LIQUID–LIQUID EXTRACTION OF METAL IONS

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I. Introduction

"A good technique is worth a thousand theories" is a debatable statement, certain to provoke a lively and acrimonious discussion at any gathering of scientists. Without attempting to resolve the argument, let it be said that development of a new and powerful technique has often opened to exploration an area of research previously inaccessible, and has frequently made it possible to prove or disprove a theory otherwise unamenable to testing.

Considering only a few of the winners of the Nobel Prize in Chemistry, it seems safe to say that, despite their many accomplishments in basic science, these men will be remembered by chemists at large because of the far-reaching consequences of techniques associated with their discoveries: V. Grignard and P. Sabatier (use of organometallic compounds in organic syntheses), H. C. Urey (separation of isotopes), W. F. Libby (dating of samples of geological importance by carbon-14 analysis), A. J. P. Martin and R. L. M. Synge (development of partition chromatography), and E. M. McMillan and G. T. Seaborg (development of procedures for production, separation, and characterization of man-made elements).

Correspondingly, in the field of liquid-liquid extraction, H. Peligot will be remembered for his observation (in 1842) that uranyl nitrate may be extracted into diethyl ether, J. W. Rothe for his study (reported in 1892) of the extraction of ferric ion from concentrated hydrochloric acid into diethyl ether, and L. C. Craig for his development of equipment for "countercurrent distribution," an operational technique of immediate value in biological and medical research and of long-term influence upon diverse chemical separations investigations.

The rapidly expanding field of liquid-liquid extraction of metal ions is now so extensive that a review of other than book length must be severely limited. On the assumption that the most valuable result of a survey may be the stimulation of further research in the field, the present treatment is largely restricted to recently reported systems not reviewed in the dual context of basic chemistry and separations application.

For analysis and discussion of the chemical and structural problems involved, up to date and thorough reviews are those by Morrison and Freiser (*187*), "Solvent extraction," 1959; Diamond and Tuck (*59*), "Extraction of inorganic compounds into organic solvents," 1960; Fomin (*88*), "Chemistry of extraction processes," 1962; Marcus (*170*), "Solvent extraction of inorganic species," 1963; and Katzin (*141*), "Solvent extraction of inorganic species," 1965.

The chemical systems, the methods of operation, and the pertinent mathematics are considered in the reviews by Martin and Holt (*174*), "Liquid-liquid extraction in inorganic chemistry," 1959; Irving and Williams (*127*), "Liquid-liquid extraction," 1961; and von Metzsch (*286*), "Solvent extraction," 1961.

The yearly journal reviews, "Extraction" in *Analytical Chemistry* and "Liquid extraction" in *Industrial and Engineering Chemistry*, are helpful complements to these fuller treatments.

"Old and new processes of multiplicative distribution (liquid-liquid extraction)," 1964, is an analysis of various ways in which multiplication of a separation effect in liquid-liquid extraction may be achieved, presented by Fischer *et al.* (*85*).

"Purification by solvent extraction" by Fletcher (*87*), 1957, treats of large-scale potentialities. Analytical applications are described by Morrison and Freiser in *Solvent Extraction in Analytical Chemistry* (*186*), 1957, and in "Extraction" (*188*), 1964, and preceding reviews of the series, and by Belcher *et al.* (*19*) in the chapter "Solvent extraction" in *New Methods of Analytical Chemistry*, 1964.

Freiser (*92*) has surveyed "Solvent extraction in radiochemical separations," and Dyrssen (*72*) has reviewed "The use of solvent extraction techniques in the study of chemical equilibria."

In "Automatic countercurrent distribution equipment," Craig *et al.* (*51*) describe in detail the design and function of the equilibration cell which made possible automation of countercurrent distribution, and Verzele and Alderweireldt (*283*) report a modification which permits both phases to flow through the train of contactors.

The extraction of mineral acids and of water, by organic phases consisting of neutral phosphorus-based extractants in an organic diluent, has been reviewed by Diamond (*59*) and Marcus (*170*).

In "The partition law in solvent extraction," 1963, McKay and Miles (*162*) compare the ratio of the independently measured activities of a solute in two immiscible liquid phases with measured partition data for the solute in the system employing these two liquid phases mutually in contact. This appears to be the first test of the thermodynamic partition law.

Complete and rigorous mathematical treatment of liquid-liquid extraction is given by Alders (*3*), Craig (*50*), and Treybal (*275*).

In addition to emphasizing chemical systems which seem of prime interest, or potential prime interest, in the field of metals separations, the present review stresses the importance of a familiarity with the various ways in which a single-stage separation effect may be multiplied.

An imposing collection of basic data concerning the extraction of metals has been gathered by liquid-liquid extraction investigators. However, with the exception of very large-scale metallurgical separations and of certain separations involved in processing in atomic energy installations, the field of applications has been left to practitioners of reversed-phase partition chromatography.

The latter statement is made not in anger but in sorrow, for in many instances a straightforward application of the "push-through" or the "countercurrent extraction" method of operation is the most efficient solution to a given separations problem. Unfamiliarity with the mechanical manipulations and the mathematical treatment appears to be the basic cause of the lack of such applications.

It is hoped that presentation of these methods of multiplication of a single-stage separation effect may lead to expanded use of liquid-liquid extraction in radiochemistry, in analytical chemistry, and in any investigation in which the degree of separation of one metal from another is a determining factor in deciding the fate of the study.

Meanwhile, reversed-phase partition chromatographers are to be commended for having established so many valuable metal separations schemes on the basis of liquid-liquid extraction data.

II. Single-Stage Extraction

A. PRINCIPLES

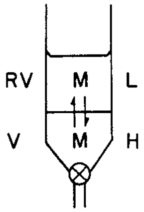
In its essentials, liquid-liquid extraction is an operation in which a dissolved substance expresses its preference between two liquids simultaneously present and available to the substance. This preference is determined by chemical and physical principles which are inviolable but in most instances are identified in a qualitative fashion only.

Consequently the behavior of a given solute in a given extraction system cannot be predicted in any but the roughest manner. However, this behavior, once determined, can be relied upon in any future experiment.

Two liquids which, following thorough mutual physical mixing, separate into two liquid phases upon becoming quiescent together constitute a *liquid-liquid extraction system.* If a solute, M, soluble in each of these liquids separately, is introduced into this system, it will (at equilibrium) *distribute* itself between the *two liquid phases* in a precise and reproducible manner. This *distribution* (or *partition*) is described mathematically by the *distribution ratio* (or *partition ratio*), for which a wide variety of symbols and defining expressions have been used.

Assume that the separatory funnel of Fig. 1 contains two liquids (L for *lighter* and H for *heavier*) which, in a settling period following thorough intermixing, will separate into two layers. A solute, M, is allowed to dissolve in this mixture and distribute between the two liquid phases during a mixing period sufficiently long to assure *empirical equilibrium distribution* (i.e., a distribution indistinguishable from the true *thermodynamic distribution* by the available methods of *measurement*).

Following a settling period to permit phase disengagement, each of the phases is analyzed for M content. Assume that a series of similar experiments, in which each variable except the quantity of M added is kept constant, has been performed, and that the quantity of M added was varied over a wide range. If the *two solutions* behave *ideally*, the ratio of the concentration of M in the light phase to that in the heavy phase will have the same value for each of the experiments, that is, $C_L/C_H = K$. (This constancy of C_L/C_H is frequently approximated very closely in practice if the solute has the same state of aggregation in the two liquid phases, and if the concentration of solute is sufficiently below the "saturated" concentration in each phase. For example, tracer-level radioactive lanthanides(III) exhibit a constant C_L/C_H over a wide range of concentration in many systems, that is, over a range in which the highest concentration in a given phase may be 10,000 times as great as the lowest, although both are in the "tracer-level" range.)



$$C_L/C_H = K, \qquad Q_H + Q_L = Q_0$$

$$Q_H = VC_H, \qquad Q_L = RVC_L$$

$$F_L = \frac{Q_L}{Q_H + Q_L} = \frac{RVC_L}{VC_H + RVC_L}$$

$$F_L = \frac{R(C_L/C_H)}{1 + R(C_L/C_H)} = \frac{RK}{1 + RK}$$

$$(RK \equiv E), \quad F_L = \frac{E}{1+E}, \quad \phi_H = 1 - F_L = \frac{1}{1+E}$$

FIG. 1. Single-stage extraction of metal M in the system: light phase (L) and heavy phase (H) of respective volumes RV and V.

B. MATHEMATICAL TREATMENT

From consideration of material balance it follows that the quantity of M in the L phase plus the quantity of M in the H phase must equal the total quantity (Q_0) of M added, that is:

$$Q_L + Q_H = Q_0 \tag{1}$$

The volumes of the H and L phases (Fig. 1) are, respectively, V and RV. Therefore, recalling that "concentration" is "quantity per unit volume," in any arbitrary units:

$$Q_H = VC_H, \qquad Q_L = RVC_L \tag{2}$$

The fraction of the total quantity of M in the separatory funnel found in the light phase (F_L) is thus:

$$F_L = Q_L/Q_0 = Q_L/(Q_L + Q_H) = RVC_L/(RVC_L + VC_H) \tag{3}$$

For the case in which the distribution ratio is a constant:

$$K = C_L/C_H \tag{4}$$

Therefore, following division of both numerator and denominator of Eq. (3) by (VC_H) and substitution of K for C_L/C_H, the fraction of the quantity of M in the L phase is expressed as

$$F_L = RK/(RK + 1) = E/(E + 1) \tag{5}$$

where the *effective distribution ratio*, E, is defined by the expression:

$$E = RK \tag{6}$$

Similarly, since the sum of the two fractions must equal unity, the fraction of the total quantity of M in the H phase (Φ_H) is expressed as:

$$\Phi_H = 1 - F_L = 1/(RK + 1) = 1/(E + 1) \tag{7}$$

Evidently if $E = 1$, $F_L = \Phi_H = 0.5$. If E is greater than unity, F_L exceeds 0.5 (M preferentially in L phase) and, if less, Φ_H exceeds 0.5 (M preferentially in H phase). These interrelationships illustrate the importance of considering E (i.e., RK), not K, in the devising of a separations scheme for solutes M and N, having respective distribution ratios K_M and K_N, $K_M > K_N$.

The technological contributions of liquid-liquid extraction techniques have involved the separation of one or more solutes from a mixture. In essence, all such separations are equivalent to the mutual separation of solutes M and N. This mutual separation is dependent upon operating the extraction system under conditions such that the RK product, E, for M is greater than unity and that for N is less than unity. It is evident that if E for solute M is *far greater* than unity and that for N is *far less* than unity, then M will appear almost exclusively in the L phase and N almost exclusively in the H phase. That is, M and N will be separated from each other quite efficiently.

Expressed in another way, the greater the ratio of their E values, the more readily may M and N be mutually separated—*provided that the two E values are suitably related to unity.* For example, if the two E values are 10,000 and 100, respectively, the N in the H phase will be purified reasonably well with respect to contamination by M (the ratio of M to N having been reduced by a factor of nearly 100), but will be obtained in only approximately 1% yield. The purification of M, with respect to N, in the L phase will be negligible.

For fixed values of E, it may be shown that maximum mutual separation of M and N is obtained when the E values are mutually reciprocal (*33*):

$$E_M E_N = 1, \text{ that is, } E_M = 1/E_N \tag{8}$$

By reference to the definition of E, Eq. (6), it is seen that the ratio of the E values is identical with the ratio of the corresponding K values. Therefore the ratio of K values of the solutes, M and N, may be considered a measure of their mutual separability. This ratio, frequently called the *separation factor*, is symbolized as β and is defined by:

$$\beta = K_M/K_N \tag{9}$$

Assuming the solutes M and N have respective K values of 100 and 0.01 ($\beta = 10{,}000$) and equal volumes of L and H phases are employed

($R = 1$), substitution in Eq. (5) indicates that 99.01% of the total M and only 0.9901% of the total N will be found in the L phase. Therefore the M-product has been obtained in 99.0% yield and has been *decontaminated* with respect to N by a factor of 100. (Similarly, N will be found in 99.0% yield, *decontaminated* with respect to M by a factor of 100, in the H phase.)

The *decontamination factor* is a numerical measure of the efficiency with which a *product* has been *cleaned up* with respect to an *undesirable impurity.* Assuming M the product and N the impurity, the decontamination factor (DF) is defined as the ratio of the quantity (Q_N/Q_M) in the starting material (feed) to the quantity (Q_N/Q_M) in the M-product. (The ratio of the quantity (Q_M/Q_N) in the M-product to the quantity (Q_M/Q_N) in the feed, sometimes called the *clean-up factor,* is an equivalent definition.)

By reference to Eq. (3), it is clear that:

$$\mathrm{DF} = (F_M/F_N), \qquad \text{for M-product in L phase} \tag{10}$$

Similarly, if N is the product and M the contaminant:

$$\mathrm{DF} = (\Phi_N/\Phi_M), \qquad \text{for N-product in H phase} \tag{11}$$

III. Multiple Extraction and Multiple Scrubbing

A. PRINCIPLES

Suppose that, in the system described, a DF of 100 is not sufficiently large or that a yield of 99% of product is not acceptable. What can be done?

By reference to Fig. 1 and Eq. (5) it will be seen that by draining the H phase, replacing it with a fresh *barren* (containing no M or N) H phase of the same volume, and agitating the phases, the M and N in the L phase (*extract*) will redistribute between the L phase and the fresh H phase (*scrub*), producing an L phase (*scrubbed extract*) containing 98.0% of the original M and only 0.0098% of the original N.

That is, the DF for M with respect to N is 10,000 after a *single extraction* followed by a *single scrub* as opposed to only 100 after a *single extraction without scrub.* (Contacting an *extract phase* with *barren opposing phase* is called *scrubbing.* In general the extract phase is primarily organic in nature and the barren opposing phase, the scrub, primarily aqueous; but this is purely a matter of definition.)

The penalty paid for increasing the DF from 100 to 10,000 by use of a single scrub was a loss in yield, the yield falling from 99.0% to 98.0%. A second scrub would result in a 97.0% yield of M-product with a DF with respect to N of 1,000,000. It is evident that *multiple scrubbing* is an effective technique for increasing the DF.

Considering the arbitrary nature of the definition of K and DF, that is, considering the L phase the extractant and M the product rather than the H phase the extractant and N the product, it is apparent from the symmetry relationships in Eqs. (5) and (7) that what *multiple scrubbing* does for DF, *multiple extraction* will do for yield, considering M as product. (Equivalent reasoning applies to N as product in the H phase.)

The answer to the demand for both increased yield and a larger DF (assuming that β cannot be increased) is the use of both *multiple extraction* and *multiple scrubbing*.

B. "PUSH-THROUGH" METHOD OF OPERATION

1. *General*

One method of operation incorporating both multiple extraction and multiple scrubbing is illustrated in Fig. 2. Because of the confusion of terms associated with it in the literature, this will be identified as the *push-through* technique in reference to the fact that a single portion of feed is *pushed* through the system by a series of scrubs. It constitutes a special case of "countercurrent distribution," which has been treated exhaustively, both experimentally and mathematically, by Craig (*50*). Its consideration here is justified on the basis of the relative simplicity of its mathematical treatment and its ready applicability to research-scale separation of radioactive nuclides.

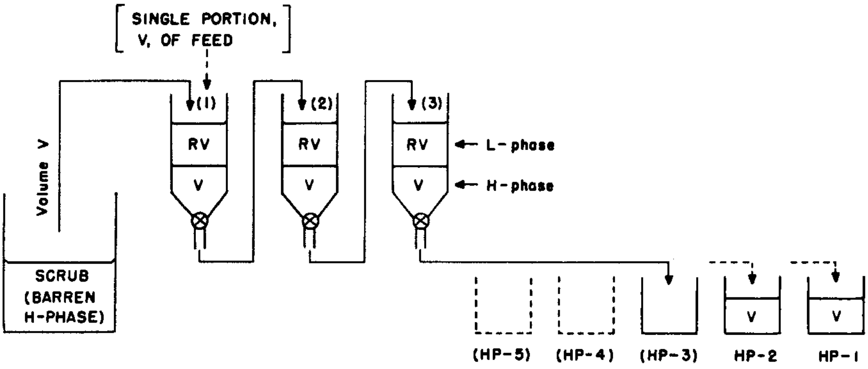


FIG. 2. Multiple extraction and multiple scrubbing: "push-through."

In Fig. 2, the three separatory funnels are numbered consecutively to the right, and the "flow" of H phase is to the right, the L phase being stationary with respect to the overall assembly.

Consider each funnel to initially contain a volume RV of barren L phase. A volume V of Feed (H phase) is introduced into Funnel 1. Following a mixing and settling cycle, the H phase is drained from Funnel 1 to Funnel 2 and a volume V of Scrub (barren H phase) is added to Funnel 1. Following a mixing and settling cycle for each of the two Funnels, the H phase of Funnel 2 is drained to Funnel 3 and that from Funnel 1 then drained to Funnel 2, following which a volume V of Scrub is added to Funnel 1. This sequence of mixing, allowing to settle, transferring N phase to the right (necessarily progressing from right to left with the transfers unless holding containers are used so that draining is not directly to a funnel), and adding a portion of Scrub is continued until the desired number of Scrubs have been employed. Note that when the depleted Feed is in Funnel 3 and ready to be drained as the first product phase, HP-1, the first Scrub is in Funnel 2 and the second Scrub in Funnel 1.

2. *Operation and Mathematical Treatment*

By a generalization of this treatment it may be shown that, after the passage of n portions of H phase through an assembly of c funnels, i.e., n H-products numbered consecutively from HP-1 to HP-a and c L-products numbered consecutively (to correspond to Funnel numbers) from LP-1 to LP-c, the fraction of solute M added to this assembly in the single portion of Feed to be found in a given product is expressed as

$$\Phi_{\mathrm{HP}-n} = B_{(c,n)}E^{n-1}/(E + 1)^{c+n-1} \tag{12}$$

for the nth H-product (c contactor), and as

$$F_{\mathrm{LP}-n} = B_{(q,a)}E^{a}/(E + 1)^{q+a-1} \tag{13}$$

for the qth L-product (a portions of H phase passed through the qth contactor). The multiplier, $B_{(q,n)}$, in the above equation is expressed as:

$$B_{(q,n)} = (q + n - 2)!/[(q - 1)!(n - 1)!] \tag{14}$$

Considering an assembly of these contactors ($c = 3$) (see Fig. 2), after a total of five H phases have traversed the assembly ($a = 5$) the funnels from left to right will contain LP-1, LP-2, and LP-3, and five products, HP-1 to HP-5, will have been withdrawn. The fraction of total M introduced into the system reporting to each of these eight products is shown in Table I.

Substitution of specific numerical values for E in the F and Φ expressions of Table I generates the F and Φ values of Table II.

For $E = 1$: The Φ value, proceeding from HP-1 to HP-5, is seen to increase to a maximum at HP-2 and HP-3, the total fraction of M reporting to the composite H-product being 0.774. The F values, proceeding from LP-1 to LP-3, increase throughout.

TABLE I

Fraction of Total M Introduced into the System Reporting to Each of the 8 Products Resulting from Transfers of 5 Portions ($a = 5$) of H Phase through 3 Stationary Portions ($c = 3$) of L Phase: General Case

L Phase		H Phase	
Product	F	Product	Φ
LP-1	$E^5/(E+1)^5$	HP-1	$1/(E+1)^3$
LP-2	$5E^5/(E+1)^6$	HP-2	$3E/(E+1)^4$
LP-3	$15E^5/(E+1)^7$	HP-3	$6E^2/(E+1)^5$
		HP-4	$10E^3/(E+1)^6$
		HP-5	$15E^4/(E+1)^7$

TABLE II

Fraction of Total M Introduced into the System Reporting to Each of the 8 Products Resulting from Transfer of 5 Portions ($a = 5$) of H Phase through 3 Stationary Portions ($c = 3$) of L Phase: Specific Values of E

	F (or Φ)			
Product	$E = 1$	$E = 2$	$E = 9$	$E = 0.1$
LP-1	0.0313	0.132	0.590	6.2×10^{-6}
LP-2	0.0781	0.219	0.295	2.8×10^{-5}
LP-3	0.117	0.219	0.089	7.7×10^{-5}
	0.226	0.570	0.974	0.000111
HP-1	0.125	0.0370	0.00100	0.751
HP-2	0.188	0.0740	0.00270	0.205
HP-3	0.188	0.0988	0.00486	0.0373
HP-4	0.156	0.110	0.00729	0.00564
HP-5	0.117	0.110	0.00984	0.000770
	0.774	0.430	0.026	1.000

For $E = 2$: The Φ value increases to 0.110 at both HP-4 and HP-5, the total fraction of M reporting to the composite H-product being 0.430. The F values behave similarly.

For $E = 9$: The Φ values increase throughout, the total fraction of M in the composite H-product being only 0.026. The LP-1 product contains better than half of the M content of the system.

For $E = 0.1$: The HP-1 product contains 75% of the total M of the system. The composite L-product contains approximately 0.011% of the total M.

3. *Applications*

A linear plot of the Φ data of Table II for a given E vs. the number of the H-product bears a formal resemblance to an ion-exchange elution curve. Similarly, a linear plot of the F data for a given E vs. the number of the L-product is formally analogous to a plot of equi-spaced sections of an ion-exchange column, sectioned after development.

From Table II it is evident that, if the Feed contained two substances, M and N, with respective E values of 9 and 0.1, the LP-1 contains 59.0% of the added M, decontaminated with respect to N by a factor of 9.5×10^4. (The DF is less in LP-2 and still less in LP-3.) The composite L-product contains 97.4% of the M with a DF of 8.8×10^3. Similarly, the HP-1 contains 75.1% of the N decontaminated with respect to M by a factor of 751.

Sometimes the analogy of gradient elution may be used in the push-through technique. Suppose, under three sets of conditions differing only in the composition of the H phase employed, the E values for substances A, B, C are (1) $E_A < 1$, $E_B \gg 1$, $E_C \gg 1$; (2) $E_B < 1$, $E_C \gg 1$; (3) $E_C < 1$. Then, by using the proper number of portions of H phase corresponding to conditions (1), (2), and (3) in succession, A, B, and C will be removed, successively, from the assembly of funnels.

Such a "gradient" separation of Th(IV), Pa(V), and U(VI), i.e., UO_2^{++}, is shown in Fig. 3. (The data used in deriving the procedure are presented in Table III.)

In this separation, the method of operation presented in Fig. 2 was employed. Each of three funnels contained 25 ml tributyl phosphate, $(n\text{-}C_4H_9O)_3PO$ (TBP), and the feed and all scrubs were used in 25-ml portions. The feed and the immediately following three scrubs were 5.0 *M*

TABLE III

EXTRACTION OF TH(IV), PA(V), AND U(VI) INTO UNDILUTED TBP, $(n\text{-}C_4H_9O)_3PO$, FROM EQUILIBRATED AQUEOUS PHASES OF VARIOUS COMPOSITION[a]

Equilibrated aqueous phase	*K* Th(IV)	*K* Pa(V)	*K* U(VI)
5.0 *M* HCl	0.006	41	50
5.0 *M* HCl + 0.5 *M* HF	—	0.13	39
4.0 *M* HCl	—	3.7	25
4.0 *M* HCl + 1.0 *M* HF	—	—	10.4
0.5 *M* HCl	—	—	0.040
0.5 *M* HCl + 1.0 *M* HF	—	—	0.0076

[a] See reference (*207*).

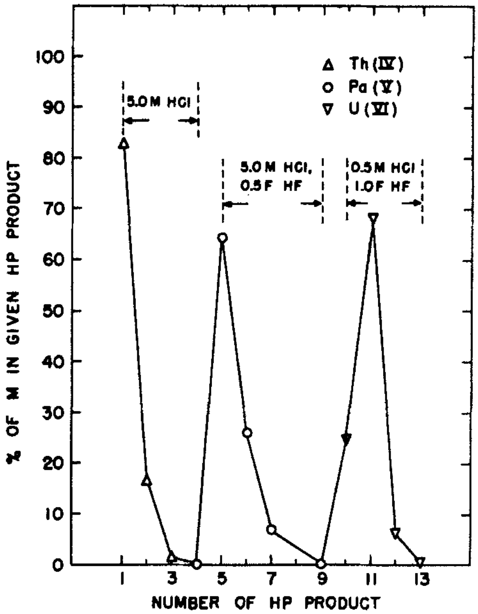


FIG. 3. "Gradient" separation of Th(IV), Pa(V), and U(VI): "push-through" (three contactors, 25 ml TBP in each, 25-ml portions of aqueous phase) (*207*).

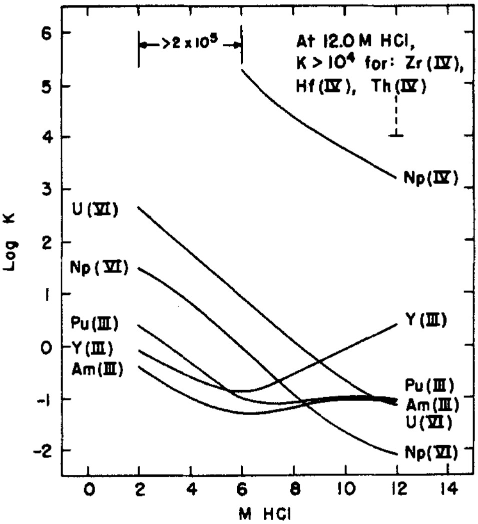


FIG. 4. Variation of log K with concentration of HCl for selected M(III), M(IV), M(VI) in the system: 0.48 F H_2MEHP (in toluene) vs. HCl (*218*). F = No. formula weights solute/liter solution.

in HCl, the next five scrubs were 5.0 *M* in HCl and 0.5 *M* in HF, and the final four scrubs were 0.5 *M* in HCl and 1.0 *M* in HF. For each of the nuclides, better than 60% yield is found in a single-product phase.

In general, separations involving metals in mutually different valence states are readily accomplished, Fig. 4 illustrating this fact for a system involving mono-2-ethyl hexyl phosphoric acid, $(C_2H_5 \cdot C_6H_{12}O)PO(OH)_2$ (H_2MEHP), as the extractant (*218*). (All lanthanides(III) lie within or close to the general region bracketed by Am(III) and Y(III); U(IV) and Pu(IV) are comparable to Th(IV) in behavior, exact data throughout the range of HCl concentration being difficult to obtain because of the problems of valence control, U(VI) and Pu(III) constituting the respective interferences.)

It is evident that neptunium, as Np(IV), is readily separable from U(VI) and from actinides(III), lanthanides(III), and Y(III) under properly chosen conditions. However, experimentally the decontamination factor (DF) of the Np product phase with respect to uranium contamination frequently levels off, with continued scrubbing with 12 *M* HCl, at approximately 500. That is, further scrubbing with 12 *M* HCl fails to remove an appreciable portion of the uranium remaining in the product. This effect has been shown to be due to the presence of U(IV), the "oxidized uranium" in 12 *M* HCl having been demonstrated, by extraction experiments, to contain 0.3–2% U(IV) after an aging period of several hours.

Following a bromate "oxidation" scrub, a further DF of approximately 500 may be obtained. Consequently, through suitable insertion of bromate oxidation scrubs in the scrub sequence, a DF with respect to uranium of any desired value may be reached. (It may be noted that if a loss in neptunium yield of 1–2% may be tolerated, only a single contactor (funnel) is required. In practice, it may be desirable to transfer the organic phase to a fresh contactor after approximately half of the scrubs have been employed, because of the tendency of trace contaminants to adhere to the walls.)

The "leveling off" of the DF of the neptunium product with respect to uranium contamination, frequently at approximately 500, due to the presence of U(IV), forcefully illustrates the importance of valence control in systems involving elements of variable valence. For example, it is extremely difficult to maintain the Pu(IV) to Pu(III) ratio in 1–6 *M* HCl below a value of 10^{-3}. Consequently, although the data of Fig. 4 indicate the ready separability of U(VI) and Pu(III) at 6 *M* HCl, a high DF of uranium product with respect to plutonium contaminant requires the presence of a reductant in the 6 *M* HCl scrubs, this reductant serving to reduce Pu(IV) in the extract to Pu(III) as Pu(III) is removed by scrubbing.

It is evident from Fig. 4 that Np(VI) is readily separable from Th(IV). Since Th exists in such systems only as Th(IV), no difficulty in purification of Np is to be expected. However, the yield of Np is dependent upon the maintenance of the hexavalent state.

Gindler *et al.* (*93*) used this H_2MEHP (in toluene) vs. HCl system in the purification of daughter ^{229}Th from parent ^{233}U and from other fissionable material in the determination of the thermal neutron fission cross-section of ^{229}Th.

A comparison of the extraction behavior of a given element in different states of oxidation is instructive. From a comparison of β values (ratio of the two K values) for a given element in two states of oxidation, as calculated from the data of Table IV, it is tempting to generalize that K values may be ordered:

$$\mathrm{M(IV)} > \mathrm{M(III)} \sim \mathrm{M(VI)} > \mathrm{M(II)}$$

However, it must be noted that even the Eu and Bk data are not strictly comparable, since the chemical systems employed are not the same. (The former data were obtained in a HCl system so that Eu(II) could be maintained, and the latter in a HNO_3 system so that Bk(IV) could be stabilized.) Further, in certain systems involving neutral extractants, such as the tributyl phosphate, $(n\text{-}C_4H_9O)_3PO$ (TBP), vs. HNO_3 system and the diethyl ether vs. NH_4NO_3 system, the K for U(VI) exceeds that for U(IV).

Although a sweeping generalization may not be made, the fact that the β for Eu(III) with respect to Eu(II), for Bk(IV) with respect to Bk(III),

TABLE IV

COMPARISON OF K VALUES FOR M IN TWO DIFFERENT VALENCE STATES UNDER SELECTED OPERATING CONDITIONS[a]

	K			
M	M(II)	M(III)	M(IV)	M(VI)
Eu[b]	3.0×10^{-3}	2.2×10^{3}	—	—
Bk[c]	—	2.3×10^{-3}	1.9×10^{3}	—
Np[d]	—	—	1.7×10^{3}	1.2×10^{-2}
U[d]	—	—	$>7 \times 10^{3}$	6.3×10^{-2}

[a] Acidic phosphorus-based extractants in carrier diluents vs. an aqueous mineral acid phase.

[b] 0.40 *F* HEH[ϕP], i.e. $(C_2H_5 \cdot C_6H_{12}O)(C_6H_5)PO(OH)$, 2-ethyl hexyl hydrogen phenyl phosphonate, in toluene vs. 0.05 *M* HCl (*201*).

[c] 0.15 *F* HDEHP, i.e. $(C_2H_5 \cdot C_6H_{12}O)_2PO(OH)$, di-2-ethyl hexyl phosphoric acid, in *n*-heptane vs. 10 *M* HNO_3 (*219*).

[d] 0.48 *F* H_2MEHP, i.e. $(C_2H_5 \cdot C_6H_{12}O)PO(OH)_2$, mono-2-ethyl hexyl phosphoric acid, in toluene vs. 12 *M* HCl (*218*).

and for Np(IV) with respect to Np(VI) approximates 10^5 in the systems represented in Table IV suggests that the mutual separation of two elements present in different valence states should be readily accomplished. The fact that M(IV) and M(III) respond differently to varying operating conditions (see Fig. 3) may be employed in effecting their mutual separation.

C. "COUNTERCURRENT EXTRACTION" METHOD OF OPERATION

1. *General*

Separations based upon β values of 10^5 (assuming the E values bear the proper relationship to unity) are readily accomplished. Those based upon β values approximating 100 may be achieved by use of multiple extraction and multiple scrubbing by the push-through technique, utilizing only a small number of contactors and relatively few scrubs; those based upon a β value of approximately 10 are in the "challenging" area.

However, a separation based upon a β value in the range 2–5 requires a method of operation not yet discussed. Such a method of operation is required for the efficient mutual separation of adjacent lanthanides(III). In the lanthanide (rare earth) series, the 15 members, differing successively by one in atomic number, are chemically similar and exist preferentially as lanthanide(III) ions. Cerium(IV) and europium(II) are sufficiently stable for study, but the usual state for each of these elements is the trivalent one.

The data of curve A of Fig. 5 pertain to one of the more promising systems with respect to the mutual separation of lanthanides(III) (*209*). The average β for one member with respect to the adjacent member one unit lower in atomic number, Z, is 2.8. (Noting that β, β^2, β^3, β^4, and β^5 are, respectively, 2.8, 7.8, 22, 61, and 172, it is evident that even the push-through technique will suffice to mutually separate lanthanides(III) which differ by four or more units in atomic number.)

The push-through method of operation may be applied to a number of solutes so as to produce a number of product phases in which the various solutes tend to concentrate discretely. (Compare the peaks of an ion-exchange elution plot.) However, the purity of a given product is not high, unless the β for the solute with respect to immediately preceding and following solutes is greatly different from unity.

In order to achieve greater discrimination (more thorough mutual separation with respect to a given pair of solutes) the advantage of multiple "product" phases must be sacrificed. In the method of operation about to be described, here referred to as *countercurrent extraction*, at *steady state* operation of the system, two product phases, L and H, each of constant composition with respect to time, are obtained.

The *cut*, among a number of solutes, may be made at any predetermined point, but the isolation of a single solute (other than one of the two terminal ones in the sequence of ascending extractability under a given set of conditions) requires *two passes* through the system. In one of these passes, this solute reports to the L phase, all solutes less extractable reporting to the H phase. In the other pass, it reports, singly, to the H phase, all solutes more extractable reporting to the L phase.

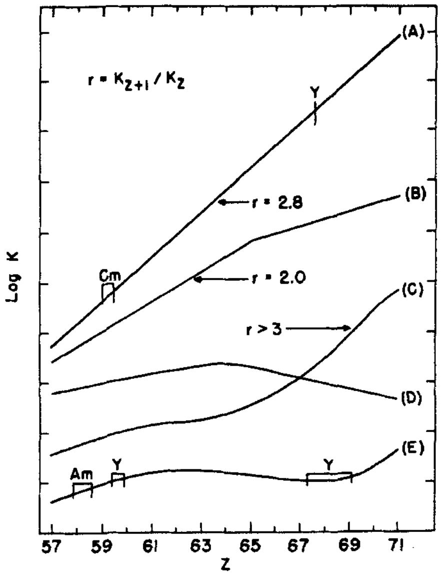


FIG. 5. Variation of log K with Z for lanthanides(III) in selected systems (smoothed curves; log K values at Z axis, respectively for curves A–E, are -7, -4, -2, -5, and 1). (A) 1.0 F HEH[ΦP] (in toluene) vs. 2.0 M HCl (*209*); (B) undiluted TBP vs. 15.6 M HNO_3 (*113*); (C) 0.0375 F HDHoEP (in benzene) vs. 0.25 M $HClO_4$ (*208*); (D) 0.71 F TBP (in CCl_4) vs. 1.96 M HNO_3 (*199*); and (E) 0.10 F H_2MEHP (in toluene) vs. 0.25 M HCl (*177*). F = No. formula wts. solute/liter solution.

(The terms "reports" and "singly" are used relatively, it being understood that each product phase contains some of each of the solutes present in the original feed, since no liquid-liquid extraction separation is "absolute.")

2. Operation and Mathematical Treatment

Countercurrent extraction is illustrated for a five-contactor system in Fig. 6. In a method of operation used in the author's laboratory the funnels are clamped in fixed equi-spaced position, mixing of the phases being accomplished by glass "pump-mix" stirrers driven by motors mounted above the funnels. The seven beakers, numbered 0–6, are placed in shallow cups attached to a board which moves easily (on glides or rollers) in a left-right line, its movement being limited by stops at the left and right, so that positions corresponding to (A) and (B) of Fig. 6 may be obtained rapidly and precisely. The position corresponding to (C) may be stabilized by use of a pin inserted to prevent movement of the board.

In the general case, any number of funnels may be employed, and the Feed may be introduced into any one. However, in the interest of mathematical simplicity, an *odd* number of funnels with Feed entry at the *central position* has been chosen for the illustration of the principle of countercurrent extraction.

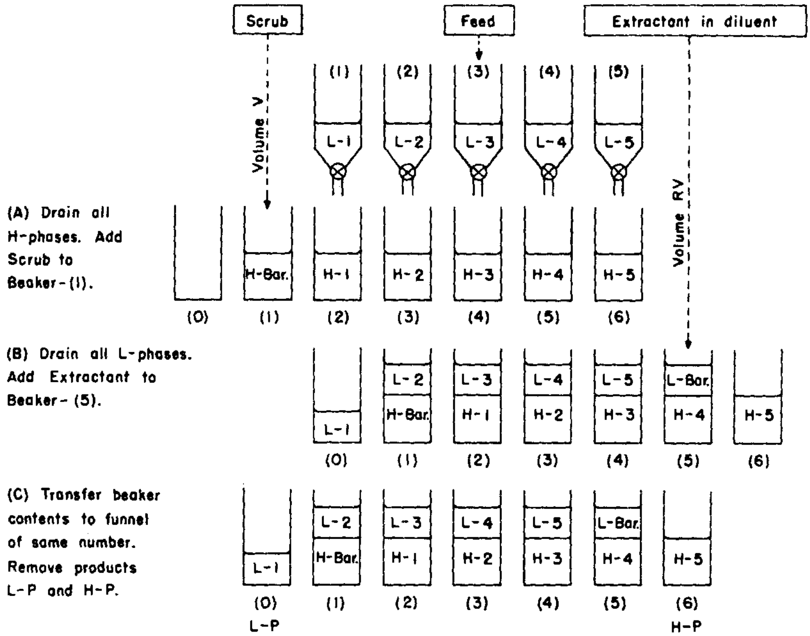


FIG. 6. Multiple extraction and multiple scrubbing: "countercurrent extraction."

Assume that at the start of the operation each of the funnels of Fig. 6 contains a volume RV of Extractant phase (L phase) and a volume V of barren Scrub phase (H phase). A portion of Feed (a volume *temporarily* considered to be negligible by comparison with V and RV) is introduced into Funnel 3. (Note that the Feed may be introduced as a solution in L or in H. In theory, a solid Feed may be introduced, but this is in general undesirable due to difficulties in assuring complete dissolution.)

Following equilibration of phases in Funnel 3, the H phase is drained to Beaker 4 (Subcycle A). The L phase is then drained to Beaker 2 (Subcycle B). (The heavy and light phases of the other funnels have meanwhile been transferred correspondingly, but at this point contain no solutes. Also, a portion, V, of Scrub (barren H phase) has been added to Beaker 1; and a portion, RV, of Extractant (barren L phase) has been added to Beaker 5.)

When the beakers are moved into Position C, Beaker 0 contains a volume RV of L phase, Beaker 6 contains a volume V of H phase, and each of the intervening beakers contains a volume RV of L phase and a volume V of H phase. The content of each beaker is then transferred to the funnel with the corresponding number.

As the result of the manipulations involved in Subcycles A, B, and C, each portion of L phase has moved one position to the left and each portion of H phase one position to the right. Note that Funnel 2 and Funnel 4, but no other funnels, now contain solutes from the Feed. A fresh portion of Feed is introduced into Funnel 3 and the entire cycle performed repetitively.

Just before addition of the third portion of Feed, solutes from *Feed portion-1* will be in *Funnels 1, 3, 5* and solutes from *Feed portion-2* will be in *Funnels 2, 4*. From consideration of Fig. 6, it is evident that all Feed portions of *odd number* will mutually interact as will all Feed portions of *even number* in an identical fashion. But odd and even *cannot* mutually interact. Therefore, if individual products, represented by Beaker 0 and Beaker 6, are kept separate as steady state operation is approached, it will be found that each odd-numbered product has an even-numbered counterpart of identical composition.

(Mathematically, the system is represented by a *double-diamond*, as opposed to a *single-diamond*. This point is stressed since, if it is mistakenly analyzed as a single diamond, it will be concluded that a given approximation to steady state operation has been reached with p through-puts (i.e., product phases produced) whereas $2p$ will be required.)

Considering a solute, M, for which RK, i.e. E, is equal to unity, it is evident that after the first transfer of Feed portion-1, the M of Feed portion-1 will be equally distributed between Funnel 2 and Funnel 4. Following the next transfer, it will be distributed in Funnels 1, 3, 5 in the ratio 1:2:1. Therefore, since M distributes equally between opposing phases, 12.5% will appear in the first L-product and 12.5% in the first H-product.

Meanwhile, 50% of the M content of Feed portion-1 has been joined by 100% of the M of Feed portion-3 in Funnel 3. Continuation of this reasoning leads to the conclusion that the M content of each funnel builds up to a limiting value which may be expressed in terms of the quantity Q present in a single portion of Feed. These limiting values are: Q for Funnel 1 and Funnel 5, $2Q$ for Funnel 2 and Funnel 4, and $3Q$ for Funnel 3.

When these limiting values have been reached, the system is operating at steady state *with respect to M which has an E of 1.*

The approach to steady state operation of a given system is a function of E. Therefore the system may be at "steady state" with respect to one solute present but not with respect to another. It has been shown that the number of through-puts required to approach steady state operation to a given approximation in such a system increases as E approaches unity, from either side (*221*). Therefore the behavior of the solute with E closest to unity may be used to establish the reliability of "steady state" data.

By definition, at steady state the quantity of solute M leaving the system in an L-product plus that in an H-product, must equal the quantity of M, Q_0, in a single portion of Feed, that is:

$$Q_{\text{L-P}} + Q_{\text{H-P}} = Q_0 \tag{15}$$

Defining "fractional yields" as before:

$$F_{\text{L}} = Q_{\text{L-P}}/Q_0, \qquad \Phi_{\text{H}} = Q_{\text{H-P}}/Q_0 \tag{16}$$

In an extension of the mathematical analysis of liquid-liquid extraction by Hunter and Nash (*118*, *119*), Bush and Densen (*33*), Golumbic (*96*), Compere and Ryland (*46*), Auer and Gardner (*9*), Scheibel (*240–242*), and Peppard and Peppard (*221*), it has been shown by Peppard *et al.* (*216*) that for the general case of:

q contactors
Feed entry at nth contactor
Scrub entry at 1st contactor
Extractant entry at qth contactor
$RK = U$, in contactors $1, \cdots, (n-1)$
$RK = P$, in contactor n
$RK = E$, in contactors $(n+1), \cdots, q$

$$F_{\text{L}} = PU^{n-1} \sum_0^{q-n} E^i \Big/ \left[\sum_0^{n-1} U^i + PU^{n-1} \sum_0^{q-n} E^i \right] \tag{17}$$

$$\Phi_{\text{H}} = \sum_0^{n-1} U^i \Big/ \left[\sum_0^{n-1} U^i + PU^{n-1} \sum_0^{q-n} E^i \right] \tag{18}$$

Assuming that all solutes are present in tracer-level concentration and that opposing L and H phases are mutually pre-equilibrated except with respect to the solutes to be studied, no volume changes will occur throughout the system. Therefore, since the Feed must be introduced in a finite volume, P may be made equal to U or to E, dependent upon the Feed being L phase or H phase, respectively.

If the volume of Feed is a sufficiently small fraction of V and of RV and if K is truly constant, then, approximately,

$$U = P = E$$

and Eqs. (17) and (18) approach:

$$F_L = E^n \sum_0^{q-n} E^i \Big/ \Big[\sum_0^{n-1} E^i + E^n \sum_0^{q-n} E^i \Big] \tag{19}$$

$$\Phi_H = \sum_0^{n-1} E^i \Big/ \Big[\sum_0^{n-1} E^i + E^n \sum_0^{q-n} E^i \Big] \tag{20}$$

Specifically, for a system with an odd number of contactors (stages) with Feed entry at the center contactor, i.e., $q = 2n - 1$, these equations reduce to the readily manipulated forms:

$$F_L = E^n/(1 + E^n) \tag{21}$$

$$\Phi_H = 1/(1 + E^n) \tag{22}$$

For the system presented in Fig. 6, therefore, in which the Feed entry is at number 3 contactor of an assembly of five contactors:

$$F_L = E^3/(1 + E^3) \tag{23}$$

$$\Phi_H = 1/(1 + E^3) \tag{24}$$

The mutual separability of two solutes, M and N, $K_M > K_N$, is illustrated in Table V for β values of 2, 4, and 8. Feed entry is at the center stage, $E_M = 1/E_N$, and Eqs. (21) and (22) are applicable. Note that, as the result of this symmetrical method of operation, the "product N" in the H phase is of the same relative yield and purity as the "product M" in the L phase.

With a β value of 2, each solute is obtained in 66.7% yield with a DF of 2.0 with respect to the other solute in a 3-stage system. A 27-stage system is required to produce a 99.2% yield of product with a DF of 127.

With a β value of 8, products in 99.8% yield with DF values of 512 are obtained in an 11-stage system; in a 27-stage system, products in greater than 99.99% yield with DF values of 2.1×10^6 are obtained.

3. *Applications*

Specific applications of countercurrent extraction to the mutual separation of lanthanides(III) may be envisioned by reference to Table V and Fig. 5. In Fig. 5, the variation of log K with atomic number for lantha-

TABLE V
Theoretical Mutual Separability of Solutes M and N, with Various β Values, as Expressed by F_L and Φ_H[a]

	$2n - 1$	M		N	
β	(q)	F_L	Φ_H	F_L	Φ_H
2	3	0.6667	0.3333	0.3333	0.6667
	7	0.8000	0.2000	0.2000	0.8000
	11	0.8889	0.1111	0.1111	0.8889
	15	0.9412	0.05882	0.05882	0.9412
	19	0.9697	0.03030	0.03030	0.9697
	23	0.9846	0.01538	0.01538	0.9846
	27	0.9922	7.752×10^{-3}	7.752×10^{-3}	0.9922
4	3	0.8000	0.2000	0.2000	0.8000
	7	0.9412	0.05882	0.05882	0.9412
	11	0.9846	0.01538	0.01538	0.9846
	15	0.9961	3.891×10^{-3}	3.891×10^{-3}	0.9961
	19	0.9990	9.756×10^{-4}	9.756×10^{-4}	0.9990
	23	0.9998	2.440×10^{-4}	2.440×10^{-4}	0.9998
	27	>0.9999	6.103×10^{-5}	6.103×10^{-5}	>0.9999
8	3	0.8889	0.1111	0.1111	0.8889
	7	0.9846	0.01538	0.01538	0.9846
	11	0.9980	1.949×10^{-3}	1.949×10^{-3}	0.9980
	15	0.9998	2.440×10^{-4}	2.440×10^{-4}	0.9998
	19	>0.9999	3.052×10^{-5}	3.052×10^{-5}	>0.9999
	23	>0.9999	3.815×10^{-6}	3.815×10^{-6}	>0.9999
	27	>0.9999	4.768×10^{-7}	4.768×10^{-7}	>0.9999

[a] Feed entry at nth stage of $(2n - 1)$ stages, $U = P = E$, $E_M = 1/E_N$. $F_L = E^n/(1 + E^n)$, $\Phi_H = 1/(1 + E^n)$.

nides(III) is shown for selected systems exhibiting widely differing separations possibilities.

Curve (B) is essentially two straight lines joining at approximately $Z = 64$ (gadolinium) (*113*). The steep left-hand portion represents a value of r (i.e., β for adjacent members) of approximately 2.0. Therefore, in this region, a pair of elements differing by one, two, and three in atomic numbers will have β values approximating 2, 4, and 8, i.e. β^1, β^2, β^3, which are the values treated in Table V.

Curve (D) represents the same basic chemical system as Curve (B), with different values of the operating variables (*199*). The plot is approximately symmetrical about $Z = 64$. Therefore, for each element on the left leg of the curve, there is a matching element of essentially the same K value on the right leg. Obviously the separations applications of such a system are limited.

Mathematically, curve (C) (*208*) resembles the curve which would result by turning curve (B) through 180° about an axis passing through the ends. That is, the right leg now offers separations possibilities, whereas the left is unpromising.

Curve (E) exhibits a maximum followed by a minimum (*177*). The total range of K values is approximately 8. (In a system recently reported (*176*) in which the curve is similar, the total range of K values is less than 4.)

Curve (A) represents a nearly constant r value for adjacent members of 2.8 throughout the lanthanide series (*209*). The total range of K values is 1×10^6.

A second system, with a straight-line plot and indicating an r of 2.5, has been reported (*217*).

A third promising system, with a "straight line of best fit plot" indicating an r for adjacent members of 2.7 and having a total K range of 1×10^6, is reported to exhibit an odd-even effect (*213*). Selected specific respective β values are: Tm(69)/Er(68), 1.5; Er(68)/Ho(67), 6.7; Tm(69)/Ho(67), 10. The 1.5 is discouragingly small, the 6.7 is far better than any previous r, and 10 is the largest r^2 value reported.

Although it is evident that adjacent members of the lanthanide series, in the trivalent state, may be separated mutually by liquid-liquid extraction, it is also evident that the amount of manipulation required in using manually operated equipment is prohibitive. Fortunately, the "continuous flow" analog of the "intermittent flow" system pictured in Fig. 6 has been automated.

One device utilizing continuous flow is the vertical column in which the barren H phase is introduced at the top and flows downward, the barren L phase is introduced at the bottom and flows upward, and the Feed is introduced at an intermediate point. The designs of such columns differ widely, including packed, rotating, and oscillating types (*273*, *274*, *277*), but the function is always the same: to allow H and L phases to intimately mix, disengage, and flow countercurrently, each infinitesimal portion of each phase then to repeat the cycle. The two products issue from the ends of the column.

Another device, of wide popularity, is the mixer-settler (*273*, *274*, *276*), which in essence is an alternating assembly of pairs of mixing and settling chambers. The arrangement is such that the physical mixture of phases from the mixing chamber of stage X flows into a settling chamber from which the discrete L and H phases then flow, respectively, into the mixing chambers of stages $(X - 1)$ and $(X + 1)$. The net result is that the L and H phases flow countercurrently and continuously. The barren L and H phases are introduced at the terminal stages, from which the two products also issue; the Feed is introduced at an intermediate stage.

D. COMPARISON OF "PUSH-THROUGH" AND "COUNTERCURRENT EXTRACTION" METHODS OF OPERATION

A comparison of "push-through" and "countercurrent extraction" techniques, with respect to areas in which one is manifestly superior to the other, is instructive.

The former has become widely accepted by analytical chemists and nuclear chemists because of its easy implementation, if a chemical system exhibiting a sufficiently large β is available. Even though a quantitative yield of the desired product may not be attainable in a system with only a few contactors, frequently the yield may be determined accurately and be sufficiently reproducible to permit use of a trustworthy correction or normalization factor. Consequently, accurate analysis is possible. Such an extraction-separation may be made solely for the purpose of eliminating interfering elements, or for effecting a concentration of the component to be determined, or for both purposes.

Sometimes a high DF with respect to one or more contaminants is the only requirement, yield being of no concern. For example, suppose an inexpensive, readily available radionuclide, A, is contaminated with radionuclide B which has a K one ninth that of A. If the E values are set at 3 and 1/3, a single extraction, followed by 11 scrubs, will produce A in 3.2% yield with a DF of 5×10^5 with respect to B. If two contactors (i.e., two portions of L phase) and a total of 12 portions of H phase are employed, A will be obtained in 12.8% yield with a DF of 2×10^5. Such a separations approach is of obvious application in obtaining a sample of radionuclide for disintegration scheme studies and half-life determination and in securing a "pure" sample for radiotracing experiments.

If the β value is sufficiently large and if the E values are properly related to unity, both high yield and large DF may be obtained with a single contactor and multiple scrubbing, as illustrated by the purification of Np based upon the data of Fig. 4.

If the β value is in the neighborhood of 3 or less, countercurrent extraction is the more feasible of the two techniques. This is especially true if the mutual separation of M and N is required, or if only M of a mixture of M, N, O, P $\cdots$ is a desired product. In general, it is the preferred "production," as contrasted with "research," method of operation.

Consider an example from actinide technology. The mutual separation of americium (Am, $Z = 95$) and curium (Cm, $Z = 96$) is a challenging problem whose solution is of great importance. A variety of uses for Cm, produced by neutron bombardment of Am, have been proposed. These include power supplies for satellites and other devices requiring a self-contained, dependable, long-lived, rugged, and light-weight energy source.

Further bombardment of Cm by neutrons and by other fundamental particles to produce radionuclides for basic studies is of importance also (*244*).

In many instances the utilization of Cm requires a preceding Cm-Am separation. Sometimes a high DF is required, but a low yield may be tolerated. In other cases a high yield is of prime importance, but a moderate DF value will suffice. In still other cases both high yield and a large DF are considered fundamental to the success of the proposed utilization.

Although few data for both Am and Cm in liquid-liquid extraction systems have been reported, it appears that the β value is in general less than 2, Cm extracting the better in most systems (*120*). If a β value of 2 may be realized in a system with acceptable physical operating characteristics, then mutual Cm-Am separation by countercurrent extraction, employing automatic equipment such as a mixer-settler, is attainable, as may be seen by reference to Table V.

Although there appears little hope of stabilizing Cm at any oxidation state other than the trivalent in a system employing an aqueous phase (*267*), the existence of Am as Am(VI) in aqueous solution has been well established (*8*, *289*). Consequently an attractive possibility in effecting the Cm-Am separation is a system separating Am(VI) from Cm(III) (*267*). From the data of Table IV and the pertinent discussion of the effect of oxidation state upon K, it may be predicted that a liquid-liquid extraction system may be devised in which the β for Am(VI) with respect to Am(III), and therefore for Am(VI) with respect to Cm(III), should be in the range 10^2–10^3 or perhaps even higher.

Such predictions have not been realized effectually, because of the difficulty encountered in maintaining Am as Am(VI) in the extraction system. In the author's laboratory, it has been found difficult to maintain ^{241}Am as Am(VI) in an aqueous phase if the Am concentration is appreciably below 0.1 mg per ml. This difficulty becomes more pronounced as the Am concentration becomes lower. Consequently, in a system in which Am(VI) extracts far better than does Cm(III), the Am(VI) extract may be scrubbed to remove contaminant Cm(III), thereby producing a "pure" Am product. However, multiple extraction to remove contaminant Am(VI) from Cm(III) fails, because of the instability of Am(VI) at low concentration. Therefore a pure Cm product cannot be obtained.

Therefore, although Cm-Am separation based upon different states of oxidation of the two elements appears promising, successful application awaits development of a system in which Am(VI) is stable at low concentration.

Meanwhile, mutual separation of Cm and Am in a system showing a β value of 2 is feasible, using countercurrent extraction. With a β of 4 (see Table V) the difficulty of the problem is decreased dramatically.

It is suggested that β values of 4 or greater might be realized if the dual effects of differential extractability and of differential aqueous phase complexing of the "bare" M(III) ions can be made mutually reinforcing. Other possibilities are systems in which one of these elements extracts as a "mixed complex" and the other does not, possibly as $MX(\text{extnt.})_2$ and $M(\text{extnt.})_3$, where X is Cl^-, ClO_4^-, NO_3^-, etc., or in which the extractant dependencies for the two elements differ, the extracted entities perhaps being $M(\text{extnt.})_3$ and $H[M(\text{extnt.})_4]$. These approaches are presently under investigation at the author's laboratory.

IV. Systems Involving Neutral Phosphorus-Based Extractants

A. Mononuclear Extractants

Extraction with neutral extractants, presumably embodying the equivalent of ion pair association plus true metal-extractant coordination, has been treated in detail by Diamond and Tuck (*59*). To the historically important and still valuable ethers, ketones, alcohols, and carboxylic esters has been added a wide range of neutral phosphorus-based extractants. These are listed in general form in Table VI, along with other phosphorus compounds, some of which have also been reported as extractants, which are included for structural comparisons.

The vertical columns, identified as A, B, and C, of Table VI, classify the phosphorus-based compounds as neutral, monoacidic, and diacidic by

TABLE VI

General Classification[a] of Mononuclear Phosphorus-Based "Extractants," Proved and Potential

Bonding class	Neutral A	Monoacidic B	Diacidic C
1	$(GO)_3P$	$[(GO)_2P(OH)]$[b]	$[(GO)P(OH)_2]$[b]
2	$(GO)_3PO$	$(GO)_2PO(OH)$	$(GO)PO(OH)_2$
3	$(GO)_2(G)PO$	$(GO)(G)PO(OH)$	$(G)PO(OH)_2$
4	$(GO)(G)_2PO$	$(G)_2PO(OH)$	—
5	$(G)_3PO$	—	—
6	$(GO)_2(H)PO$	$(GO)(H)PO(OH)$	—
7	$(GO)(G)(H)PO$	$(G)(H)PO(OH)$	—
8	$(G)_2HPO$	—	—
9	$(GO)(H)_2PO$	—	—
10	$(G)(H)_2PO$	—	—

[a] G is a generalized organic group containing a C atom attached directly to P or to an oxygen atom which is attached to P. For simplicity, G, G′, and G″ have been represented as G, it being understood, for example, that (GO)(G)PO(OH) may be (GO)(G′)-PO(OH), and $(GO)(G)_2PO$ may be (GO)(G′)(G″)PO, etc.

[b] Brackets indicate nonexistence of this structure, Class 1B and Class 1C being found, respectively, as Class 6A and Class 6B.

reference to the formula. The horizontal groupings, identified by the numerals 1, 2, · · · 10, are based upon types of bond involved. (Class 1 includes "tricoordinate" phosphorus and all others "tetracoordinate" phosphorus, assuming the simple monomeric formula.)

For example, Class 1 and Class 2 involve no C-P or H-P bonds; Class 3, one C-P bond; Class 4, two C-P bonds; Class 7, one C-P bond and one H-P bond; Class 9, two H-P bonds; etc. In general, the nomenclature which will be used in referring to these compounds is that used in *Chemical Abstracts.*

The most widely studied of these neutral phosphorus-based extractants is tributyl phosphate, i.e., tri-*n*-butyl phosphate, $(n\text{-}C_4H_9O)_3PO$, an example of Class 2A of Table VI. Accepted usage has established TBP as the symbolic representation of this compound.

It is generally assumed to function as an extractant through metal coordination involving the unique oxygen (*32*), thereby occupying one coordination position on the metal (*111*). For example, Healy and McKay (*111*) consider Am(III) to be hexacoordinate in the extracted species, $Am(NO_3)_3(TBP)_3$.

In some studies and applications, undiluted TBP has been employed. However, the extractant phase is more generally a solution of TBP in a carrier diluent such as an aliphatic or aromatic hydrocarbon or carbon tetrachloride (the term carrier diluent is used, rather than inert diluent, since the *K* for a given element under otherwise identical sets of conditions may vary widely as the diluent is changed) (*4*, *270*).

The first recorded instance of the application of TBP as an extractant for metal ions was the extraction of Ce(IV) from an aqueous nitrate phase into undiluted TBP, reported by Warf (*290*).

Typical extraction stoichiometries from an aqueous nitrate phase might be represented as

$$M^{+2} + 2NO_3^- + 3TBP \rightleftharpoons M(NO_3)_2(TBP)_3 \qquad (25)$$

$$MO_2^{+2} + 2NO_3^- + 2TBP \rightleftharpoons MO_2(NO_3)_2(TBP)_2 \qquad (26)$$

$$M^{+3} + 3NO_3^- + 3TBP \rightleftharpoons M(NO_3)_3(TBP)_3 \qquad (27)$$

$$M^{+4} + 4NO_3^- + 2TBP \rightleftharpoons M(NO_3)_4(TBP)_2 \qquad (28)$$

the charged species being considered to be in the aqueous phase and the uncharged in the organic phase, respectively assumed to be H and L phases. (Whether the organic is L or H phase is dependent upon the diluent employed and the nature of the aqueous phase, i.e., salt content, etc. Usually the TBP extractant phase is the L phase.)

Extracted metallic species shown to conform to these stoichiometries are (Eq. 25) Co(II) (*110*); (Eq. 26) U(VI), Np(VI), and Pu(VI) (*111*); (Eq. 27) Am(III) and Y(III) (*111*), Pu(III) (*22*), and lanthanides(III) in general (*113*, *239*); and (Eq. 28) Th(IV), Np(IV), and Pu(IV) (*2*), Zr(IV) (*1*).

Consider the extraction represented by Eq. (26). If MO_2^{+2} is the only M(VI) species present in the aqueous phase and $MO_2(NO_3)_2(TBP)_2$ the only M(VI) species present in the organic phase, then

$$K = [MO_2(NO_3)_2(TBP)_2]_O/[MO_2^{+2}]_A \tag{29}$$

Hence, from mass law consideration,

$$K = k[NO_3^-]_A^2[TBP]_O^2 \tag{30}$$

The assumption that $K \propto [TBP]^q$ was utilized in deriving all of the quoted stoichiometries. However, whether the K is proportional to $[NO_3^-]^p$ is dependent upon whether appreciable complexing of the metal by nitrate occurs in the aqueous phase.

The complexing of UO_2^{+2} by nitrate at unit ionic strength is small (*55*), and therefore Eq. (30) holds very well for both the NO_3^- and TBP for U(VI) (*212*). On the other hand, complexing of Th(IV) by nitrate in the aqueous phase may not be ignored (*56*, *90*, *91*, *304*). Therefore, the K for Th is expressed as

$$K = [Th(NO_3)_4(TBP)_2]/\{[Th^{+4}] + [Th(NO_3)^{+3}] + \cdots\} \tag{31}$$

from which it follows that

$$K = k\{1 + k_1[NO_3^-] + \cdots\}^{-1}[NO_3^-]^4[TBP]^2 \tag{32}$$

where k_1 is the stability constant for $Th(NO_3)^{+3}$, etc. Fomin and Maiorova (*90*, *91*) have used a TBP vs. aqueous nitrate extraction system in determining the stability constants of the various nitrate complexes of Th.

In addition to M(II,III,IV,VI), M(V) as exemplified by Pa(V) is of both practical and theoretical importance in TBP vs. HNO_3 extraction systems (*106*). Hardy *et al.* (*106*) reported the K for Pa(V) into a solution of TBP in odorless kerosene from aqueous HNO_3 solutions to be second-power dependent upon the concentration of TBP. They suggest the possibility that a series of nitrate complexes, ranging from $Pa(OH)_2(NO_3)^{+2}$ to $Pa(OH)_2(NO_3)_4^{-1}$, in rapid equilibrium with one another, are present in the aqueous phase and that $Pa(OH)_2(NO_3)_3$ is extracted by TBP. (For purposes of this discussion, the equivalence of $Pa(OH)_2^{+3}$ and PaO^{+3} is assumed.)

Accordingly, in terms of concentration of nitrate ion and of TBP, the equation for the extraction of Pa(V) is of the form of Eq. (32). However, it is perhaps more instructive to represent the extraction, as postulated by Hardy *et al.* (*106*), as:

$$PaO(NO_3)_3 + 2TBP \rightleftharpoons PaO(NO_3)_3(TBP)_2 \tag{33}$$

An extensive investigation of 100% TBP (i.e., without diluent) as an extractant for metals from solutions of HNO_3 and $Ca(NO_3)_2$ was reported by Bernström and Rydberg (*21*). The cations studied were those of Ca(II), Sr(II), La(III), Zr(IV), Th(IV), Pu(IV), Nb(V), U(VI), and Pu(VI). The extraction curves were ". . . discussed with respect to the different complexes formed and to the possibility of using the investigated systems for separating plutonium and uranium from the fission products."

Extractants of Class 5A have been shown to function much as those of Class 2A, except that for identical G groups the phosphine oxides (Class 5A) are better extractants than the phosphates (Class 2A). Assuming the extracting ability of the molecule to be determined by the ability of the oxygen atom of the $P \rightarrow O$ to accept hydrogen bonds, i.e., by the basicity of this oxygen, the K, for a given metallic cation in an otherwise fixed system of extractant (in carrier diluent) vs. an aqueous nitrate phase, should increase with successive removal of O atoms, in the sequence:

$$(GO)_3PO < (GO)_2(G)PO < (GO)(G)_2PO < (G)_3PO \qquad (34)$$

This was first shown to be true for the extraction of U(VI) andP u(IV) by Burger (*32*), who correlated the K values with phosphoryl-bond stretching frequencies.

As TBP is the most widely studied phosphate, TOPO, tri-*n*-octyl phosphine oxide, $(n\text{-}C_8H_{17})_3PO$, is the most frequently reported phosphine oxide in metals extraction studies. In general, Eqs. (26–28) are applicable. For example, in a TOPO vs. aqueous nitrate system, Ishimori *et al.* (*134*) found the K values for Am(III) and Eu(III) to be essentially third-power extractant dependent; Martin *et al.* (*173*) reported the K values for Pu(IV) and Pu(VI) as second-power extractant dependent. Similarly, Saisho (*235*) reported second-power extractant dependencies for Zr(IV) and Hf(IV). However, Zingaro and White (*305*) found a third-power TOPO dependency for Th(IV), to be compared with the second-power TBP dependency.

The higher K for a given metallic cation in an otherwise identical system shown by phosphine oxides (Class 5A) as compared with phosphates (Class 2A) is paralleled by a higher K for HNO_3 (*292*). Consequently, in the interpretation of extractant and nitrate dependency data, corrections for tie-up of extractant by HNO_3 are even more important than in TBP vs. aqueous nitrate systems.

A study of tri-*n*-butyl phosphine oxide, $(n\text{-}C_4H_9)_3PO$ (TBPO), in carbon tetrachloride as extractant for Pu(III) and Pu(IV) from HNO_3 has been reported by Umezawa (*278*).

The monograph by White and Ross (*292*) reviews a large portion of the TOPO literature preceding 1961. From this review it is evident that TOPO vs. aqueous mineral acid systems offers great promise in separations of interest to the nuclear chemist. However, it must be emphasized that, for many separations applications, ridding the TOPO of acidic impurities is imperative. In the author's laboratory, a sample of TOPO obtained from a commercial source showed zero titer in a titration with standard NaOH. However, a portion of this was treated by a procedure designed to remove acidic impurities, possibly di-*n*-octyl phosphinic acid (see Class 4B of Table VI). Under otherwise identical conditions, ^{230}Th was extracted from an aqueous nitrate solution by the purified sample with a K of 0.2 and by the "as received" sample with a K of 7×10^2.

Dialkyl alkyl phosphonates (Class 3A) have been studied as extractants, from aqueous mineral acids, of U(VI) (*212, 250, 264*), Mo(VI) (*194*), Th(IV) (*166, 250*), and Zr(IV) and Hf(IV) (*299*).

Burger (*32*) reported the extraction of Pu(IV) and Pu(VI) from an aqueous nitrate phase by butyl dibutyl phosphinate and by ethyl dihexyl phosphinate, examples of Class 4A. However, studies of members of this class are sparse, probably because the compounds have not been readily available.

How widely applicable the proposed generalization of Eq. (34) will prove, when tested for a variety of metallic cations for a large range of electronegativities for G, for both minimal and maximal steric effects in G, and for systems employing various diluents, should prove of great interest. Compounds of Classes 2A, 3A, and 5A are commercially available. Certain Class 4B compounds are commercially available and may be esterified by the carbodiimide technique (*149–151*) to form the corresponding Class 4A compound. Consequently the initial phases of such a study should not prove difficult.

Of the remaining neutral, or A, compounds of Table VI, only those of Class 1A have been reported as extractants, to the author's knowledge. Handley and Dean (*104*) studied the extraction of Cu(I) halides from an aqueous halide phase into a solution of triphenyl phosphite, $(C_6H_5O)_3P$, in carbon tetrachloride. From their saturation data, indicating a 1:1 ratio of extractant to Cu in the extracted entity, and from data on extraction of bromide-82 with the Cu(I), it may be concluded that the extraction stoichiometry is:

$$\mathrm{CuX} + (\mathrm{RO})_3\mathrm{P} \rightleftharpoons \mathrm{CuX} \cdot \mathrm{P(OR)}_3 \tag{35}$$

Presumably the bonding is through the electron pair on the P, but this has not been demonstrated.

It should be pointed out that such a study is possible because of the stability of triphenyl phosphite in an aqueous mineral acid system. Presumably stability is to be expected of other aromatic phosphites also. However, the investigation cannot be extended to include alkyl phosphites, because they react in contact with aqueous mineral acid (*7*), to form members of Class 6A:

$$(RO)_3P + HOH \rightarrow (RO)_2(H)PO + ROH \qquad (36)$$

The $(RO)_2(H)PO$ may very well be a valuable extractant in its own right, but it is important that its properties not be mistaken for those of $(RO)_3P$. Postulation of the product as $(RO)_2P(OH)$ has been shown to be in error (*6*, *53*). The structure is discussed at length by Doak and Freedman (*60*).

Although the utility of $(GO)_3P$ in liquid-liquid extraction is limited by the instability of so many members, the corresponding compounds without C-O-P bonds, i.e. $(G)_3P$, $(G)_2(H)P$, and $(G)(H)_2P$, may be widely applicable. Although these compounds have been studied as addends in coordination chemistry, they have not been exploited as extractants. If triphenyl phosphite, $(C_6H_5O)_3P$, functions as an extractant because of the pair of electrons on the P, then presumably triphenyl phosphine, $(C_6H_5)_3P$, should be the better of the two extractants. (Triphenyl phosphine oxide, $(C_6H_5)_3PO$, is a far better extractant than is triphenyl phosphate, $(C_6H_5O)_3PO$.)

Monothio compounds, in which S replaces the unique O of the Class A compounds of Table VI, should offer an entirely different range of separations possibilities, since the electron-donating tendency of S in the $P \rightharpoonup S$ group is very small compared with that of the O in the $P \rightharpoonup O$ group. Handley and Dean (*103*) have reported the extraction of Ag(I) and Hg(II) by triisooctyl thiophosphate, $(C_8H_{17}O)_3PS$ (TOTP), from aqueous HNO_3. From the observed extractant dependencies, they postulate:

$$Ag^+ + NO_3^- + TOTP \rightleftharpoons Ag(NO_3)(TOTP) \qquad (37)$$

$$Hg^{+2} + 2NO_3^- + 2TOTP \rightleftharpoons Hg(NO_3)_2(TOTP)_2 \qquad (38)$$

(These stoichiometries are not intended to imply first- and second-power nitrate dependencies of the respective distribution ratios, since nitrate dependencies at constant ionic strength were not reported.) The system was found to be highly selective for Ag(I) and Hg(II) from the 35 elements listed, including Ca(II), Zn(II), La(III), Th(IV), Zr(IV), Nb(V), and Mo(VI).

Although a large proportion of the "neutral phosphorus extractant" systems reported employ an aqueous nitrate phase, aqueous chloride, perchlorate, and thiocyanate phases have also been shown to be effective. Kertes and Halpern (*148*) showed TBP to extract U(VI) from an aqueous chloride solution as $UO_2Cl_2(TBP)_2$. Peppard *et al.* demonstrated the mutual separation of Sc(III), Th(IV), and Zr(IV) (*216*) and of Th(IV), Pa(V), and U(VI) (*207*) in a TBP vs. HCl system. Reznik *et al.* (*231*) employed TBP vs. aqueous HNO_3, HCl, and mixed HNO_3-HCl phases in a study of Zr(IV) extraction. They reported $Zr(NO_3)_4(TBP)_2$ and $ZrCl_4(TBP)_2$ and "mixed nitrate-chloride complexes" corresponding to $Zr(NO_3)_3Cl(TBP)_2$ and $Zr(NO_3)_2Cl_2(TBP)_2$ as the respective extracted species. Ishimori and Sammour (*135*) studied the countercurrent separation of fission products in the TBP vs. HCl system; Majumdar and De (*164*) report $FeCl_3(TBP)_3$ and $H[FeCl_4(TBP)_2]$ as extractable species from 2 *M* and 6 *M* HCl, respectively. Ishimori *et al.* (*139*) made "a radiochemical survey on the extraction behavior of almost sixty chemical elements" in the 1% TBPO, tributyl phosphine oxide, $(n\text{-}C_4H_9)_3PO$, in toluene vs. HCl system.

Distribution ratios for Ce(III), La(III), Y(III), Zr(IV), and Th(IV) from perchloric acid solution into TBP were reported by Siekierski (*254*). Hesford and McKay (*114*) postulated $UO_2(ClO_4)_2(TBP)_2$ as an extracted entity in a TBP vs. aqueous perchlorate system but point out that other solvates may also form. Naito and Suzuki (*192*) report $UO_2(ClO_4)_2(TBP)_4$.

Yoshida (*301*) studied the extraction of lanthanides(III) into a kerosene solution of TBP from an aqueous thiocyanate phase. He pictured the extraction of Eu(III) as:

$$Eu^{+3} + 3SCN^- + 4TBP \rightleftharpoons Eu(SCN)_3(TBP)_4 \qquad (39)$$

His plot of log *K* vs. *Z* for the lanthanide(III) series, excepting Pm(III), has a saw-tooth appearance, suggestive of an odd-even effect, especially in the $Z = 62\text{–}69$ region.

The first odd-even effect in the extraction of lanthanides(III) to be noted was reported by Hesford *et al.* (*113*) for the TBP vs. dilute HNO_3 system. In reference to their observation of "an alternation in extractability between elements of odd and even atomic number" they state, "Our impression is . . . that a single smooth curve can always be drawn through the points for the odd-*Z* elements, but that there is often a discontinuity at gadolinium among the results for the even-*Z* elements."

Structural effects have been reported by Siddall in "The effects of altering alkyl substituents in trialkyl phosphates on the extraction of actinides" (*251*), and by Nomura and Hara in "The effect of organic substituents and structure of organophosphorus compounds on their extraction abilities for uranium" (*197*). Examples of specific metals separations applications of TBP systems are "Separating hafnium from zirconium, solvent extraction with tributyl phosphate" (*49*); "Separation of monazite rare earths by solvent extraction" (*25*); "Recovery of neptunium-237 from process residues by solvent extraction" (*86*); and "Separation of transcurium elements from large quantities of curium, by liquid-liquid extraction" (*129*).

Ishimori and Sammour (*136*) report the separation of ^{233}U and ^{233}Pa from irradiated thorium in the tributyl phosphine oxide (TBPO) vs. HCl system by a "discontinuous countercurrent extraction technique"; Siddall (*252*) devotes a chapter to "Solvent extraction processes based on tri-*n*-butyl phosphate."

B. Dinuclear Extractants

If neutral mononuclear phosphorus-based extractants function as coordinating ligands through the unique O, i.e. the O of $P \rightharpoonup O$, then presumably a dinuclear compound with the $P \rightharpoonup O$ groupings suitably joined to permit chelation through the two O atoms to the metal atom to be extracted should be an even more effective extractant.

Saisho (*234*) studied the extraction of Zr(IV), Y(III), and lanthanides(III) as nitrates by tetra-*n*-butyl ethylene diphosphonate (TBEDP), which is a representative of

$$(X)_2(O)P{-}Y{-}P(O)(X)_2$$
(I)

where Y is $—CH_2CH_2—$, and X is $n\text{-}C_4H_9O—$. Since the "TBEDP . . . was used without further purification," i.e., as received from a commercial supplier, it must be considered suspect with respect to acidic impurities. Such an acidic impurity, perhaps

$$(X)_2(O)P{-}Y{-}P(O)(X)(OH)$$
(II)

i.e., tri-*n*-butyl hydrogen ethylene diphosphonate, would, if present even in the parts per thousand range, probably be the dominant extractant for tracer-level radionuclides in the low acid range. In addition, it would probably impose an inverse hydrogen ion dependency.

Consequently, whether the high K values for lanthanides(III) in the acidity region of approximately 0.1–0.5 M HNO_3 are due to the main extractant or to acidic impurity or impurities is open to serious question, as pointed out by Siddall (*253*).

Siddall (*253*), working with the same extractant without diluent, found the K for Ce(III) to rise steadily from 0.4 M HNO_3 to 4 M HNO_3, whereas Saisho reported the K to decrease in this range in the 0.2 M extractant (kerosene) vs. HNO_3 system. In a study of the effect of the length of Y, Siddall (*253*) used four compounds in which X was $n\text{-}C_4H_9O—$ and Y was $—CH_2—$, $—CH_2CH_2—$, $—CH_2CH_2CH_2—$, and $—CH_2CH_2CH_2CH_2—$. As extractants for Ce(III) from aqueous HNO_3, the last two diphosphonates were only slightly superior to dibutyl butyl phosphonate, which may be written as

$$(n\text{-}C_4H_9O)_2(O)P(n\text{-}C_4H_9)$$
(III)

to emphasize the resemblance to the diphosphonate structure. At 5 *M* HNO_3, in the ethylene diphosphonate and the methylene diphosphonate systems, the *K* for Ce(III) was, respectively, 20 and 200 times that in the dibutyl butyl phosphonate system. Presumably a stable six-membered ring is formed by chelation of the methylene diphosphonate with a central M atom, resulting in a relatively high *K* value. However, as the ring size increases to 7, 8, and 9 members, the effectiveness of a diphosphonate approaches that of a phosphonate. In the same study, the effectiveness of a combined phosphoryl and carbonyl extractant was demonstrated for Ce(III), the compounds being

$$(X)_2(O)P\text{—}(CH_2)_n\text{—}C(O)(X)$$

(IV)

where *n* was 0 or 1, and X was n-C_4H_9O

The major objection to a diphosphonate as an extractant in basic studies is that contamination by an acidic impurity, which may well be the dominant extractant for a tracer-level metal, is difficult to avoid. (An extractant which is of acceptable purity at the beginning of a determination of *K* may undergo sufficient hydrolysis during equilibration with the aqueous mineral acid phase to form an acidic extractant which then controls the extraction.)

Consequently the diphosphine oxides, structurally equivalent to the diphosphonate except that X is attached to P by a C-P bond, should be more trustworthy in studies involving tracer-level metals. These compounds have been investigated as extractants by Mrochek *et al.* (*190*), who refer to them as *gem*-bis(disubstituted phosphinyl)alkanes. Specifically, bis(di-*n*-hexyl phosphinyl)methane, $[(C_6H_{13})_2P(O)]_2CH_2$ (symbolized as HDPM), in 1,2-dichlorobenzene diluent was studied as an extractant for U(VI) from the four aqueous mineral acids HCl, $HClO_4$, H_2SO_4, and HNO_3. Throughout the region 1–9 *M* $HClO_4$, the *K* into 0.05 *M* extractant is greater than 4,000. Correspondingly, the *K* into 0.05 *M* TOPO, $(n\text{-}C_8H_{17})_3PO$, decreases from 7 to 0.6. However, in the HNO_3 system, TOPO is somewhat the more effective of the two as an extractant for U(VI) throughout the 1–7 *M* acid region.

In the presence of excess extractant, the extraction of U(VI) from HNO_3 is described by:

$$UO_2^{+2} + 2NO_3^- + 2HDPM \rightleftharpoons UO_2(NO_3)_2(HDPM)_2 \qquad (40)$$

Since UO_2^{+2} has been shown to extract in the TBP vs. HNO_3 system with a second-power dependence upon TBP concentration, it might have been expected that Eq. (40) would involve only one HDPM. Mrochek *et al.* (*190*) report a monosolvate, but conclude that a disolvate is formed in the presence of excess extractant.

V. Systems Involving Acidic Phosphorus-Based Extractants

A. MONONUCLEAR EXTRACTANTS

1. *General*

Acidic phosphorus-based extractants, as extractants for metallic cations, were discovered by accident. In at least two instances the discovery resulted from observation of interferences in TBP vs. mineral acid extraction systems.

For example, in early experiments with tracer-level Th(IV) in the undiluted TBP vs. HCl system in the author's laboratory, the dependence of *K* upon concentration of HCl was studied, using eight approximately equi-spaced concentrations varying from 1.0 *M* to 12 *M*. In each experiment, the α-active ^{230}Th was initially in the aqueous phase. The *K* values increased from $\sim 4 \times 10^{-4}$ at 1.0 *M* HCl to ~20 at 12 *M* HCl. All of the separated organic extracts in the $K > 0.1$ range were set aside for determination of *K* values by the reverse or scrubbing technique the following day. Each of these extracts, approximately 18 hours old, was then contacted with the pertinent barren scrub (aqueous HCl of the same concentration as initially used). The resultant *K* values were all greater than 500. These "anomalous" reverse *K* values were shown to be due to hydrolysis products of TBP.

Concurrently, in U. S. Atomic Energy-sponsored investigations, certain interferences in the TBP vs. HNO_3 metals separation process were shown to be due to hydrolysis products of TBP.

Stewart and Hicks (*269*) first reported, in a U.S.A.E.C. classified document issued in 1950 and declassified in 1957, the extraction of U(VI) by dibutyl ether solutions of dibutyl phosphoric acid, $(n\text{-}C_4H_9O)_2PO(OH)$ (HDBP), and of monobutyl phosphoric acid, $(n\text{-}C_4H_9O)PO(OH)_2$ (H_2MBP), from an aqueous mineral acid phase. From their extractant dependency and hydrogen ion dependency data and the fact that *K* did not vary as the nitrate concentration varied from zero to 0.5 *M*, in a 0.5 *M* constant ionic strength nitrate plus perchlorate medium, they concluded that the extraction with HDBP could be represented as

$$UO_2^{+2} + 2HY \rightleftharpoons UO_2Y_2 + 2H^+ \tag{41}$$

where HY represents HDBP, and the charged species are in the aqueous phase and the uncharged species in the organic phase. Assuming HDBP to be dimeric in dibutyl ether, Eq. (41) should be rewritten as:

$$UO_2^{+2} + 2(HY)_2 \rightleftharpoons UO_2(HY_2)_2 + 2H^+ \tag{42}$$

(Although no state of aggregation study has been reported for dibutyl ether as a diluent, it seems probable, on the basis of diisopropyl ether data (*77*), that HDBP is dimeric in this diluent.)

The method of mutually separating mono- and diacidic esters of phosphoric acid reported by Stewart and Hicks (*269*) and Stewart and Crandall (*268*), based upon distribution between two mutually immiscible liquid phases such as dibutyl ether and diethylene glycol, has proved invaluable in obtaining extractants of the required purity.

Scadden and Ballou (*238*) reported the use of a dibutyl ether solution of mixed mono- and dibutyl phosphoric acids in the isolation of zirconium and niobium from other fission products, and in the separation of the "yttrium group" lanthanides from the "lanthanum group" lanthanides.

Dyrssen *et al.* (*68*, *74*, *77*) have shown HDBP to be dimeric in *n*-hexane, carbon tetrachloride, chloroform, isopropyl ether, methyl isobutyl ketone, and TBP, and to be essentially monomeric in methyl isobutyl carbinol. Peppard *et al.* (*200*) have shown di-2-ethyl hexyl phosphoric acid, $(2\text{-}C_2H_5\cdot C_6H_{12}O)_2PO(OH)$ (HDEHP), to be dimeric and mono-2-ethyl hexyl phosphoric acid, $(2\text{-}C_2H_5\cdot C_6H_{12}O)PO(OH)_2$ (H_2MEHP), to be polymeric in dry benzene. They further reported both HDEHP and H_2MEHP to be monomeric in methyl alcohol and dimeric in acetone, and H_2MEHP to be hexameric in benzene (*82*). Baes (*11*) reported HDEHP as primarily dimeric (partially trimeric) in *n*-octane.

Peppard *et al.* (*82*) found several members of Class 3B, (GO)(G)PO(OH), to be dimeric in benzene. Kosolapoff and Powell (*155*) reported $(G)_2PO(OH)$, representative of Class 4B, to be dimeric in naphthalene; they also reported (G)(H)PO(OH), Class 7B, to be trimers and $(G)PO(OH)_2$, Class 3C, to be polymers approximating hexamers in naphthalene.

Generalizing from the examples of Table VI and the reported states of aggregation, letting X represent G or GO, the compounds $(X)_2PO(OH)$ tend to approximate dimers in all diluents except alcohols, in which they are monomers; the compounds $(X)PO(OH)_2$ tend to approximate (or exceed) hexamers in hydrocarbons, etc., dimers in ketones, and monomers in alcohols. It must be realized that these generalizations are based upon a very modest collection of data.

The dimers of $(X)_2PO(OH)$ are considered to be based upon the PO(OH) function, by analogy with the dimers of carboxylic acids based upon the CO(OH) function. The bonding is pictured as

$$\text{(1)O—P—O—H} \cdots \text{O—P—O—H(8)}$$

(V)

with the O(1) joined in similar fashion to the H(8) to form an eight-membered ring which may be shown, without distinction as to the origin of the H atoms, for the molecule as:

$$(X)_2P(—O—H—O)_2P(X)_2$$
(VI)

Perhaps the monomer, in alcohol, should be postulated similarly as

$$(X)_2P(—O—H—O)_2(H)(R)_2$$
(VII)

assuming the formula $X_2PO(OH)\cdot 2ROH$.

2. *Monoacidic Extractants, $(X)_2PO(OH)$*

The studies of HDBP by Stewart and Hicks (*269*) and Scadden and Ballou (*238*) were followed by an investigation of di-2-ethyl hexyl phosphoric acid, $(2\text{-}C_2H_5\cdot C_6H_{12}O)_2PO(OH)$ (HDEHP), as an extractant for lanthanides(III) by Peppard *et al.* (*217*). The $\log K$ vs. Z curve in the 0.75 F HDEHP (toluene) vs. 0.5 M HCl system was represented as a straight line of slope 0.40, i.e., average separation factor for adjacent members of 2.5 (cf. Fig. 3). Their representation of the extraction is in error, since they were unaware of the dimeric nature of HDEHP. In a later paper (*206*) they represent the extraction as

$$M^{+3} + 3(HY)_2 \rightleftharpoons M(HY_2)_3 + 3H^+ \tag{43}$$

analogous to Eq. (42).

In both Eq. (42) and Eq. (43) and in others to be discussed, HY_2^- is to be considered equivalent to $Y^-\cdot HY$, so that $M(HY_2)_3$, $M(Y)(HY_2)_2(HY)$, $MY_2(HY_2)(HY)_2$, and $MY_3(HY)_3$ are alternate representations of the extracted species. The choice of HY_2^- in the formula as written is based upon the supposition, not in any way proved, that mono-ionized dimers are present in the extracted entity.

In a similar study of HDBP in dibutyl ether, Duyckaerts *et al.* (*63*) reported the separation factor for adjacent rare earths to be 2.6 in the "heavy" region and 1.95 in the "light." The plots are presented in a later paper (*62*). They found the extraction to be represented by Eq. (43) (*63*). The same extraction stoichiometry for Eu(III) in HDBP (diluent) vs. HNO_3 was found by Dyrssen and Liem (*78*) for *n*-hexane, carbon tetrachloride, chloroform, and diisopropyl ether as diluent. In methyl isobutyl carbinol, in which the HDBP is primarily monomeric, they postulated two extracted entities, MY_3 and $MY_3(HY)_3$, the latter being an alternative representation of $M(HY_2)_3$, and suggested that the former is dominant at low concentrations of extractant. Dyrssen (*67*) also showed the extraction of Y(III) from HNO_3 into a chloroform solution of HDBP to follow Eq. (43).

From the reports of Dyrssen and Krasovec (*75*) on HDBP vs. aqueous perchlorate, Baes *et al.* (*13*) on HDEHP vs. aqueous perchlorate, Sato

(*236*) on HDEHP vs. aqueous sulfate, and Peppard *et al.* (*212*) on HDEHP vs. aqueous perchlorate, nitrate, and chloride, the extraction of U(VI) in systems employing a nonmonomerizing diluent may be represented by Eq. (42).

Consideration of Eqs. (42–43) suggests the generalized expression

$$M_A^{+p} + p(HY)_{2,O} \rightleftharpoons M(HY_2)_{p,O} + pH_A^+ \tag{44}$$

for the extraction of a cation with charge $+p$, the subscripts A and O referring, respectively, to the equilibrated aqueous and organic phases, and HY, in this instance, representing a Class 2B compound of Table VI, i.e., $(GO)_2PO(OH)$.

However, the K for the extraction of Th(IV) into a toluene solution of di[*p*-(1,1,3,3-tetramethyl butyl)phenyl] phosphoric acid $(p\text{-}C_8H_{17}\cdot C_6H_4O)_2\text{-}PO(OH)$ (HDOϕP), from aqueous perchlorate, chloride, and nitrate phases is third-power extractant dependent, not fourth-power. The expected inverse fourth-power hydrogen ion dependency is observed (*214*). The extraction is thus represented as

$$Th_A^{+4} + 3(HY)_{2,O} \rightleftharpoons ThY_2(HY_2)_{2,O} + 4H_A^+ \tag{45}$$

without intent to imply a proved structure of the extracted entity, which may be $ThY_4(HY)_2$, etc.

In an otherwise similar system in which HDEHP is the extractant, the extraction of Th(IV) from aqueous perchlorate and chloride phases of low acidity is represented by Eq. (45), but the extraction from an aqueous nitrate phase involves a "mixed complex" (*214*),

$$Th_A^{+4} + X_A^- + 3(HY)_{2,O} \rightleftharpoons Th(X)(HY_2)_{3,O} + 3H_A^+ \tag{46}$$

where $X^- = NO_3^-$.

At 0.1 M H^+ the K for Th(IV) from 1.0 M (HX + NaX) into a toluene solution of HDEHP of fixed concentration is in the approximate ratio 0.3:1:50 for $X = Cl^-$, ClO_4^-, NO_3^-, respectively. (The corresponding ratios in the HDOϕP system are approximately 0.3:1:0.2.)

Presumably in the HDEHP (toluene) vs. aqueous nitrate system the extraction stoichiometries represented by Eq. (45) and Eq. (46) are both involved, but the latter is dominant throughout the range of hydrogen ion concentrations investigated. The data for the chloride and perchlorate systems in the high concentration of hydrogen ion region are consistent with the postulation of both $ThY_2(HY_2)_2$ and $Th(X)(HY_2)_3$, the dominant extraction being expressed by Eq. (45) in the low acidity region and by Eq. (46) in the high (*214*).

Dyrssen and Liem (*79*) in analogous studies with HDBP report the Th(IV) mixed perchlorate complex and mixed nitrate complex to extract essentially identically.

Dreze and Duyckaerts (*61*) report $Th(NO_3)_2(HY_2)_2$, where HY is di-*n*-butyl phosphoric acid (HDBP), as the extracted species in a benzene solution of HDBP.

In contrast to the *K* for Th(IV) which has an extractant dependency smaller than the charge on the cation, the *K* for Ca(II), Sr(II), and Ba(II) has an extractant dependency greater than the charge on the cation. In the HDEHP (xylene) vs. aqueous chloride system, the extraction of Ca(II) may be represented (*215*) as

$$M_A^{+2} + 3(HY)_{2,O} \rightleftharpoons M(HY_2)_2(HY)_{2,O} + 2H_A^+ \tag{47}$$

recalling that the extracted entity might be written alternatively as $M(Y)(HY_2)(HY)_3$, etc.

Considering the coordination number of Ca(II) to be 6, the extracted entity might be postulated as $M(HY_2)_2(HY)_2$ containing two mono-ionized dimers, each occupying two coordination positions, and two un-ionized monomers, each occupying one, by analogy with the Sr(II) compound, $Sr(oxine)_2(H\ oxine)_2$, reported by Dyrssen (*65*). One difficulty presented by this postulation is that presumably there would be a "free" OH group, i.e., not hydrogen-bonded, on each of these un-ionized monomers. Considering the strong tendency toward hydrogen bond formation by $(X)_2PO(OH)$ (*83*), free OH groups seem unlikely. Perhaps one OH is hydrogen-bonded to the other, as in ROH dimers and trimers. If so, the structure would be formally similar to

$$H[M(HY_2)_3]$$

(VIII)

in which the "unique" H is coordinated to a specific O which then has a coordination number of 3.

This postulation must be modified in order to explain the 2.5-power extractant dependency of the *K* for Ca(II) and for Sr(II) in the HDOΦP (xylene) vs. aqueous chloride system (*215*):

$$M_A^{+2} + 2.5(HY)_{2,O} \rightleftharpoons M(HY_2)_2(HY)_O + 2H_A^+ \tag{48}$$

One possibility is that the $M(HY_2)_2(HY)$ contains 1 mole of H_2O, the formulation then being equivalent to

$$H[M(HY_2)_2(Y)(H_2O)]$$

(IX)

by analogy with compound VIII, it being understood again that the "unique" H is coordinated to one of the O atoms. In this system, the *K* for Ba(II) is 3.0-power extractant dependent (*215*).

In the same system, Eu(II) is extracted with a third-power extractant dependency, the extraction being represented by Eq. (47) (*201*). The extraction of Eu(III) is also third-power extractant dependent, being represented by Eq. (43) (*206*).

Mason *et al.* (*176*) studied the extraction of M^{+2}, M^{+3}, and Th^{+4} in the HDEHP (*n*-decyl alcohol) vs. aqueous chloride system. Since this extractant in alcohol solution is primarily monomeric, extractant dependencies less than the charge on the cation should be impossible unless the extracted species contains chloride. The extractant dependency of the *K* for Th(IV) was analyzed as a composite of fourth-power and sixth-power, the extraction being represented as:

$$Th_A^{+4} + 4HY_O \rightleftharpoons ThY_{4,O} + 4H_A^+ \tag{49}$$

$$Th_A^{+4} + 6HY_O \rightleftharpoons ThY_2(HY_2)_{2,O} + 4H_A^+ \tag{50}$$

Note that the extractant dependency in Eq. (50) is not twice that of Eq. (49) but twice that found in a "dimer mechanism" extraction, Eq. (45).

Similarly UO_2^{+2} was shown to extract with second-power and fourth-power extractant dependencies and lanthanides(III), Y(III), Sc(III), and Am(III) with third-power and sixth-power extractant dependencies. Both UO_2^{+2} and Ca^{+2} are extracted with second-power and fourth-power extractant dependencies in the HDOϕP (*n*-decyl alcohol) vs. aqueous chloride system (*176*).

Consequently the "monomeric" extraction of U(VI), Ca(II), lanthanides(III), Y(III), Sc(III), and Am(III) may be represented as:

$$M_A^{+p} + pHY_O \rightleftharpoons MY_{p,O} + pH_A^+ \tag{51}$$

$$M^{+p} + 2pHY_O \rightleftharpoons M(HY_2)_p + pH_A^+ \tag{52}$$

It is apparent that the extraction represented by Eq. (52) becomes more important, relative to that represented by Eq. (51), as the concentration of extractant is increased.

If the plot of observed *K* values, as a log *K* vs. log *F* of extractant plot, is analyzed into two straight-line plots corresponding to the extraction represented by Eqs. (51–52), the two straight lines intersect. The point of intersection, in terms of log *F* of extractant, varies with variation in M(III). In the lanthanide(III) series, this point of intersection shifts toward lower concentration of extractant with increasing *Z*.

As a consequence of this difference in operational extractant dependency of the *K* values for two lanthanides(III), the β for the pair of elements is a function of the concentration of extractant. For example, in the HDEHP (*n*-decyl alcohol) vs. 0.025 *M* HCl system, the β for Tm(III) with respect to Eu(III) is approximately 2 at 0.06 *F* HDEHP and approximately 100 at 0.6 *F* HDEHP. Exploitation of such differences in extractant dependencies for two elements in their mutual separation seems promising.

In both the HDOϕP and HDEHP systems, i.e., extractant (in *n*-decyl alcohol) vs. 0.025 *M* HCl, the plot of log *K* vs. *Z* for lanthanides(III) is best represented as separate odd-*Z* and even-*Z* curves.

Class 3B extractants (Table VI), (GO)(G)PO(OH), have not been investigated extensively, but reported studies indicate stoichiometries similar to those found in $(GO)_2PO(OH)$ systems. For example (*209*), the extraction of Pm(III), Cm(III), and Cf(III) is represented by Eq. (43) in the HG[GP] (toluene) vs. aqueous chloride system, where HG[GP] is 2-ethyl hexyl hydrogen 2-ethyl hexyl phosphonate (HEH[EHP], X), 2-ethyl hexyl hydrogen chloromethyl phosphonate (HEH[ClMP], XI), or 2-ethyl hexyl hydrogen phenyl phosphonate (HEH[ϕP], XII):

$(2\text{-}C_2H_5\cdot C_6H_{12}O)(2\text{-}C_2H_5\cdot C_6H_{12})PO(OH)$ (HEH[EHP])
(X)

$(2\text{-}C_2H_5\cdot C_6H_{12}O)(ClCH_2)PO(OH)$ (HEH[ClMP])
(XI)

$(2\text{-}C_2H_5\cdot C_6H_{12}O)(C_6H_5)PO(OH)$ (HEH[ϕP])
(XII)

The HEH[ϕP] (toluene) vs. 1.0 *M* (NaCl + HCl) system has been demonstrated to differentiate in favor of Cf with respect to Cm by a factor of approximately 105 (*209, 210*). This β value of 105 may be compared with that of 47 reported for the HDEHP (toluene) vs. 0.25 *M* HCl system (*205*).

In the 1.0 *F* HEH[ϕP] (toluene) vs. 2.0 *M* HCl system (Fig. 5), the β for a given lanthanide(III) with respect to the adjacent member of lower *Z* is approximately 2.8 (*209*). With respect to β values throughout the lanthanide series, this is the most promising liquid–liquid extraction separations system yet reported.

In Th(IV) experiments with HEH[EHP] (X), extraction of mixed complexes appears to be favored more than in HDEHP systems, the separate extracted species containing one nitrate group, two nitrate groups, one chloride group, and one perchlorate group being reported (*220*).

Like those of Class 3B, extractants of Class 4B, $(G)_2PO(OH)$ (Table VI), have not been investigated in depth. In a study of di-*n*-octyl phosphinic acid, $(n\text{-}C_8H_{17})_2PO(OH)$ (H[DOP]), in benzene solution, the extractant dependency of *K* from an aqueous acidic chloride medium was found to be 2.0-power for U(VI) but 2.5-power, rather than the expected 3.0-power, for Ce(III), Eu(III), Tm(III), Yb(III), Y(III), Am(III), and Cm(III) (*213*). The extraction of U(VI) was found to follow Eq. (42), but that of the M(III) examples was represented as:

$$M_A^{+3} + 2.5(HY)_{2,O} \rightleftharpoons MY(HY_2)_{2,O} + 3H_A^+ \qquad (53)$$

For comparison, it may be noted that the extraction of Eu(III) and Am(III) in the bis(hexoxy-ethyl) phosphoric acid (HDHoEP, XIII) in benzene vs. aqueous perchlorate or chloride system (*208*) is also expressed by Eq. (53). Both H[DOP] (*213*) and HDHoEP (*208*) have been proved dimeric in dry benzene.

$$(n\text{-}C_6H_{13}\text{—O—}C_2H_5\text{—O})_2PO(OH) \qquad \text{(HDHoEP)}$$

(XIII)

Blake *et al.* (*24*) showed the extraction of U(VI) from aqueous sulfate solution into a carbon tetrachloride solution of extractant to be better by a factor approximating 2 for $(G)_2PO(OH)$ as compared with $(GO)_2PO(OH)$, where G is $n\text{-}C_8H_{17}$ or $2\text{-}C_2H_5{\cdot}C_6H_{12}$.

Baes (*10*) has surveyed "The extraction of metallic species by dialkyl phosphoric acids," treating the effects of varying the diluent, varying the G in $(GO)_2PO(OH)$, adding synergists, and varying the ion size and ion charge of the cation to be extracted. Among more restricted reviews pertinent to this discussion are "Some mechanisms of extraction of M(II), (III),(IV),(VI) metals by acidic organophosphorus compounds" (*202*), "Structural aspects of organophosphorus extractants and their metallic complexes as deduced from spectral and molecular weight studies" (*83*), and "Types of acidic organophosphorus extractants and their applications to transuranic separations" (*178*).

"Mutual separation of yttrium-91 and promethium-147 by countercurrent solvent extraction in pulse column" by use of the HDEHP (toluene) vs. aqueous HNO_3 system has been reported by Mandil *et al.* (*165*).

The HDOϕP (toluene) vs. 1.0 *M* ($HX + HClO_4$) system, where X^- is Cl^- or NO_3^-, has been used in determining the stability constant of MX^{+2} in the aqueous phase for La, Ce, Pr, Eu, Tm, Yb, Lu, and Am (*211*).

Blake *et al.* (*24*) reported "relative acidity" data, defined as apparent pH at half-neutralization in 70% ethanol, for a variety of $(X)_2PO(OH)$, where X is G or GO. The respective values reported for $(n\text{-}C_8H_{17}O)_2PO(OH)$ and $(n\text{-}C_8H_{17})_2PO(OH)$ are 2.9 and 5.2, and those for $(2\text{-}C_2H_5{\cdot}C_6H_{12}O)_2\text{-}PO(OH)$ and $(2\text{-}C_2H_5{\cdot}C_6H_{12})_2PO(OH)$ are 3.2 and 5.6. In a system employing carbon tetrachloride as diluent and an aqueous sulfate solution as opposing phase, the phosphinic acid, $(G)_2PO(OH)$, extracted U(VI) with a K approximately twice that found for the dialkyl phosphate, $(GO)_2PO(OH)$.

This small difference in K for U(VI) associated with an apparent acidity difference of approximately 2.3 pK units is surprising. In support of this finding, 2-ethyl hexyl hydrogen 2-ethyl hexyl phosphonate (HEH[EHP], XIV), which would be expected to have a pK between that of the corresponding phosphate and phosphinic acid, has been shown to extract U(VI) with a K approximately twice that shown by HDEHP for aqueous perchlorate, nitrate, or chloride solutions (*212*).

$$(2\text{-}C_2H_5{\cdot}C_6H_{12}O)(2\text{-}C_2H_5{\cdot}C_6H_{12})PO(OH) \qquad \text{(HEH[EHP])}$$

(XIV)

In contrast to U(VI), the M(III) elements reported by Peppard *et al.* (*213*) show a marked decrease in K as C-P bonds replace C-O-P, the order being:

$$(GO)_2PO(OH) > (GO)(G)PO(OH) > (G)_2PO(OH)$$

(XV)

Perhaps a detailed study of K for a variety of elements under a standard set of conditions as a function of the "acidity" of the extractant may furnish a clue concerning the bonding present in the extracted species. Consider the equation

$$K_{obs} = K_S F_{ex}{}^b/[H^+]_A{}^p \tag{54}$$

as relating the observed K, K_{obs}, of M^{+p} as a function of the concentration of extractant, F_{ex}, in the organic phase, expressed in formality units, and the concentration of hydrogen ion in the aqueous phase, $[H^+]_A$. It is evident that if the diluent, ionic strength of the aqueous phase, and the temperature are fixed, then K_S values for a given cation in systems involving different extractants may be compared if both p and b have the same values in each of the systems considered. (Note that p and b may be but are not necessarily equal to each other.)

Such a compilation of K_S values for a number of cations could then be considered as a function of the "acidity" of the extractant in the hope of finding useful correlations. A study of the "Variation of the pK_A of (X)(Y)PO(OH) with X and Y in 75 and 95% ethanol" recently reported (*204*) may prove useful here. The average effect of interposing an oxygen atom between G and P to transform a G-P structure to a G-O-P structure was found to be -1.10 pK units where G is cyclo-hexyl. Therefore the difference to be expected for two such interpositions is -2.20 pK units. Specifically, for $(\text{cyclo-}C_6H_{11}\text{-}O)_2PO(OH)$ and $(\text{cyclo-}C_6H_{11})_2PO(OH)$ the pK values as measured are 3.81 and 5.92 (in 75% ethanol) and 4.43 and 6.64 (in 90% ethanol), the respective pK differences corresponding to interposition of two oxygen atoms being -2.12 and -2.21. These differences may be compared with the value of -2.3 observed by Blake for the *n*-octyl compounds (*24*).

In this pK_A study, Peppard *et al.* (*204*) assigned a values to the groups phenoxy (ϕO), hydrogen (H), cyclo-hexoxy (CHO), phenyl (ϕ), and cyclohexyl (CH) to be used in the pK_A expressions for (X)(Y)PO(OH):

$$pK_A = 2.00 - \sum a, \text{ in } 75\%\ C_2H_5OH \tag{55}$$

$$pK_A = 2.60 - \sum a, \text{ in } 95\%\ C_2H_5OH \tag{56}$$

The values are: ϕO (0.30), H (0.00), CHO (-0.85), ϕ (-1.05), and CH (-1.95).

The difference in measured $\mathrm{p}K_A$ values for (cyclo-$C_6H_{11})_2PO(OH)$ and (cyclo-C_6H_{11})(H)PO(OH) is 2.01 in 75% ethanol and 2.11 in 95% ethanol. Consequently it would be expected that in general an alkyl hydrogen phosphinic acid (Class 7B of Table VI) would be considerably more acidic, perhaps by approximately two pK units, than the corresponding dialkyl phosphinic acid, Class 4B. (Analogously, an aryl hydrogen phosphinic acid might be predicted to be more acidic than the corresponding diaryl phosphinic acid by perhaps one pK unit.)

If it is assumed that increasing acidity, as measured by decreasing $\mathrm{p}K_A$ values, is accompanied by increasing K_S values, as defined by Eq. (54), for M(III) cations, then *n*-octyl hydrogen phosphinic acid, H[(O)(H)P], and 2-ethyl hexyl hydrogen phosphinic acid, H[(EH)(H)P], should be far better extractants than the corresponding dialkyl phosphinic acids.

(n-C_8H_{17})(H)PO(OH) (H[(O)(H)P]
(XVI)

(2-$C_2H_5 \cdot C_6H_6$)(H)PO(OH) (H[(EH)(H)P])
(XVII)

Unpublished investigations in the author's laboratory show that in systems involving H[(O)(H)P], XVI, in benzene vs. aqueous chloride phase, Am(III), Cm(III), and Pm(III) are extracted according to Eq. (43), assuming the extractant to be dimeric. However, the extractant dependency for lanthanides(III) decreases with increasing Z, being 3.0 for Pm, 2.7 for Eu, 2.3 for Tm, and 2.3 for Lu. The hydrogen ion dependencies are all inverse third-power. The variation of extractant dependency with Z is even more noticeable in the system utilizing H[(EH)(H)P], XVII. Here, the power of the extractant dependency is: Ce (2.9), Pm (2.7), Eu (2.6), Tm (2.2), and Lu (2.2). The corresponding actinide values are: Am (2.7) and Cm (2.7).

As a result of the variation of extractant dependence with Z, the dependence being smaller at higher Z, the $\log K$ vs. Z curve for lanthanides(III) is "steeper" in the 0.0187 F extractant vs. 0.100 M HCl system than in the 0.300 F extractant vs. 0.25 M HCl system.

In a 0.10 F extractant (benzene) vs. 0.25 M HCl system, the K for Y(III) in the H[(O)(H)P] system is at least 500 times as great as that in the H[DOP] system. It is therefore imperative that the H[DOP] used in studying tracer-level M(III) elements be scrupulously freed from H[(O)(H)P].

Handley and Dean (*105*) report *O,O'*-dialkyl phosphorodithioc acids, $(RO)_2PS(SH)$, as extractants (in carbon tetrachloride) for metal ions from HCl and H_2SO_4. In this ". . . preliminary survey of the distribution of elements as dialkyl phosphorodithioates into CCl_4 from HCl and H_2SO_4

media . . . ," 42 elements were studied. Stoichiometric parameters were not reported in detail except for Zn(II), for which the K was found to vary directly as the square of the concentration of extractant and inversely as the square of the hydrogen ion concentration.

3. Diacidic Extractants, $(X)PO(OH)_2$

Reported studies of $(X)PO(OH)_2$ compounds, either $(GO)PO(OH)_2$, Class 1C of Table VI, or $(G)PO(OH)_2$, Class 2C, as extractants for metallic cations are few.

Blake *et al.* (*24*) presented extraction data for U(VI) from an aqueous sulfate phase into carbon tetrachloride or kerosene solutions of seven $(GO)PO(OH)_2$ samples. They point out, "In extractions by monoalkyl phosphoric and phosphonic acids, the U(VI) extraction coefficient varies as the first to second power of the extractant concentration. This indicates that the U(VI) extraction complexes contain at least as many organophosphorus groups as the aggregates of the unreacted organophosphoric acid. Since these monoalkyl acids (H_2X) are considerably more associated than the dialkyl acids, this means that the extraction complex cannot be the simple salt UO_2X or $UO_2(HX)_2$, but must contain additional molecules of the extractant."

Peppard *et al.* (*206*) have postulated an "infinite polymer" mode of extraction of lanthanides(III), actinides(III), scandium(III), and yttrium(III) from aqueous mineral acid phases into a toluene solution of mono-2-ethyl hexyl phosphoric acid (H_2MEHP, XVIII). The extraction was expressed as

$$(2\text{-}C_2H_5 \cdot C_6H_{12}O)PO(OH)_2 \qquad (H_2MEHP)$$

(XVIII)

$$M_A^{+p} + (H_2Y)_{x,O} \rightleftharpoons M(H_{2x-p}Y_x)_O + pH_A^+ \tag{57}$$

assuming that x is a large number, i.e., that H_2MEHP is a very large polymer in "wet" toluene, since it was shown that contacting a toluene solution of H_2MEHP with pure water results in the formation of a gel-like solid.

Alternatively, if it is assumed that $x = 6$ in the equilibrated organic phase, i.e., wet toluene, as it is in dry benzene (*82*) and that the extractant is attached to M as mono-ionized dimers, $H_3Y_2^-$, then the extraction may be represented as:

$$M_A^{+p} + (p/3)(H_2Y)_{6,O} \rightleftharpoons M(H_3Y_2)_{p,O} + pH_A^+ \tag{58}$$

In Eq. (57) the indicated extractant dependency is first-power for all values of p, whereas in Eq. (58) it is first-power for M^{+3} but 4/3-power for M^{+4}, such as Th(IV), and 2/3-power for M^{+2}, such as UO_2^{+2} and Ca^{+2}.

Both Eq. (57) and Eq. (58) are consistent with the observed first-power extractant dependencies in the extraction of M(III) cations. However, Eq. (57) is favored, since a highly polymeric form of H_2MEHP in the equilibrated organic phase seems likely.

Although in their report of the extraction of M(III) cations by H_2MEHP in toluene, Peppard *et al.* (*206*) present their hydrogen ion dependency data as pertaining to constant ionic strength in the aqueous phase, this presentation is almost certainly in error.

In an extension of the H_2MEHP work, accompanying an H_2[EHP] study, the *K* values for these M(III) cations were found to have an inverse hydrogen ion dependency slightly in excess of third-power for nonconstant ionic strength conditions, i.e., the aqueous phase containing only HX, the log *K* vs. log $[H^+]$ plot being closely approximated by a straight line. However, in the corresponding 1.0 *M* (HX + NaX) system, the inverse hydrogen ion dependency is much less than third-power. Although these data were obtained with a sample of H_2MEHP different from that used in the reported study, and the reported data may therefore be in error due to the action of unidentified impurities, it seems more likely that nonconstant ionic strength data were mistakenly identified as constant ionic strength data in the preparation of the manuscript.

Equations (57) and (58) should therefore be considered as pertaining to nonconstant ionic strength aqueous phases containing only HX.

In later work with H_2MEHP (XVIII) (in *n*-decyl alcohol) vs. 0.05 *M* HCl, the extraction of Am(III) and Eu(III) by a monomer mechanism was demonstrated (*177*), the extraction being presented as

$$M_A^{+3} + 3(H_2Y)_O \rightleftharpoons M(HY)_{3,O} + 3H_A^+ \qquad (59)$$

with the extractant dependency exceeding third-power in the region beyond 0.3 *F* H_2MEHP.

The variation of *K* value with diluent in this instance is dramatically large, the *K* value for Eu(III) for a 0.1 *F* H_2MEHP (in diluent) vs. 0.05 *M* HCl system being at least 10^5 times greater with toluene as diluent than with *n*-decyl alcohol as diluent.

Warren and Suttle (*291*), working with $(GO)PO(OH)_2$ where G is *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}, *n*-C_6H_{13}, and *n*-C_8H_{17}, in *n*-amyl alcohol as diluent, reported the extraction of Y(III) and La(III) from aqueous HNO_3 as

$$M_A^{+3} + 4H_2Y_O \rightleftharpoons HM(HY)_{4,O} + 3H_A^+ \qquad (60)$$

and that of Sc(III) as in Eq. (59).

Their conclusions and those of Mason *et al.* (*177*), although in apparent conflict, are seen to be compatible when it is noted that their Sc data were obtained in the extractant concentration range lower than that employed by Mason *et al.* (*177*), and therefore Eq. (59) is obeyed, but their Y and La data were obtained in the extractant concentration range in which Mason *et al.* (*177*) noted an increasing extractant dependency.

The large diluent effect found in replacing a hydrocarbon by an alcohol has been utilized in returning a cation of otherwise awkwardly high K from a solution of H_2MEHP in hydrocarbon diluent to an aqueous phase, the extract being diluted with 2-ethyl hexanol-1 which serves as an antisynergist or negative synergist (*203*). For example, a solution of H_2MEHP in a diluent such as carbon tetrachloride, chlorobenzene, toluene, or *n*-heptane is contacted with a sample of acidified human urine in analysis for certain M(III), M(IV), and M(VI) radioactive metals. The antisynergistic effect of 2-ethyl hexanol-1 may then be used in effecting the removal to the aqueous phase of M(III), followed by M(VI), followed by M(IV), as the concentration of antisynergist is increased (*203*).

Some of the metals separations possibilities inherent in the H_2MEHP (toluene) vs. aqueous HCl system are shown in Fig. 4. In this system, the K for Np(IV) is approximately first-power dependent upon the concentration of extractant. Therefore dilution of the extract with toluene is without effect in aiding the return of Np to an aqueous phase, since the RK product remains essentially constant. Oxidation to Np(VI) and re-extraction of the element in this state of oxidation are a feasible solution to the problem. A more direct solution, however, is addition of the antisynergist. For example, in the 0.24 F H_2MEHP (toluene) vs. 1.0 M H_2SO_4 system, the K for Np(IV) is 2×10^4. In an otherwise similar system in which the extractant is 0.24 F H_2MEHP + 1.8 F TBP, the K is $\sim$0.15. As an antisynergist the TBP depresses the K for Np(IV) in this system by a factor exceeding 10^5 (*218*).

In the 0.48 F H_2MEHP (toluene) vs. HCl system, the K for Pm(III) is larger than that for Am(III) throughout the range of HCl concentration greater than 2.0 M. In the plot of log K vs. M HCl, the curves for both M(III) elements display a flat minimum in the 5–7 M HCl region. However, to the right of this region the curves diverge. Consequently, although the β for Pm with respect to Am is less than 2 at 2.0 M HCl (*218*), it is approximately 6 at 12.0 M HCl (*178*). At 13.5 M HCl, the β in the same system at 2°C is 20 (*205*).

Baybarz and Leuze (*17*) replaced the aqueous HCl phase by an aqueous 10 M LiCl solution containing HCl and used xylene as the diluent. They reported, "Rare earth elements are extracted from 10 M LiCl solutions (with HCl ranging from 0.5 to 1.0 M) into 0.5 M mono-2-ethyl hexyl orthophosphoric acid in xylene carrier. The americium and curium remain in the lithium chloride solution. Americium is separated from all rare earths, and curium from all rare earths except lanthanum by countercurrent extraction." (Note that their expression 0.5 M H_2MEHP means 0.5 F H_2MEHP.)

Mason and Peppard (*178*) report that in the 0.5 F H_2MEHP (toluene) vs. 10.3 M NH_4CNS system, the respective K values for Pm and Am(III) are 8.3 and 0.163, the β value being 51.

In regard to extraction of metallic cations by solutions of phosphonic acids, Class 2C of Table VI, Peppard and Mason (*202*) state, "A study now in progress in the authors' laboratory of $H_2[EHP]$, $(EH)PO(OH)_2$, shows many similarities but some striking differences with respect to the H_2MEHP studies. For example, hydrogen ion dependencies in the chloride and perchlorate systems (nonconstant ionic strength, utilizing only HX) are parallel, being slightly greater than third-power for lanthanides(III) and actinides(III). However, the extractant dependency for lanthanides(III) and actinides(III) in the $H_2[EHP]$ system employing toluene as carrier diluent is approximately second-power, not first-power, as with H_2MEHP. The log K vs. Z curve appears similarly unpromising for $H_2[EHP]$, from a separations viewpoint." The detailed study upon which these comments were based has not yet been published.

Rao *et al.* (*230*) have studied the extraction of Am(III), Eu(III), Tm(III), Ca(II), and U(VI) by 2-ethyl hexyl phosphonic acid, $H_2[EHP]$ (XIX), and by H_2MEHP in a dimerizing diluent from aqueous HCl. The diluent was methyl isobutyl ketone.

$$(2\text{-}C_2H_5\cdot C_6H_{12})PO(OH)_2 \qquad (H_2[EHP])$$

(XIX)

The extraction of M(III) by H_2MEHP was presented as

$$M_A^{+3} + 2.5(H_2Y)_{2,O} \rightleftharpoons M(HY)(H_3Y_2)_{2,O} + 3H_A^+ \tag{61}$$

and by $H_2[EHP]$ as

$$M_A^{+3} + 3(H_2Y)_{2,O} \rightleftharpoons M(H_3Y_2)_{3,O} + 3H_A^+ \tag{62}$$

and that of Ca(II) and U(VI) by both H_2MEHP and $H_2[EHP]$ as:

$$M_A^{+2} + 2(H_2Y)_{2,O} \rightleftharpoons M(H_3Y_2)_{2,O} + 2H_A^+ \tag{63}$$

Both systems show some promise for application to mutual separations of lanthanides(III) in the Ho-Lu region.

B. DINUCLEAR EXTRACTANTS

The acidic dinuclear compounds,

$$(HO)(X)(O)P{-}Y{-}P(O)(X)(OH) \qquad\qquad (X)_2(O)P{-}Y{-}P(O)(OH)_2$$

(XX) (XXI)

$$(X)_2(O)P{-}Y{-}P(O)(X)(OH)$$

(XXII)

where Y is an alkyl chain or an oxygen atom, are considered together. It may be noted that the dinuclear compounds, XX and XXI, are mutually isomeric. Of these, only XX has been reported as an extractant, and no extractions by the monoacidic compound XXII have been noted.

Grdenic and Korpar (*100*) reported the extraction of U(IV) into a ligroin solution of symmetrical di-*n*-octyl pyrophosphoric acid, a specific example of XX with Y = *O* and X = $n\text{-}C_8H_{17}O$, from aqueous sulfuric acid solution. They concluded that the extractable species is a complex compound defined by the formula $U(Oct_2HP_2O_7)_4$, or, if XX is symbolized by H_2Z, as $U(HZ)_4$.

Gorican and Grdenic (*98*) then studied symmetrical di-*n*-octyl methylene diphosphonate, an example of XX, with Y = CH_2 and X = $n\text{-}C_8H_{17}O$, stating, "Although dioctyl dihydrogen pyrophosphate can be used as a complex-forming agent in liquid-liquid extraction of uranium, it has the serious inconvenience of being easily hydrolyzed by the acid aqueous phase." For M(IV) = U, Th, Zr, or Ce in the quadrivalent state, they reported the extractable species as $H_4[MZ_4]$, which may be considered equivalent to $M[HZ]_4$, where H_2Z represents un-ionized XX. They also isolated Na_4ThZ_4, where the X in XX was C_2H_5O.

Grdenic and Jagodic (*99*) in a study of "Separation of germanium from arsenic by solvent extraction with dioctyl methylene bisphosphonic acid" suggest the formulation of the extracted germanium species as $H_2[GeZ_3]$ and that of a mixed sodium-germanium compound as $Na_2[GeZ_3]$, where H_2Z represents XX. With excess $GeCl_4$ a gelatinous precipitate, "probably a polymer" (*99*), with a composition corresponding to GeZ_2 was formed.

In the absence of data concerning the state of aggregation of H_2Z and of extractant dependency data, expressions for the extractions discussed cannot be written.

VI. Systems Involving Sulfonic Acids, $(G)SO_2(OH)$, as Extractants

Reported studies of $(G)SO_2(OH)$ compounds, where G is a generalized organic group attached directly to the sulfur atom, as extractants for metallic cations are few.

Boyd and Lindenbaum (*28*), in discussing liquid-liquid extraction systems from the ion-exchange viewpoint, considered solutions of di-2-ethyl hexyl phosphoric acid (HDEHP) and of dinonyl naphthalene sulfonic acid, later symbolized by White *et al.* (*294*) as HD (XXIII), as respective analogs of weak-acid and strong-acid resinous cation exchangers.

$$(C_9H_{19})_2C_{10}H_5SO_2(OH) \qquad (HD)$$
(XXIII)

White *et al.* (*294*), employing a *n*-heptane solution of HD vs. aqueous perchloric acid system, found the extraction of Co(II), Zn(II), Mn(II), Fe(III), and In(III) to be represented as:

$$M_A^{+p} + (HD)_{x,O} \rightleftharpoons M(H_{x-p}D_x)_O + pH_A^+ \qquad (64)$$

Note the similarity of Eq. (64) to Eq. (57), which is one representation of the extraction of M^{+p} by H_2MEHP. Both H_2MEHP and HD are assumed to be highly polymeric in these interpretations. Note also that Eq. (64) pertains to aqueous $HClO_4$, not to ($HClO_4 + NaClO_4$) of constant ionic strength.

Ishimori *et al.* (*132*), using dodecyl benzene sulfonic acid (DBSA) as the extractant in a diluent composed of diethyl ether and ethyl acetate (1:1), reported the extraction of M^+, M^{+2}, and M^{+3} from mineral acids to be represented as

n-$C_{12}H_{25}{\cdot}C_6H_4SO_2(OH)$ (DBSA)(HA)
(XXIV)

$$M_A^+ + (HA)_{2,O} \rightleftharpoons M(HA_2)_O + H_A^+ \qquad (65)$$

$$M_A^{+2} + 2(HA)_{2,O} \rightleftharpoons M(HA_2)_{2,O} + 2H_A^+ \qquad (66)$$

$$M_A^{+3} + 2(HA)_{2,O} \rightleftharpoons MA_2(HA_2)_O + 3H_A^+ \qquad (67)$$

assuming the extractant to be dimeric in the organic phase.

The assumptions of polymers in *n*-heptane by White *et al.* (*294*), and of dimers in a diethyl ether–ethyl acetate diluent by Ishimori *et al.* (*132*), correspond roughly to the previously discussed assumptions that H_2MEHP is highly polymeric in wet toluene but dimeric in methyl isobutyl ketone.

The dodecyl benzene sulfonic acid (DBSA) study was extended by Ishimori *et al.* (*133*) to include approximately 60 elements, the extraction system being a 3% DBSA solution in a 1:1 diethyl ether–ethyl acetate mixture vs. aqueous HCl.

Using DBSA in (1:1) diethyl ether–ethyl acetate vs. aqueous HCl, HNO_3, and $HClO_4$, Nakamura (*193*) studied the extraction of Np(IV), (V), and (VI) and compared the results with those for Th(IV), Pa(V), and U(VI). He concluded, "To sum up, the ionic charges of Np(IV), (V), and (VI) were shown to be +4, +1, and +2, and the chemical species in dilute acid solutions are supposed to be Np^{+4}, NpO_2^+, and NpO_2^{+2}. A dissimilarity was recognized between Np(V) and Pa(V)."

VII. Systems Involving Amines and Amine Oxides as Extractants

A. General

In 1948 Smith and Page (*260*) reported their study of "The acid-binding properties of long-chain aliphatic amines." They considered the system of amine in hydrocarbon diluent vs. an immiscible aqueous phase as analogous to a resinous anion exchanger vs. an aqueous phase, and demonstrated the mutual separation of hydrohalic acid and glutamic acid, the former reporting to the amine phase.

In his investigation "Long-chain amines, versatile acid extractants," Moore (*179*) suggests, "The acid-binding properties of these bases depend on the fact that their salts with acids are almost insoluble in water, but readily soluble in organic solvents such as chloroform. In its simplest form the reaction is thought to be as follows:

$$R_3N + HA \rightleftharpoons R_3N{\cdot}HA \qquad (68)$$

where R = a long chain aliphatic or aromatic group, and A = the anion of either a simple acid or a complex metal acid, such as $FeCl_4^-$."

In 1952 Leddicotte and Moore (*158*) reported "A new solvent extraction method for the separation of niobium and tantalum," stating, "We wish to make a preliminary report of the separation of niobium and tantalum by a new solvent extraction technique. It has been found that niobium may be extracted essentially quantitatively from strong hydrochloric acid with a solution of methyldioctylamine in xylene. Under these conditions the extraction of tantalum appears to be negligible. The niobium may then be 'stripped' from the organic phase with nitric acid, sulfuric acid or dilute hydrochloric acid."

With this report, the currently rapidly expanding field of extraction of metals into an amine solution from an aqueous solution of a mineral acid and/or its salt, or of a carboxylic acid and/or its salt, was opened.

The stoichiometry of extraction by amine oxides is considered to resemble that of extraction by amines very closely.

B. Amines and Amine Oxides

In an extension of the Leddicotte and Moore (*158*) work, Ellenburg *et al.* (*80*) in 1954 demonstrated a β for Nb(V) with respect to Ta(V) of 3.4×10^4 for the system 8% tribenzylamine (XXV) in methylene chloride

$$(C_6H_5CH_2)_3N \qquad (TBA)$$
(XXV)

vs. 11 *M* HCl, the respective *K* values being 80.50 and 2.3×10^{-3}. In a system involving the same organic phase but 4.5 *M* H_2SO_4, the β was 1.9×10^2, the respective *K* values being 0.58 and 3×10^{-3}.

Moore (*180*) followed in 1958 with the paper, "Liquid-liquid extraction of uranium and plutonium from hydrochloric acid solution with triisooctylamine." He pointed out, "Inasmuch as thorium does not form anionic complexes with the chloride ion, it was reasoned that the extraction of anionic uranyl complexes from hydrochloric acid solutions would result in a clean separation of these two elements."

He reported that the *K* values for Th(IV) and U(VI) in the 5% triisooctylamine in xylene vs. 6 *M* HCl system were respectively 1×10^2 and

$\sim 1 \times 10^{-2}$, adding that Sr(II), lanthanides(III), Am(III), and Cm(III) did not extract appreciably, whereas "Those elements which form anionic complexes at the particular hydrochloric acid concentration used for the extraction of uranium would, of course, extract also."

His observation that triisooctylamine-xylene solution, previously saturated with hydrochloric acid, extracted U(VI) at least as efficiently as did the untreated amine was of far-reaching consequence, since it led to the investigation of solutions of amine hydrochloride vs. aqueous LiCl. These latter systems show great promise in actinide-lanthanide separations.

The paper "Solvent extraction with alkyl amines" by Coleman *et al.* (*45*) treats the "control of extraction by amine structure," one example being "Whereas rare earth sulfates are extracted only by primary amines . . . , the nitrates are extracted only by tertiary amines."

The extraction isotherms for U(VI) in the amine (in aromatic diluent) vs. an aqueous sulfate phase indicated a limiting association of each uranium atom with 4–6 formula weights of amine. But the K of U(VI) was approximately first-power. Coleman *et al.* (*45*) suggested, "The obvious hypothesis to account for this is that the amine salts associate into aggregates, which remain in stable colloidal dispersion but in effect constitute a separate phase of nearly constant composition. However, direct evaluation of the average molecular weights . . . shows that not all of the amine salts concerned are aggregated, and hence the explanation cannot be quite so simple."

Keder (*142*) considers the hydrochloride of tri-*n*-octylamine (XXVI)

$$(n\text{-}C_8H_{17})_3N \qquad (\text{TOA})$$

(XXVI)

as monomeric in wet xylene when he represents the extraction of M^{+p} in the tri-*n*-octylamine in xylene vs. aqueous HCl system as:

$$M^{+p} + pA^- + nR_3NH{\cdot}A \rightleftharpoons (R_3NH)_nMA_{n+p} \tag{69}$$

From a study of K vs. vol% TOA in xylene, he concludes that $n = 2$ for U, Np, and Pu in both the tetravalent and hexavalent states, the complex anions in the extracted species presumably being MCl_6^{-2} and $MO_2Cl_4^{-2}$, respectively.

Similarly, Wilson and Keder (*297*) conclude that U(IV), which is extracted from 4 M HNO_3 by TOA in xylene with a second-power extractant dependency, is extracted as $U(NO_3)_6^{-2}$.

The question of the state of aggregation of the amine salt in the organic phase is an important one currently under investigation in a number of laboratories. Keder and Wilson (*144*), quoting the work of Högfeldt *et al.* (*115*) on polymers of the type $(TLA{\cdot}HNO_3)_i$ found in solutions of trilaurylamine (XXVII), state, "In *m*-xylene the degree of aggregation found is small, but in *n*-octane solutions the aggregates are perhaps a factor of ten higher."

$(n\text{-}C_{12}H_{25})_3N$ (TLA)
(XXVII)

If the state of aggregation of the amine salt is strongly dependent upon the nature of the diluent, then an extraction stoichiometry, as deduced from extraction dependency data, for a given metal in an otherwise fixed system may be expected to vary with the diluent employed. This important point must be kept in mind when considering reported stoichiometries which appear to be in mutual conflict. An example is noted by Keder *et al.* (*143*), who state, ". . . the amine dependence of extraction of U(VI) from 4 *M* HNO_3 by TOA-nitrobenzene solutions is greatly different from that by TOA-xylene solutions."

Duyckaerts *et al.* (*64*), studying TLA·HCl, the hydrochloride of XXVII, in benzene and toluene, concluded, "The amine salt exists partially in an associated form." However, the assumption of monomeric TLA·HCl does not lead to appreciable error, the authors concluding from their study of actinides(III), "The extraction coefficients of actinides increase with the second power of amine salt concentration in the organic phase which means that the complex contains two molecules of amine per metal atom."

The extraction of lanthanides(III) and actinides(III), in a toluene solution of the hydrochloride of TLA (XXVII) vs. an aqueous chloride solution, has been interpreted by Müller *et al.* (*191*) as equivalent to

$$M^{+3} + 3Cl^- + 2R_3N{\cdot}HCl \rightleftharpoons MCl_3{\cdot}(R_3NHCl)_2 \qquad (70)$$

where the charged species are considered to be in the aqueous phase and the uncharged in the organic.

Without attempting to distinguish between $MCl_3{\cdot}(R_3NHCl)_2$, $(R_3NH)(MCl_4){\cdot}(R_3NHCl)$, and $(R_3NH)_2MCl_5$ as the proper representation of the extracted species in Eq. (70), it may be noted that Eq. (70) is Eq. (69) with $p = 3$ and $n = 2$. It is concluded that, if the tertiary amine is monomeric, the extraction of actinides in the tertiary amine hydrochloride (in diluent) vs. aqueous chloride solution system is second-power dependent upon the concentration of amine salt in the organic phase for M(III), M(IV), and M(VI).

Moore (*183*) first reported the application of amine extractants to the separation of actinides(III) from lanthanides(III), the system being triisooctylamine in xylene vs. a concentrated LiCl plus dilute HCl aqueous solution. In an extension of the study Baybarz *et al.* (*18*), using the hydrochloride of Alamine 336 (a commercial tertiary amine with three straight-chain alkyls, principally C_8H_{17} and $C_{10}H_{21}$, obtained from General

Mills, Inc., Kankakee, Ill.) in diethyl benzene vs. aqueous 10 *F* LiCl solution, showed the group β for actinides(III) with respect to lanthanides(III) to be at least 100. See the (B) curves of Fig. 7.

The comparison of this "anionic" system with a "cationic" system employing a monoacidic phosphorus-based extractant (*209*), the (A) curves presented in Fig. 7, accents the following points:

(1) The lanthanide(III) curves differ greatly in the two systems, the one system showing great promise, the other no promise, for mutual separation of lanthanides.

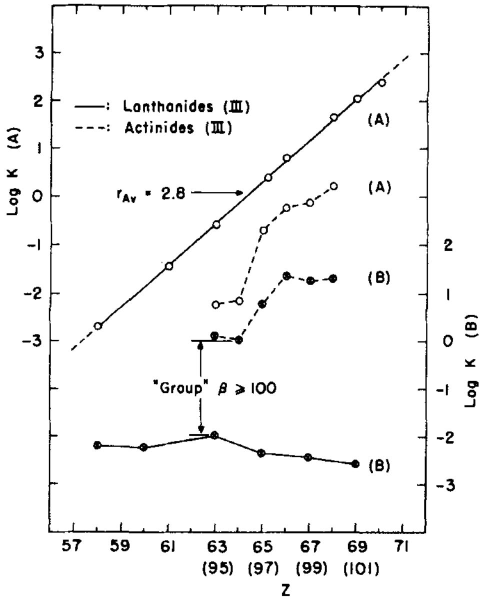


FIG. 7. Variation of log *K* with *Z* for lanthanides(III) and actinides(III) in the systems: (A) 1.0 *F* HEH[ΦP] (in toluene) vs. 2.0 *M* HCl, (B) 0.6 *F* "Alamine 336" hydrochloride (in diethyl benzene) vs. 10.0 *F* LiCl [(A), lanthanides, Peppard *et al.* (*209*); (A), actinides, Baybarz (*16*), "normalized" to benzene diluent; (B), both curves, Baybarz *et al.* (*18*).]

(2) The actinide(III) curves resemble each other somewhat, both showing promise for mutual actinide(III) separations in the *Z* = 96–98 region.

(3) The relative order of extraction of Am and Cm, and of 98 and 99, differs in the two systems.

(4) As plotted, the relative positions of actinide and lanthanide curves differ in the two systems.

(5) The concept of group β is meaningless in considering the (A) curves, since for each actinide there is one or more lanthanides with a nearly identical K, whereas the group β for the (B) curves is at least 100.

Baybarz *et al.* (*18*) reported the K values for M(III) to be directly proportional to the square of the amine hydrochloride concentration in the organic phase and to the 17th power of the LiCl concentration in the aqueous phase and inversely proportional to the 1.3–2.0 power of the acid concentration in the aqueous phase.

In studying the effect of diluent in the 0.5 F triisooctylamine hydrochloride (diluent) vs. 8 N LiCl + 2 N $AlCl_3$ system, they found the respective K values for Am(III) to be 0.27, 0.45, 0.65, 1.35, and 1.80 for benzene, toluene, xylene, diethyl benzene, and diisopropyl benzene. With carbon tetrachloride as diluent the K was less than 0.001.

A far-ranging study of the diluent effect in such systems has been reported by Smulek and Siekierski (*261*) in their paper, "The influence of diluent on the extraction of iron(III) from hydrochloric acid solutions by tertiary amines."

Baybarz *et al.* (*18*) describe a process, based upon the tertiary amine hydrochloride (diluent) vs. LiCl system, for recovery of transplutonium elements, summarizing, "The flowsheet has been tested in batch countercurrent extraction and in mini mixer-settlers with tracer-level runs. With 6 extraction and 6 scrub stages an americium recovery of 99.99% with a rare earth decontamination factor of $>10^4$ was consistently achieved."

In a paper titled "Application of amine and phosphonate extractants to transplutonium element production," Leuze *et al.* (*160*) discuss a production-scale separations scheme in which the two systems presented in Fig. 7 are integrated into a composite process.

Extraction by a tertiary amine (in diluent) from an aqueous nitrate solution has been reported by Sato (*237*), Lloyd and Mason (*161*), Baroncelli *et al.* (*14*), Verstegen (*282*), and Vdovenko *et al.* (*280*) for U(VI); by Wilson (*296*) for Pu(IV); and by Verstegen (*282*) for Cu(II), Cd(II), Fe(III), and Th(IV).

The extraction of oxalato complexes of Ni(II), Co(II), Co(III), and Fe(III) by long-chain alkyl amines has been investigated by Bryan and Good (*31*). The extraction of Co(III) and of Fe(III) was represented as:

$$3R_3NHA + M(C_2O_4)_3^{-3} \rightleftharpoons (R_3NH)_3[M(C_2O_4)_3] + 3A^- \qquad (71)$$

Moore (*181*) considered the extraction of U(VI) from an aqueous acetate solution into a xylene solution of triisooctylamine to be equivalent to:

$$R_3N + H[UO_2(OAc)_3] \rightleftharpoons (R_3NH)[UO_2(OAc)_3] \qquad (72)$$

The extraction of Pu(IV) from an aqueous H_2SO_4 solution by TOA (XXVI) in carbon tetrachloride was represented by Shevchenko and Zhdanov (*249*) as:

$$(R_3NH)_2SO_4 + Pu^{+4} + 2SO_4^{-2} \rightleftharpoons (R_3NH)_2Pu(SO_4)_2 \qquad (73)$$

$$2R_3NH_2SO_4 + Pu^{+4} + 2SO_4^{-2} \rightleftharpoons (R_3NH)_2Pu(SO_4)_2 + 2H^+ + SO_4^{-2} \qquad (74)$$

Vdovenko *et al.* (*281*) in a similar study employing a primary amine (a mixture of C_7 to C_9 aliphatic amines) considered the extraction of Pu(IV) as equivalent to:

$$2(RNH_3)_2SO_4 + Pu(SO_4)_2 \rightleftharpoons (RNH_3)_4Pu(SO_4)_4 \qquad (75)$$

Wilson *et al.* (*295*) in their paper, "Solvent extraction with quaternary ammonium halides," liken the extraction from concentrated hydrochloric acid to anion exchange, on a resinous exchanger, in the same aqueous medium. They summarize, "A comparison of the characteristic curves of all the metals studied in this paper . . . with those studied by Kraus *et al.* suggests that the mechanism of distribution by solvent extraction with quaternary ammonium halides is similar to the mechanism of distribution by elution chromatography with anion exchange resins. These quaternary ammonium halides can be called 'liquid anion exchangers.' Also, qualitative predictions about separations in one system should apply to the other system." (The Kraus (*156*) study referred to is the paper "Anion exchange studies of the fission products.") Good *et al.* (*97*) also consider such extractions as occurring through "liquid anion exchange."

Maeck *et al.* (*163*) made a survey study of the extraction of 57 metallic ions by three quaternary amines, tetrapropyl, tetrabutyl, and tetrahexyl, in methyl isobutyl ketone diluent from five aqueous media, HNO_3, H_2SO_4, HF, HCl, and NaOH. The data should prove useful in the derivation of analytical separations schemes.

Similar survey studies have been made by Ishimori *et al.* for tertiary amines (in xylene) vs. HCl systems (*137*), and for tertiary amine (in xylene) vs. H_2SO_4 systems (*130*).

Kennedy and Perkins (*147*) found a tertiary amine oxide, Alamine 336 oxide, to differ only marginally from the corresponding tertiary amine, Alamine 336, in extraction behavior with respect to U(VI). The system was extractant in dibutyl carbitol (DBC) vs. HNO_3.

Outstanding general reviews in the field are "High molecular weight amines, versatile modern extractants" by Moore (*184*), "Amine extraction in reprocessing" by Coleman (*43*), and "Recent uses of liquid ion exchangers in inorganic analysis" by Green (*101*).

The needs of the nuclear chemist with vexing separations problems are more specifically met by "Liquid-liquid extraction with high-molecular-weight amines" by Moore (*182*).

VIII. Miscellaneous Systems

A. ORGANIC EXTRACTANT (IN DILUENT) VS. FUSED SALT

The observation by Gruen *et al.* (*102*), that certain transition metal ions including Co(II), Fe(III), Nd(III), and U(VI) may be extracted nearly quantitatively from fused $LiNO_3$-KNO_3 eutectic at 150°C into undiluted tri-*n*-butyl phosphate (TBP), appears to be the first literature reference to a system composed of organic extractant vs. fused salt. In an extension of this study, Isaac *et al.* (*128*) used a mixture of polyphenyls as carrier diluent for the TBP extractant.

Isaac *et al.* (*128*) report the dependence of K upon the concentration of TBP in the organic phase to be second-power for Li(I), Co(II), and U(VI) and third-power for Nd(III), Eu(III), Am(III), and Cm(III). It was found difficult to operate the system with an acceptable material balance with respect to the tracer metal ion under investigation, the authors stating, ". . . all the distribution coefficients listed . . . were determined using concentrations of metal ions in the range 10^{-3} M or with tracer concentrations supported by a suitable carrier. Carriers were found to be necessary to maintain tracer quantities of any of the elements investigated in the molten salt solutions. A reaction between the molten $LiNO_3$-KNO_3 phase and the Pyrex container was postulated to account for the lack of material balances when tracer quantities of metal ions were used without carrier. Different container materials such as quartz, Teflon, and stainless steel were tried, without significantly changing the results obtained with Pyrex. . . . The best results were obtained when a Pyrex tube, which had been contacted two or three times with the molten salt phase, was employed with radioactive tracer."

They report a separation factor, β, of 3.2 for Cm(III) with respect to Am(III), pointing out that it "is the best ever found in liquid-liquid extractions." It will be recalled (from Section III,D) that the β for this pair is usually less than 2. A value of 3.2 therefore seems excitingly large.

However, it should be noted that their data in a system involving 1.4% by weight of NH_4NO_3 in the eutectic are inconsistent with this value, the β apparently being less than unity. (If the K for Cm in their Table IV is "normalized" to 0.084 M free TBP, on the assumption of a third-power TBP dependence, so that it may be compared with that for Am, the respective Cm and Am values are 9.3 and 10.3, corresponding to a β value of 0.90.) The data of their Table VI are also inconsistent with a Cm(III)/

Am(III) β value of 3.2, but this is presumably due to errors in the table, specifically in the Eu(III)/Am(III) β values.

Considering the acknowledged material balance difficulties encountered in the study, a β value based upon Cm and Am *K* values determined in separate experiments, not involving a normalizing element, must be considered suspect.

If Eu(III) had been present in both the Cm(III) and Am(III) experiments, then if the two *K* values for Eu were nearly identical the ratio of the normalized Cm and Am *K* values should be reasonably accurate. Note that Cm and Am are α-active and Eu β-active, so that the radiometric assays are readily made.

Another approach is the determination of *K* values, through α pulse analysis, of Cm and Am simultaneously present. A β value thus determined in a single experiment is directly applicable to separations calculations.

B. PARTITION CHROMATOGRAPHY

1. *Neutral Phosphorus-Based Stationary Phase*

Application of partition chromatography to the mutual separation of metals appears to date from the publication in 1959 of a paper by Siekierski and Kotlinska (*256*), titled "Separation of mixtures of zirconium and niobium by reversed-phase partition chromatography." The authors present the rationale, "An extraction technique which allows for separating substances having similar chemical properties is often used for separating mixtures of inorganic cations. But in the case where the distribution constants differ only slightly, however, the extraction process must be repeated through quite a few runs on the countercurrent principle using a series of separatory funnels, for example, or an extraction tower. These methods are not very convenient, so that the ion-exchange technique is most often resorted to under laboratory conditions. The merits of extraction and of the chromatographic technique are combined in partition chromatography, particularly in reversed-phase partition chromatography, where the organic solvent phase is the stationary phase."

Using tributyl phosphate (TBP) adsorbed on "siliconated silica gel" as the stationary phase and aqueous nitric acid as eluting agent, they demonstrated the mutual separation of Nb and Zr, Nb appearing first. Although the Nb fraction was purified acceptably well, the tailing of Nb resulted in a Zr product of poor grade. This difficulty was eliminated through use of a nitric acid eluting agent containing H_2O_2, the Nb tailing being eliminated.

The authors conclude, "Separation of a mixture of cations having similar chemical properties by means of partition chromatography using

TBP as the stationary phase is thus entirely within the realm of possibility. Since many cations in the form of different salts (nitrates, chlorides, bromides) are extracted with the aid of TBP, it may be anticipated that the technique described above will prove to be of more extended value. At the present time, studies are in progress in our laboratory on the application of this technique to the separation of rare earths."

Siekierski and Fidelis (*255*) followed in 1960 with the paper "Separation of some rare earths by reversed-phase partition chromatography," describing the use of TBP as the stationary phase and aqueous HNO_3 as the mobile phase. They state, ". . . reversed-phase partition chromatography in the system TBP-HNO_3 may be successfully applied to the separation of small quantities of some rare earths. It is possible to separate the neighboring rare earths from Pm to Tb, and with a change of acid concentration from Ce to Tb, excluding Pr. It should be emphasized that the effluent from the column in this method does not contain any salts but only HNO_3 which is readily removed by evaporation and that the procedure is not time-consuming and may be carried out at room temperature." They emphasize the very low value of the separation factor for the Eu-Gd pair.

Martynenko *et al.* (*175*) in 1959 reported "Chromatographic separation of rare earth elements by means of tributyl phosphate," differing from the preceding techniques in that a TBP solution of rare earth nitrates was fed to a column of particulate silica gel and followed by TBP as eluting agent.

Fidelis and Siekierski (*84*) in 1961 showed the applicability of the TBP (stationary phase) vs. HNO_3 (mobile phase) system to the separation of heavy rare earths, demonstrating the mutual separation of all of the members Gd-Lu by elution with 11.5 M HNO_3. (The position of Y was between Er and Tm.) They calculate separation factors of pairs of neighboring members with 12.3 M HNO_3 as eluting agent to be: Tb-Dy (1.5), Dy-Ho (1.33), Ho-Er (1.4), Er-Tm (1.53), Tm-Yb (1.4), and Yb-Lu (1.23). They point out that the factor 1.23 for Yb-Lu is exceptionally small, and that the Yb-Lu pair ". . . plays the same role among the heavy rare earths as the Eu-Gd pair does among the light rare earths."

They also studied the TBP (stationary phase) vs. aqueous HCl (mobile phase) system for the heavy rare earths, reporting separation factors (a) with 11.8 M HCl Er-Tm (1.6), Tm-Yb (1.94), and Yb-Lu (1.48), and (b) with 12.3 M HCl Er-Tm (1.86) and Tm-Yb (2.52). Again the Yb-Lu pair has a smaller separation factor than does the Tm-Yb pair. Note that the value 2.52 for Tm-Yb in the 12.3 M HCl elution is unusually large.

Reasoning ". . . from the fact that scandium is well extracted into TBP from HCl solutions (*216*) and extraction of calcium should be much worse, since there is generally a significant difference in extractability between di- and trivalent cations," Siekierski and Sochacka (*257*) successfully applied the TBP (stationary phase) vs. HCl (mobile phase) to the separation of carrier-free Ca(II) from macro amounts of Sc(III).

Beranová and Novák (*20*), employing a sorbent "formed by swelling the styrene divinyl benzene copolymer in tributyl phosphate solution" and aqueous HNO_3 as eluting agent, studied uranium and the fission products ^{116}Ru, ^{95}Zr-Nb, ^{90}Sr-Y, ^{144}Ce, and ^{137}Cs and concluded that the technique ". . . appears suitable for the decontamination of uranium from the fission products in 5 *M* nitric acid medium."

Cerrai and Testa (*39*) used tri-*n*-octyl phosphine oxide (TOPO) on Whatman No. 1, type CRL/1, chromatographic paper as support and three different mineral acids as eluents. They made a systematic study and reported, "Curves of the R_F values as functions of the acidity of the eluent are given for about fifty metal ions. The acids used were HCl, HNO_3 and H_2SO_4. . . . Generally, the higher the extraction coefficient E_a° of TOPO for a given element at the selected acidity, the lower the R_F value."

Kennedy (*145*) used the solid polymer of triallyl phosphate, $(CH_2{=}CH{-}CH_2O)_3PO$, symbolizing it as $\overline{TAP}$, as adsorbent for uranyl nitrate, cobaltous nitrate, lithium chloride, and ferric chloride from solutions of the salts in acetone, acetone-ether, and alcohol. He points out that the distribution coefficients for these salts between $\overline{TAP}$ and acetone are high, 10–1,000 in favor of the polymer.

2. Acidic Phosphorus-Based Stationary Phase

Pierce and Peck (*225*) observed, "Investigations into the use of alkyl phosphoric acids as metal extractants have shown that there are relatively large differences between the stabilities of the complexes of individual rare earths with di(2-ethylhexyl) orthophosphoric acid (HDEHP), the separation factor for any adjacent pair being about 2.5 (*217*). This figure suggests that it should be feasible to devise a comparatively simple scheme for rare earth separations based on a multi-stage extraction procedure utilizing HDEHP as extractant."

They immobilized the HDEHP on a poly(vinyl chloride/vinyl acetate) copolymer as column packing and used aqueous perchloric acid as eluting agent. At 60°C a mixture of all of the irradiated lanthanides(III) from La to Gd (with the exception of Pm) was separated by gradient elution, the concentration of $HClO_4$ ranging from 0.320 to 0.810 *M*. (The first element to appear in the effluent is La.) The authors conclude, ". . . gradient elution greatly reduced overlap of the elements in the effluent, and permitted a separation to be achieved, even for the europium-gadolinium pair. . . ."

The same authors (*226*) followed with a paper describing the separation of all 15 lanthanides(III) in a similar system employing gradient elution by $HClO_4$ ranging in concentration from 0.195 to 6.87 *M*. They comment, "It can be seen that the elements terbium to lutetium, like the light rare earths, are eluted in the order of increasing atomic number, which is also the order of increasing distribution ratio for the lanthanides, when partitioning between aqueous hydrochloric acid and a solution of HDEHP in toluene, at constant acidity and HDEHP concentration" (*217*).

In two succeeding papers, Pierce and Hobbs (*223*) and Pierce *et al.* (*227*) explore the HDEHP (stationary phase) vs. aqueous $HClO_4$ (mobile phase) in detail.

The reaction between metal ion and column material is considered to be

$$M_A^{+p} + pHL_O \rightleftharpoons ML_{p,O} + pH_A^+ \tag{76}$$

where the subscripts A and O refer to aqueous and solid phases and HL represents HDEHP in this instance.

In terms of the zone migration parameter, R_M, Pierce and Hobbs (*223*) express the reaction as equivalent to

$$R_M = K_c + p \log [HL]_O - n \log [H^+]_A \tag{77}$$

where K_c is a constant characteristic of the specific column employed, and R_M is defined (*15*) as

$$R_M = \log (1/R_F - 1) \tag{78}$$

R_F being the experimentally determined ratio of the rate of movement of the fronts of solute and eluting agent (*40*, *159*, *224*). Note that if the solute front moves as rapidly as the eluting agent front, $R_F = 1$. [In the Pierce and Hobbs paper (*223*, p. 78), the definition of R_M is a misprint, the term "log" having been omitted.]

If the concentration of hydrogen ion is varied but all other conditions remain fixed, a plot of R_M vs. log $[H^+]$ should have a slope of -3 for M^{+3}, according to Eq. (77). This hydrogen ion dependence was demonstrated for Eu^{+3} at six different loadings of HDEHP ranging over a factor of 6. With respect to the dependence of R_M upon concentration of HDEHP the authors state, "No attempt was made to relate R_M to $[HL]_O$ since the nature of the non-aqueous phase is not yet known, but . . . an increase in column loading is accompanied by an increase in R_M."

Pierce *et al.* (*227*) studied the variation of R_M with $\log[H^+]$ for all 15 lanthanides(III), in both $HClO_4$ and HCl systems, and found the slope of R_M vs. $\log[H^+]$ to have an average value of -3.13 ± 0.29 for the $HClO_4$ system and -2.73 ± 0.37 for the HCl system. (Note that these experiments included only HX, not HX + NaX at constant ionic strength.)

Their plot of 3 log[H^+], at $R_M = 1$, vs. Z for the 15 lanthanides(III) is represented reasonably well by a straight line corresponding to an average separation factor for adjacent members of 2.44 and 2.11 in $HClO_4$ and HCl systems, respectively.

They summarize a comprehensive comparison of liquid-liquid extraction data and reversed-phase chromatographic data, ". . . it can be seen that the relative positions of the points derived from solvent extraction results correspond well with those taken from elution measurements. . . . Thus, generally, similar separation factors are obtained in the two systems, which is of interest, since liquid-liquid measurements are derived from equilibrium determinations with the HDEHP dissolved in toluene, whereas for elutions, the aqueous phase flowed past the reagent which was immobilized on a solid. Further, the results suggest that it should be possible to predict the behavior of elements on these columns from liquid-liquid results, if the position of the elution maximum for one element is known at a given acidity, together with the liquid extraction data for this and the other elements to be eluted."

In evaluating their reversed-phase system with respect to conventional ion exchangers they point out, "A disadvantage of the reversed phase system described in this paper compared with conventional ion-exchangers for the separation of macro quantities of rare earths is . . . the relatively low capacity of HDEHP-Corvic columns for the extraction of metals . . . . Nevertheless, the reliability of the system, the order of elution of the elements, the simplicity of the eluting phase and the generally higher separation factors for adjacent elements have resulted in the reversed phase partition technique providing a more satisfactory means for the routine separation of rare earths, prior to analytical determination, in several cases."

Cerrai *et al.* (*41*) report a similar study involving HDEHP immobilized on cellulose powder as the stationary phase and aqueous HCl as eluent. Winchester (*298*), using aqueous HCl or HNO_3 as eluent vs. HDEHP (which he symbolized as DEP), "held on dichlorodimethylsilane-treated diatomaceous silica columns," reports, "Separation factors observed are similar to those in solvent extraction using DEP, and the kinetics of the elution are rapid. Columns are easily prepared and are stable and long-lived." He concludes, "Application of the DEP rare earth chromatographic procedure to neutron activation analysis in geochemistry is now in progress."

Sochacka and Siekierski (*262*) studied the factors affecting plate height in the HDEHP (on kieselguhr) vs. aqueous HCl or HNO_3 system. They found that with up to 10% of HDEHP (with respect to the mass of kieselguhr) the height of the plate is about 0.33 mm, making it possible to obtain very efficient separation of adjacent rare earths at room temperature. However, the width of the elution peak of a heavy rare earth is much greater with HCl than with HNO_3 as eluting agent, especially at room temperature.

Siekierski and Sochacka (*258*), in a detailed lanthanide(III) study of the factors affecting the height of the plate in HDEHP (on kieselguhr) vs. aqueous HNO_3, $HClO_4$, HCl, and H_2SO_4, showed that the plate height is essentially independent of Z in HNO_3 and $HClO_4$ systems, being in the 0.3–0.5 mm range. The plate height in the HCl system is 0.3–0.4 mm for the members La-Gd, but the succeeding values are (in mm): Tb (0.78), Dy (1.4), Ho (1.7), Er (4.0), Tm (3.6), Yb (6.0), Lu (4.4), and Y (6.0). Comparable results are presented for the H_2SO_4 system. The authors explain the larger plate height associated with the heavy rare earths as being due to kinetic effects, suggesting that Cl^- and $SO_4^=$ anions are held in the inner coordination shell of the cation in the aqueous phase and must be displaced before the cation becomes fixed in the HDEHP phase. The NO_3^- and ClO_4^- anions are assumed to be in the outer coordination sphere and therefore more readily dislodged.

However, it should be noted that Pierce *et al.* (*227*) found the average of the slopes of R_M vs. log$[H^+]$ to be -2.73 ± 0.37 in the HCl system, but those of the heavier rare earths were flatter than those of the lighter. (In liquid-liquid extraction studies of HDEHP, he found the average slope of log K vs. log$[H^+]$ to be -3.57 ± 0.25. Since the study involved only HCl, not a constant ionic strength medium, a slope more steep than -3.0 is to be expected.) Consequently, an alternative explanation of the higher plate heights for the heavy rare earths may be based upon the assumption that MCl^{+2} rather than, or in addition to, M^{+3} is fixed in the HDEHP phase. The reaction might be represented as:

$$M_A^{+3} + Cl_A^- + 2HL_O \rightleftharpoons MClL_{2,O} + 2H_A^+ \tag{79}$$

The relative importance of Eq. (79) is assumed to be a function of Z. A similar explanation of the H_2SO_4 data might be offered. (Compare Eqs. (80) and (81) in a later discussion.)

Moskvin (*189*) used a Jones reductor in conjunction with the HDEHP (fixed on Teflon) vs. aqueous HCl + NH_4Cl system, demonstrating the separation of europium, as Eu(II), from lanthanides(III), the Eu(II) being in the early fractions. The author points out, "In those cases when europium is present in trace amounts it cannot be separated. This is evidently explained by the presence in the solutions of elementary oxygen, which oxidizes the europium after it has passed through the reducer."

This technique may be compared with the corresponding liquid-liquid extraction technique reported by Peppard *et al.* (*201*), in which Eu(II) reports preferentially to the aqueous phase and lanthanides(III) to the HDEHP (in toluene) phase. In this latter system, the separation of Eu(II) in the 10^{-10} M range was demonstrated, Cr(II) being employed as a holding reductant. Perhaps the Moskvin (*189*) separation might be extended into the tracer range by use of a holding reductant.

Hulet (*117*) demonstrated the mutual separation of Am and Cm, as Am(VI) and Cm(III), by use of the HDEHP (immobilized on a diatomaceous silica product) vs. aqueous HNO_3 system, using $(NH_4)_2S_2O_8$ as holding oxidant. Similarly, Bk was isolated as Bk(IV) from "all transuranic elements and fission products except cerium."

Kooi and Boden (*154*) used a similar system in the mutual separation of Bk(III) and Ce(III).

In their study of alkaline earths in the system HDEHP (immobilized on paper) vs. HCl, Cerrai and Ghersini (*35*) noted that the plot of $\log(1/R_F - 1)$ vs. $\log[H^+]$ had in general a slope less steep than -2. In explanation, they postulated the extraction as a composite of:

$$M^{+2} + 3(HY)_{2,O} \rightleftharpoons MY_2 \cdot 4HY_O + 2H^+ \tag{80}$$

$$MCl^{+1} + 3(HY)_{2,O} \rightleftharpoons MCl(Y \cdot HY) \cdot 4HY_O + 2H^+ \tag{81}$$

Cerrai and Ghersini (*36*) later demonstrated the applicability of the same system to the separation of the M(III) elements Al, Ga, In, and Tl.

Separation of lanthanides(III) by the HDEHP (immobilized) vs. HCl system was adapted to thin-layer chromatography (TLC) by Pierce and Flint (*222*). The results may be compared with those of Daneels *et al.* (*54*), who used silica gel impregnated with buffers or acids as the stationary phase and a solution of HDEHP in carbon tetrachloride as the eluent in a TLC separation of lanthanides(III).

3. Amine Stationary Phase

Testa (*272*) first reported the separation of metallic cations by use of the amine (immobilized on paper) vs. aqueous HCl system. He correlated his R_F values with distribution ratios reported for the same elements in anion resin vs. aqueous HCl systems (*156*) and summarized, "Chromatographic paper treated with a liquid anion exchange (tri-*n*-octylamine) behaves like an anionic resin film; consequently many separations of cations that form anionic complexes can also be carried out by means of this new chromatographic procedure. Many examples are reported, among which the separation of the very similar elements zirconium and hafnium is of great significance. It is anticipated that it will be possible to isolate traces of complexed metals from large quantities of non-complexed elements."

Cerrai and Testa (*37*) followed with a report of the chromatographic separation of U(VI), Th(IV), and lanthanides(III) using the tri-*n*-octylamine (TOA, XXVI) impregnated paper vs. aqueous HNO_3 system. They suggest the possibility of using columns filled with cellulose powder treated with TOA as anionic resin columns.

In a closely following paper they (*38*) report the use of tri-*n*-octylamine cellulose (TOAC) in metals separations using HCl and HNO_3 as eluents. They describe the preparation of TOAC and the procedure used for determining exchange capacity. This exchange capacity was found to be 3–4 times lower than that of the common anionic resins. They point to its stability in 8–10 *M* HCl and 5–7 *M* HNO_3 as an advantage of TOAC.

Brinkman and de Vries (*29*) applied the thin-layer technique using amine-impregnated silica gel on glass microscope slides, the eluent being aqueous HCl.

4. General Treatment of the Technique

For historical background and a rigorous introduction, the papers by Martin and Synge (*171*) and Martin (*172*) are highly recommended. In addition to papers quoted in preceding sections, those by Vink (*284, 285*) on the theory of partition chromatography and on numerical calculations will be found valuable.

Familiarity with thin-layer chromatography (TLC) may be gained from the papers by Bolliger and Bolliger (*27*), Peifer (*198*), and Russel (*233*).

Cerrai (*34*), in a paper "Liquid ion exchangers: separation on inert supports impregnated with liquid ion exchangers," reviews the work on TOPO, HDEHP, and TOA as stationary phases. In his conclusions he states, "The results presented in this review show . . . what can be accomplished in the field of chemical separation by reversed-phase partition chromatography . . . . The principal merits of such processes are their simplicity and versatility . . . . The development of these techniques has allowed not only the separation of many similar elements from one another, but also the separation of ions of the same element, present in two different states of valency. Further development may also be concerned with processes involving electron exchange chromatography."

IX. Synergism and Antisynergism

In 1954 Cuninghame *et al.* (*52*) in a study of the extraction of Nd(III) and Pr(III) by the β-diketone, thenoyltrifluoroacetone (HTTA, XXVIII), noted a greatly enhanced extraction in a system containing a small concentration of tri-*n*-butyl phosphate (TBP) in the organic phase. For example, in the 0.2 *F* HTTA (in kerosene) vs. an aqueous $HNO_3 + 1\ M\ NH_4NO_3$ phase of pH 3.55 system in which the organic phase contained TBP in

$$(C_4H_3S)CO(CH_2)C_3{,}OCF \qquad \text{HTTA}$$

(XXVIII)

various concentrations (expressed in formality units), the *K* for Nd(III) increased with the formality, *F*, of TBP: 0.30 (no TBP), 0.87 (0.005 *F*), 2.6 (0.01 *F*), 9.4 (0.02 *F*), and 110 (0.04 *F*). Note that at the highest TBP concentration the ratio of TBP to HTTA, in formality units, is only 0.20. The *K* for Nd(III) into 0.04 *F* TBP (in the absence of HTTA) from the same aqueous phase is not reported, but from the reported data for 100% TBP it might be expected to be less than 0.01.

This enhancement of the *K* by a factor of approximately 350 appears to be the first recorded instance of a very large synergistic effect in the liquid-liquid extraction of metals.

In 1958 Blake *et al.* (*24*) reported the enhanced extraction of U(VI) in the presence of neutral organophosphorus reagents, in dialkyl phosphoric acid (in hydrocarbon diluent) vs. aqueous mineral acid systems. Specifically, neutral phosphates, phosphonates, phosphinates, and phosphine oxides, respectively members of Classes 2A, 3A, 4A, and 5A of Table VI, were shown to increase the *K* for U(VI) in the system 0.1 *F* HDEHP (in kerosene) vs. 0.5 *F* aqueous sulfate at pH 1.0. For example, in the presence of 0.05 *F* tri-*n*-butyl phosphine oxide (TBPO) the *K* for U(VI) is 7.0×10^3, and in the absence of synergist is 1.35×10^2. The synergistic enhancement factor is approximately 50.

The authors state, "An important property of the dialkylphosphoric acids is that in combination with neutral organophosphorus reagents a strong (synergistic) enhancement of U(VI) extraction can be obtained, the extraction power of the mixture being greater than the sum of the extraction powers of the separate reagents. . . . The order of synergistic enhancement is seen to be

$$(RO)_3PO < R(RO)_2PO < R_2(RO)PO < R_3PO$$

which is also the order of increasing base strength of the phosphoryl oxygen. . . . The property of synergistic enhancement of extraction coefficient seems limited to dialkylphosphoric acid–neutral reagent combinations. The phosphinic acids tested show no synergistic enhancement. . . ."

They suggest that the effect is due to addition of the neutral reagent (synergist) to the uranyl–dialkyl phosphate complex through hydrogen bonding, and that hydrogen bonding between the synergist and the extractant accounts for the antisynergistic effect noted in systems containing a high concentration of the neutral reagent.

In this paper and in another by Blake *et al.* (*23*), it is reported that with monoalkyl phosphoric acids, Class 2C of Table VI, an immediate antagonistic decrease in K, that is, an antisynergistic effect, is found upon addition of a neutral reagent.

This enhancement effect, variously called the "synergic" and "synergistic" effect, has been studied for U(VI) in systems employing a monoacidic extractant of Class 2B of Table VI as extractant and a neutral compound of Class 2A or Class 5A of Table VI as synergist by Dyrssen and Kuca (*76*), Deane *et al.* (*58*), Kennedy and Deane (*146*), Siekierski and Taube (*259*), Baes (*12*), and Zangen (*302*). Siekierski and Taube (*259*) and Taube (*271*) extended the study to Pu(IV) and Pu(VI); Zangen (*303*) studied Ca(II) and Ba(II), selected lanthanides(III) and actinides(III), and Th(IV). Zangen concludes, ". . . only lanthanides with $Z > 64$ and Ba failed to show any synergistic phenomena. In general, the synergism was much less pronounced than in the case of U(VI)."

Each of these studies in general reports a region of positive effect followed by one of negative effect, that is, synergistic and antisynergistic regions.

The antisynergistic effect of TBP upon the extraction of Np(IV) by mono-2-ethyl hexyl phosphoric acid (H_2MEHP, XVIII) (in toluene) from an aqueous HCl solution was reported by Peppard *et al.* (*218*). The study of H_2MEHP as extractant was extended by Mason *et al.* (*177*), who employed *n*-decanol, TBP, and TOPO as synergistic agents in the extraction of selected lanthanides(III), Y(III), Am(III), Cm(III), Th(IV), and U(VI). In no instance was a large positive effect noted, but the negative effects were quite large.

In 1959 Irving and Edgington (*121*) reported a preliminary survey of the extraction of U(VI) into 0.02 F HTTA (in cyclohexane) from 0.01 M HNO_3 as affected by the presence of TBP or TBPO in the organic phase. They noted that 0.003 F TBP enhanced the K for U(VI) 5000-fold and that TBPO is even more effective. The extracted species were shown to be $UO_2(TTA)_2(TBP)$ and $UO_2(TTA)_2(TBPO)_3$.

They (*122*) reported an extension of this work in 1960 and included a penetrating analysis of various proposed explanations of "synergism" in liquid-liquid extraction, concluding, "Synergic effects are well known in many biochemical systems where the association of two drugs, two insecticides, two germicides or a toxic and a non-toxic component exert effects which would not have been predicted from the behavior of the substances considered severally. No general explanation of such complex phenomena has been given and indeed no such universal explanation is to be expected, for to take a special case, particular physiological symptoms may be produced by several different stimuli. For similar reasons we would not suppose that all cases of synergic enhancement of solvent extraction will be explicable in the same terms, even using the rather general model we have proposed. . . ."

In 1961 the same authors (*123*) report the synergistic enhancement by TBP, in the HTTA (in cyclohexane) vs. aqueous HNO_3 system, of the extraction of Pu(VI), Np(IV), Th(IV), Am(III), Pm(III), and Eu(III). When TBP was replaced by TBPO, the extracted species were $M(TTA)_3(TBPO)$ and $M(TTA)_2(NO_3)(TBPO)_3$ where $M = Eu^{+3}$, Am^{+3}. Similarly, in explaining the extraction of Np(IV) and Pu(IV) the extracted species were considered to be $M(TTA)_4$, $M(TTA)_3(NO_3)(TBP)$, and $M(TTA)_2(NO_3)_2(TBPO)_2$. They conclude in part, "That the basic reasons for the enhancement in solvent extraction will not always be due simply to a replacement of coordinated water by a less hydrophilic group, or to a simple increase in coordination number due to the attachment of a neutral hydrophobic ligand will be obvious from the variety of behaviour indicated above. Clearly the interplay of these factors with steric and stability considerations must now be regarded as the basis of any comprehensive theoretical treatment of the phenomena which have yet to be fully exploited in analytical chemistry."

Perhaps the final dozen words of the preceding statement will prove most prophetic. Almost certainly, synergism in liquid-liquid extraction, in both its positive and negative aspects, will prove important in the field of separations chemistry of vital interest to the analytical chemist.

Irving and Edgington, in three other papers dealing with synergic effects in HTTA extraction, report upon trivalent plutonium, americium, and europium (*126*), upon tetravalent actinides (*124*), and upon plutonium(VI) and neptunium(V) (*125*).

Also in 1961 Healy (*107*) reported "Synergism in the solvent extraction of di-, tri-, and tetra-valent metal ions—I. Synergic effects of different phosphate esters," in which the HTTA (in benzene) vs. aqueous HCl system was used. His results and conclusions were very similar to those of Irving and Edgington. He accompanied this study with ". . . II. Synergic effects in so-called inert diluents" (*108*) and concluded, "The extracted species $M(TTA)_nS_x$ is the same, whatever 'inert' diluent is used, but the partition coefficients of the metal ion vary over several powers of ten, sometimes by a factor much greater than that obtained by the synergic effect itself. The effect, on the extraction, of so-called 'inert' diluent such as cyclohexane, hexane, carbon tetrachloride, benzene and chloroform has been studied under various conditions. In all cases, the distribution ratio decreases as the diluent is changed from cyclohexane in the above sequence, chloroform giving the lowest partition coefficient."

An extensive study of antisynergism in HTTA systems was reported by Healy *et al.* (*112*), and Healy and Ferraro (*109*) reported ultraviolet and visible absorption spectrophotometric measurements of dilute solutions of the uranyl, thorium, and neodymium complexes. Ferraro and Healy (*81*) followed with a study of the infrared spectra.

Manning (*167*), in a study of the HTTA (in kerosene) vs. HNO_3 system, found steric effects (as exhibited by the synergists) to be important, concluding, "Both steric and synergic effects operate in the extraction of the lanthanides, yttrium and scandium by mixtures of HTTA and coordinating organophosphorus reagents. The former effects lead to poor separation factors, and synergic systems generally would seem to possess little practical application to the improved separation of the metals. An exception might be in cases where the lower lanthanide chelates form disolvates and the higher, monosolvates."

Similar systems, in which tri-*n*-octylamine (TOA) serves as the synergist, have been reported by Newman and Klotz (*195, 196*); Walker and Li (*288*) have reported the preparation of $Zn(TTA)_2(TOPO)$ and $Cu(TTA)_2(TOPO)$.

Dyrssen (*73*) utilized the antisynergistic effect of an alcohol, methyl isobutyl carbinol, to return Y(III) from the HDBP (in chloroform) extract to an aqueous phase.

In a study of the extraction of Sc(III) by mixtures of oxine (8-quinolinol) and neutral organophosphorus reagents in hexone (methyl isobutyl ketone) from dilute HCl, Manning and Pranowo (*169*) represent the extraction as

$$\mathrm{Sc_A}^{+3} + \mathrm{Cl_A}^{-} + 2\mathrm{HO}x_{\mathrm{O}} + 2S_{\mathrm{O}} \rightleftharpoons \mathrm{ScClO}x_2S_{2,\mathrm{O}} + 2\mathrm{H_A}^{+} \qquad (82)$$

where S is the synergist. The extraction of the "mixed complex" containing chloride from aqueous $1.24 \times 10^{-3}\ M$ HCl indicates the need for caution in interpreting synergism data, and for precise determinations of hydrogen ion dependency data.

The synergistic behavior of protactinium in mixed solvents has been reported by Goble and Maddock (*94*). This study was concerned with extraction from aqueous HCl by a variety of two component mixtures of neutral solvents.

X. Investigation of Complexes

In 1949 Connick and McVey (*47*), working with Zr(IV), inaugurated the HTTA extraction method of determining complexity constants. In their rationale they explain, "From a search of the literature we have been forced to the conclusion that the formula of not a single aqueous zirconium(IV) species has been unambiguously identified up to the present time . . . . The purpose of the present research was to determine the formulas of the zirconium species existing in acidic aqueous solutions and to study the complexing of zirconium(IV) by a number of the more common anions . . . . The usual procedures for the determination of the formulas of species in solution . . . are not readily applicable in the case of zirconium because of the great tendency for hydrolysis to take place except in quite acidic solutions."

They outline the procedure, "The experimental method involves the measurement of an equilibrium in which zirconium(IV) is distributed between the aqueous phase being investigated and an organic phase containing a chelating agent. The zirconium is inappreciably complexed by the chelating agent when in the aqueous phase, yet forms a chelate which is soluble in the organic phase and which is in equilibrium with whatever species exist in the aqueous phase. Any complexing of species in the aqueous phase is quantitatively reflected in a decrease of the extraction of the zirconium in the organic phase."

In essence the extraction into HTTA (in benzene) from perchloric acid was represented as:

$$Zr(OH)_{n,A}{}^{+(4-n)} + 4HTTA_O \rightleftharpoons Zr(TTA)_{4,O} + (4 - n)H_A{}^+ + nH_2O_A \qquad (83)$$

They concluded that at low zirconium concentrations the average zirconium species lies between Zr^{+4} and $Zr(OH)^{+3}$.

(Connick and Reas (*48*) extended the method to the study of the hydrolysis and polymerization of zirconium in perchloric acid solution.)

By studying the effect of incremental replacement of $HClO_4$ by H_2SO_4, keeping the ionic strength essentially constant, Connick and McVey (*47*) evaluated the respective equilibrium constants for

$$Zr^{+4} + HSO_4{}^- \rightleftharpoons Zr(SO_4)^{+2} + H^+ \qquad (84)$$

$$ZrSO_4{}^{+2} + HSO_4{}^- \rightleftharpoons Zr(SO_4)_2 + H^+ \qquad (85)$$

$$Zr(SO_4)_2 + HSO_4{}^- \rightleftharpoons Zr(SO_4)_3{}^{-2} + H^+ \qquad (86)$$

as 4.6×10^{-2}, 53, and 1.

Similarly, through use of HF in place of H_2SO_4, the complexes ZrF^{+3}, $ZrF_2{}^{+2}$, and $ZrF_3{}^+$ were shown to be unusually stable. The $ZrCl^{+3}$ and $Zr(NO_3)^{+3}$ complexes were shown to have small stability constants, perhaps 2.0.

Prophetically, the authors suggest, "The method used in the present study is clearly a powerful one and it should find applications in the study of many similar systems."

In 1950 Day and Stoughton (*56*) reported stability constants for Th(IV) complexes, with chloride, fluoride, nitrate, chlorate, bromate, iodate, acetate, chloroacetate, dichloroacetate, and trichloroacetate ions, using the HTTA (in benzene) vs. ($HClO_4$ + HX) system. They cited evidence for the existence of $Th(NO_3)F^{+2}$ and $Th(NO_3)F_2{}^+$.

In their study of acetate complexing they found, ". . . the presence of acetic acid in the aqueous phase increases the extractability of the chelated product formed between thorium and TTA." For example, under otherwise identical conditions the K from a 0.5 M acetic + 0.5 M $HClO_4$ phase is 1.4 times that from 0.5 M $HClO_4$. This effect has been reported in detail by Goldstein *et al.* (*95*).

Similar HTTA studies of complexing of metals by a variety of common anions have been reported for Th(IV) by Zebroski *et al.* (*304*) and Waggener and Stoughton (*287*), for Hf(IV) by Varga and Hume (*279*), for U(IV) by Day *et al.* (*57*), for U(VI) by Day and Powers (*55*), and for Eu(III) by Manning and Monk (*168*).

Analogously, Bogucki *et al.* (*26*) used the HTTA (in cyclohexane) vs. a buffered aqueous phase containing 1,2-pyrocatechol-3,5-disulfonic acid ("Tiron") to determine the molecular complexity in the aqueous phase of the 1:1.5 Th(IV)-Tiron chelate. Their results show it to be binuclear at pH 4.3.

In an approach somewhat less direct than that used in HTTA systems, extraction by TBP has been used by Solovkin (*263*) in the determination of hydrolysis constants of Zr(IV) and of stability constants of Zr(IV) complexes with nitrate and chloride ions. Similarly, Prokhorova and Brezhneva (*229*) determined the stability constants of the nitrate complexes of Hf(IV).

Extraction by TBP was used in the study of the nitrate complexes of Th(IV) by Fomin and Maiorova (*90, 91*), of Ce(III) by Fomin *et al.* (*89*), and of Pu(III) by Shevchenko *et al.* (*248*) and Laxminarayanan *et al.* (*157*).

Peppard *et al.* (*211*) determined the stability constants of MX^{+2} for La, Ce, Pr, Eu, Tm, Yb, Lu, and Am, where $X = Cl^-$, NO_3^-, using the di[*p*-(1,1,3,3-tetramethyl butyl)phenyl] phosphoric acid (HDOΦP) (in toluene) vs. ($HClO_4$ + HX) system. In essence the theory is that utilized in the HTTA system.

White *et al.* (*293*) studied the chloride and nitrate complexes of Fe(III) and In(III) by use of the dinonyl naphthalene sulfonic acid (HD, XXIII) (in benzene) vs. ($HClO_4$ + HX) system. Choppin and Unrein (*42*) determined similarly the stability constants of $CeCl^{+2}$, $CeBr^{+2}$, $EuCl^{+2}$, $EuBr^{+2}$, EuI^{+2}, YCl^{+2}, and YBr^{+2}.

Extraction by a mixture of secondary amines (in toluene) from an aqueous ($NaNO_3$ + $NaClO_4$ + 0.2 M HNO_3) phase, $\mu = 6.7$, was used by Brothers *et al.* (*30*) in their investigation of the complexing of Pu(IV) by nitrate ion.

Sekine (*245*) has demonstrated the use of a "synergistic" system, employing HTTA and TBP, in the study of trivalent La, Eu, Lu, and Am complexes with oxalate, sulfate, chloride, and thiocyanate ions.

Antikainen and Dyrssen (*5*) studied the hydrolysis of Ag^+ by varying the concentration of OH^- in the extraction system quinoline (in benzene) vs. 3 M ($NaClO_4$ + NaOH).

The extent of hydration of salts, as measured by liquid-liquid extraction techniques, has been reported by Rozen *et al.* (*232*) and Yates *et al.* (*300*).

Further examples of liquid-liquid extraction as a tool in the study of metal complexes may be found in the review "Investigation of complex formation in solution by the distribution method" by Zozulya and Peshkova (*306*).

XI. Concluding Comments

Because of space limitations this review has not included extraction of water and of mineral acids by neutral phosphorus-based extractants. For an excellent survey of this important field, the chapter by Diamond and Tuck (*59*) is recommended.

Important recent comprehensive papers, concerning extractants other than phosphorus-based compounds and amines, are "Systematic study of the solvent extraction of metal β-diketonates," by Starý and Hladký (*266*); "Systematic study of the solvent extraction of metal oxinates," by Starý (*265*); "A theoretical approach to the solvent extraction of metal chelates," by Schweitzer (*243*); "A summary of TTA extraction coefficients," by Poskanzer and Foreman (*228*); and a series of papers on the use of tropolone and β-isopropyl tropolone as extractants for metal ions by Dyrssen *et al.* (*66, 69–71, 246, 247*).

Moore, who made the pioneering applications of amine vs. chloride systems to the separation of actinides(III) as a group from lanthanides(III) as a group (Section VII,B), has recently described a "New approach to separation of trivalent actinide elements from lanthanide elements, selective liquid-liquid extraction with tricaprylmethylammonium thiocyanate" (*185*).

Baybarz and Leuze (*17*) have reported "Separation of transplutonium and rare earth elements by liquid-liquid extraction," and Horner *et al.* (*116*) have described "Fission product recovery from waste solutions by solvent extraction."

A "periodic table" type of survey has been made by Kimura (*152, 153*) for the HDEHP (in toluene) vs. HCl system, by Ishimori and Watanabe (*138*) for the 100% TBP vs. HNO_3 system, by Ishimori *et al.* (*140*) for the 100% TBP vs. HCl system, by Ishimori *et al.* (*131*) for various systems employing neutral phosphates and phosphine oxides and amines as extractants, and by Ishimori *et al.* (*130*) for various amine vs. H_2SO_4 systems.

In recent reviews Coleman *et al.* (*44*) and Green (*101*) have assessed the use of liquid ion exchangers in inorganic analysis. These papers are especially recommended because of the breadth of treatment which makes them of immediate value to the working analyst.

And finally, to deliver the coup de grace to the term "inert diluent," the diluent effect has been elucidated by Taube (*270*) in "The influence of diluent polarity on the extraction of neptunium and uranium compounds to organic media," by Alimarin and Zolotov (*4*) in "The influence of the nature of the organic solvent on the extraction of chelate compounds," and by Smulek and Siekierski (*261*) in "The influence of diluent on the extraction of iron(III) from hydrochloric acid solutions by tertiary amines."

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