and (B) Tm(III) from 0.10 F HCl.

70

39

95

96

Yb(III)

Am(III)

Cm(III)

Y(III)

FIG. 7.—Variation of $\log K$ with Z for lanthanides (III) in the 0.30 F H[DOP] in benzene vs. 0.050 F HCl system. Straight line drawn with respect to odd-Z lanthanides.

 1.4×10^{5}

 9.7×10^{3}

2.1

3.6

TABLE 1.— K_s values for trivalent Am, Cm, Ce, Eu, Yb, Tm and Y and for U(VI) in the H[DOP] in benzene vs. 1.0 M (HCl + NaCl) system at 22 \pm 2°C.								
M(III): 1	$K_s = K[\mathrm{H^+}]^3/\mathrm{F}_\mathrm{H}^2$	$[DOP]^{5}$. U(VI): K,	$= K[\mathrm{H^+}]^2/\mathrm{F^2_{H[DOP]}}$					
Z	М	Ks	$(K_{\rm M}/K_{\rm Ce(III)})$					
58	Ce(III)	5.8×10^{-6}	1.0					
63	Eu(III)	$7\cdot4$ $ imes$ 10 $^{-4}$	$1.3 imes 10^2$					
69	Tm(III)	$2\cdot3 imes10^{-1}$	$4.0 imes10^4$					

 $8.3 imes 10^{-1}$

 5.6×10^{-2}

 $1.2\,\times\,10^{-5}$

 $2\cdot 1 \times 10^{+5}$

92	U(VI)	$5.2 imes10^3$	$9.0 imes 10^8$
61	Pm(III)*	9.3×10^{-5}	16.0
* K _s fo	or Pm(III) calcul	ated by multiplyin	g the K_s for Ce(III)
ur the meti	2 V 1V 160	in the sustains non	managered law The 7

by the ratio $K_{\rm Pm}/K_{\rm Ce}$, 16.0, in the system represented by Fig. 7.

In Fig. 7, a plot of log K vs. Z for lanthanides (III) in the 0.30 F H[DOP] vs. 0.050 F HCl system is represented as a straight line for odd-Z elements. (The dashed section is intended to emphasize the absence of the median even-Z element, gadolinium, Z = 64.) The straight line indicates a hypothetical β of 2.7 for adjacent lanthanides (III), $\beta = K_{Z+1}/K_Z$, or a β of $(2.7)^2$ for successive odd-Z lanthanides.

The even-Z elements lie above the line drawn for the odd-Z elements. An odd-even effect in a K vs. Z study of lanthanides (III) has been reported recently for two HY in n-decanol vs. dilute HCl systems, the HY extractants being HDEHP, (2-ethyl hexyl $O_2PO(OH)$, and HDO ΦP , (*p*-octyl phenyl $O_2PO(OH)$.⁽¹⁴⁾ However, in these systems cross-overs of the separate odd-Z and even-Z curves occur.

DISCUSSION

Probably the most important aspect of the study presently reported employing H[DOP], as compared with studies employing HDEHP and HEH[EHP], is the unexpected 2.5-power extractant dependency for M(III), Expressions (1) and (3), and Figs. 4–6. The authors are not aware of any reported example of a system employing a monoacidic phosphorus-based extractant in which the extraction dependency for M(III) is less than third-power, except a system utilizing di hexoxyethyl phosphoric acid, $(n-C_6H_{12}OC_2H_4O)_2PO(OH)$, HDHoEP.⁽¹⁵⁾

It was assumed that HDHoEP extracted M(III) with a 2.5 power dependency, rather than a third-power dependency, because of participation of the ether oxygen atoms of the hexoxy ethyl groups in coordination with the metal atom, thereby stabilizing one monomeric ligand, Y, Expression (1).⁽¹⁵⁾ In the case of H[DOP] the 2.5-power extractant dependency may be explained on a geometric basis, the supposition being that the O--P-O angle in the Y⁻ ligand is of the proper value in H[DOP] to favour co-ordination by Y⁻ over that by HY₂⁻. Similarly, then, the O--P-O angle in the Y⁻ ligand of HDEHP and of HEH[EHP] must be assumed to be an unfavourable value.

Why the extractant dependency is not 1.5-power, the extracted entity being MY_3 , on the basis of this reasoning remains unresolved. Perhaps co-ordination by one Y⁻ distorts the bond angles of the M atom sufficiently that a second Y⁻ may not be accommodated, while the HY_2^- ligand is free to buckle and can, therefore, be stably attached. In this connection it may be noted that the extractant dependency for Th(IV) is third-power, rather than fourth-power, for systems involving HDEHP, both in perchlorate systems and nitrate systems, the extracted entities being respectively postulated as ThY₂(HY₂)₂ and Th(NO₃)(HY₂)₃.⁽¹⁶⁾

Because of the 2.5-power extractant dependency, direct comparison of the relative extractant powers of HDEHP, HEH[EHP] and H[DOP] for M(III) is not possible. However, comparison of K_s values, calculated as shown, may be made, Table 2. Intercomparison for U(VI), for which the stoichiometry of extraction is the same for all three extractants, shows the K to increase with increasing number of C—P bonds. (A similar effect was noted by BLAKE *et al.*^(13b,c) in the extraction of U(VI) by phosphoric and phosphinic acids where the groups were n-octyl and 2-ethyl hexyl.) The K values for Pm(III) and Cm(III) decrease, respectively, by factors of approximately 40 and 100 as one C—P bond is introduced but do not change further with a second C—P bond. No special significance can be attached to this latter fact, however, since the extraction stoichiometry is different for the third extractant.

It is evident, further, that interpretation of the comparison is complicated by the difference in diluent and the difference in isomeric G groups. In general, in otherwise

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Diluent	НҮ	K _s			K _s (HY)/K _s (HDEHP)		
		Pm(III)	Cm(III)	U(VI)	Pm(III)	Cm(III)	U(VI)
Toluene Toluene Benzene	HDEHP* HEH[EHP]* H[DOP]†	$6.3 imes 10^{-3} \ 1.5 imes 10^{-4} \ 1.9 imes 10^{-4}$	$\begin{array}{c} 3{\cdot}4 \times 10^{-3} \\ 3{\cdot}4 \times 10^{-5} \\ 4{\cdot}2 \times 10^{-5} \end{array}$	$\begin{array}{c} 9.5 imes 10^2 \ 1.7 imes 10^3 \ 9.4 imes 10^3 \end{array}$	1.00 0.024 0.030	1.00 0.010 0.012	1.00 1.8 9.9

TABLE 2.—COMPARATIVE K_s values for Pm(III), Cm(III), and U(VI) in HDEHP, HEH[EHP] and H[DOP] in carrier diluent vs. 1.0 M (NaClO₄ + HClO₄) systems

* Pm(III) and Cm(III) data from Ref. 4 and U(VI) data from Ref. 3.

† K_s for 1.0 M (NaCl + HCl) converted to K_s for 1.0 M (NaClO₄ + HClO₄) by multiplication of data from Table 1 by factor of 2.0 for Pm(III) and Cm(III) and by factor of 1.8 for U(VI). See Table 1 of Ref. 4 and page 1392 of Ref. 3, respectively, for the origin of these factors.

identical systems employing phosphorus-based HY extractants, in toluene or benzene, the extraction of M(III) is greater in that employing toluene. In the extraction of Tb(III) by $(GO)(C_6H_5)PO(OH)$ and by $(GO)(ClCH_2)PO(OH)$ where G is n-octyl or 2-ethyl hexyl, the K_8 is 7–9 times greater for n-octyl than for 2-ethyl hexyl.⁽¹⁷⁾

Whether the 2·5-power extractant dependency for M(III) will be exhibited by H[DEHP], (2-ethyl hexyl)₂PO(OH), and whether the corresponding K_s for M(III) will be markedly less than in a system involving HEH[EHP] thus become important questions. By intercomparison of data for (GO)₂PO(OH), (GO)(G)PO(OH) and (G)₂PO-(OH) for M(III) extraction, and for U(VI), the steric hindrance factor and the P--C vs. P-O--C factor should become, at least qualitatively, mutually separable.

Preparation of H[DEHP] in a state of purity suitable for such a comparison has not thus far proved possible by the alkene addition to hypophosphorous acid, H₂PO-(OH), technique,^(10,12) presumably because of products formed due to telomerization.⁽¹¹⁾ GRIFFIN and WELLS⁽¹¹⁾ report the formation of 2-hexyl decyl phosphonic acid as an impurity in the synthesis of n-octyl phosphonic acid from n-octene and phosphorous acid, HPO(OH)₂. It might, therefore, be expected that a hexadecyl phosphinic acid, (C₁₆H₃₃)(H)PO(OH), should be found as an impurity in the preparation of (C₈H₁₇)₂ PO(OH) and accompanying (C₈H₁₇)(H)PO(OH). In the liquid–liquid extraction purification procedure the (C₈H₁₇)(H)PO(OH) is eliminated, but the (C₁₆H₃₃)(H)PO(OH) would be expected to accompany the product (C₈H₁₇)₂PO(OH).

In the case of H[DOP] the product is a solid and may be recrystallized to remove the (hexadecyl)(H)PO(OH) contaminant. However, H[DEHP] is a liquid, and to date purification of a product made by alkene addition to hypophosphorous acid has proved impossible.

An attempt to prepare H[DEHP] of the required purity by oxidation of the corresponding di 2-ethyl hexyl phosphine oxide, $(EH)_2(H)PO$, prepared by the Grignard technique of WILLIAMS and HAMILTON^(10.12) will be made.

⁽¹⁷⁾ D. F. PEPPARD, in Science and Technology of Rare Earths 1, pp. 89–109. Pergamon Oxford (1963).