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COMMISSION ON EQUILIBRIUM DATA*

Critical Evaluation of Equilibrium Constants in Solution
Part B: Equilibrium Constants of Liquid-Liquid Distribution Systems

CRITICAL EVALUATION OF SOME EQUILIBRIUM CONSTANTS INVOLVING ACIDIC ORGANOPHOSPHORUS EXTRACTANTS

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CONTENTS

I. INTRODUCTION

I.1. GENERAL CONSIDERATIONS

Acidic organophosphorus compounds have been extensively studied as extractants for numerous metals, and have been shown to exhibit a good extraction and separation efficiency. Many authors have reported equilibrium constants characterizing the distribution of metals and of the extractants themselves in two-liquid-phase systems, and an essential part of the data has been compiled in recent years (71K,74Ma). The compilations, of course, include data of different accuracy and reliability and a critical evaluation of the published equilibrium constants would be useful. The primary aim of the evaluation is the choice and recommendation of the best value of each constant. For this purpose values determined independently by different authors must be compared, taking into account the precision and care with which experiments have been performed and evaluated. However, such a comparison is possible only for frequently used extractants, like di-n-butyl and bis(2-ethylhexyl) phosphoric acids, and is also limited to some metals, and a strict following of the above criterion would leave a large number of equilibrium constants unassessed. Since this would be a serious restriction of the evaluation work, an attempt is made here to extend the assessment also to equilibrium constants published by one author or team of authors. On the basis of his own experience in the field, the present author feels to be in a position to perceive possible sources of errors in the experimental procedure and the evaluation of results, provided that both are properly described in the original paper, and to judge to some extent the plausibility of conclusions made by the original authors. The benefit of such an effort could at least be a warning to the reader of erroneous or quite irrelevant equilibrium constants, which unfortunately are not rare in the chemical literature. The equilibrium constants will thus be divided into three categories:

i) Recommended values, obtained in evaluating numerical data reported independently in several sources.

ii) Tentative values, reported by one author or team of authors, but obtained from results of a careful experimental work which are graphically or numerically well documented; it must be obvious that possible error sources have been avoided both in the experiments and in the numerical or graphical evaluation of the results. The equilibrium constants must obey well known correlations with the nature and properties of the diluent, extractant and metal extracted. Moreover, the definition of the constant must be in accord with the chemistry of the system, i.e. it must reflect the true nature of species participating in the distribution equilibrium.

iii) Unacceptable values including those determined under erroneous assumptions or calculated from erroneous data, those describing the distribution of a solute between two liquid phases quite well, but not expressing the actual chemical reactions correctly, and those which cannot be assesed because of a lack of information.

In this work equilibrium constants were not in all cases simply taken from the original source. In many cases the experimental results, if presented numerically or graphically well, were reevaluated in a simple computer treatment in order to check the evaluation made by the authors. In the reevaluation the dependencies of the distribution ratio on the hydrogen ion and extractant concentrations were not treated separately, as it is usual in a graphical treatment, but as many constants as possible were optimized simultaneously.

The precision of the constants, if not given in the original source, could only be roughly estimated from the scatter of the experimental results and the accuracy of analytical methods used. With few exceptions no statistical treatment was done in this work, because of a low number of independent measurements.

This work is only partially based on the two previous compilations (71K, 74Ma). Recent data, to the end of 1978, were also included and in many cases equilibrium constants, although not calculated by the original authors, were gained from the original data and included here.

I.2. SYMBOLS AND DEFINITIONS

A bar over a symbol or formula denotes quantities referring to, or species present in the organic phase.

HA, A^-	monoacidic organophosphorus extractant and its anion respectively
HX, X^-	perchloric, nitric or hydrochloric acids and their anions respectively
B	neutral organophosphorus compound
M^{z+}	cation of a z-valent metal
I	ionic strength
F	formula weight dm^{-3}, concentration unit for acidic organophosphorus extractants
[ ]	concentration, mol dm^{-3} or g-ion dm^{-3}
( )	thermodynamic activity on the molar scale
D_M, D_A	distribution ratio of a metal or an organophosphorus extractant respectively
$\bar{C}_{A,i}$	initial analytical concentration of an extractant in the organic phase, formula weight dm^{-3}
$\bar{C}_A$, C_A	equilibrium analytical concentrations of an extractant in the organic and aqueous phases respectively, formula weight dm^{-3}
$\bar{C}_{dim}$	equilibrium concentration of dimeric extractant in the organic phase, mol dm^{-3}
$\bar{C}_B$	equilibrium analytical concentration of a neutral organophosphorus compound in the organic phase, mol dm^{-3}

$K_2 = [\overline{(HA)_2}][\overline{HA}]^{-2}$, dimerization constant

$K_D = [\overline{HA}][HA]^{-1}$, partition coefficient

$K_a = [H^+][A^-][HA]^{-1}$, acid dissociation constant

$K_{u,z} = [\overline{MA_z\cdot(2u-z)HA}][H^+]^z[M^{z+}]^{-1}[\overline{(HA)_2}]^{-u} = D_M[H^+]^z\,\bar{C}_{dim}^{-u}$, equilibrium constant of a two-liquid-phase reaction of M^{z+} with a dimeric extractant without participation of X^-

$K_{v,u,z} = [\overline{MA_{(z-v)}X_v\cdot(2u+v-z)HA}][H^+]^{z-v}[M^{z+}]^{-1}[\overline{(HA)_2}]^{-u}[X^-]^{-v} = D_M[H^+]^z[X^-]^{-v}\,\bar{C}_{dim}^{-u}$, equilibrium constant of a two-liquid-phase reaction of M^{z+} with a dimeric extractant with participation of X^-

${}^mK_{u,z} = [\overline{MA_z\cdot(u-z)HA}][H^+]^z[M^{z+}]^{-1}[\overline{HA}]^{-u} = D_M[H^+]^z\,\bar{C}_A^{-u}$, equlibrium constant of a two-liquid-phase reaction of M^{z+} with a monomeric extractant (e.g. in an alcohol diluent) without participation of X^-

${}^mK_{v,u,z} = [\overline{MA_{(z-v)}X_v\cdot(u+v-z)HA}][H^+]^{z-v}[M^{z+}]^{-1}[\overline{HA}]^{-u}[X^-]^{-v} = D_M[H^+]^{z-v}[X^-]^{-v}\,\bar{C}_A^{-u}$, equilibrium constant of a two-liquid-phase reaction of M^{z+} with a monomeric extractant with participation of X^-

$\beta_n = [MA_n^{z-n}][A^-]^{-n}[M^{z+}]^{-1}$, concentration stability constant of a complex formed in the aqueous phase by M^{z+} with A^-

$K_{s,1.5} = S_0[\overline{(HA)_2}]^{-1.5}$, equilibrium constant of the reaction of MA_3 with a dimeric extractant in an organic solution; S_0 is the solubility of MA_3 in pure diluent

$S = (M^{3+})(A^-)^3$, thermodynamic solubility product of MA_3

K_a, K_D, $K_{u,z}$, β_n etc. are concentration equilibrium constants determined at a constant ionic strength or in a reasonably narrow ionic strength range. The corresponding thermodynamic constants are defined analogously, but with thermodynamic activities on the molar scale instead of concentrations.

I.3. ABBREVIATIONS OF EXTRACTANTS AND DILUENTS

Organic radicals are abbreviated as follows:

E	ethyl	Hp	*n*-heptyl	C-P	chlorophenyl
P	propyl	O	*n*-octyl	pC,oC	*p*-cresyl, *o*-cresyl
B	*n*-butyl	N	*n*-nonyl	Ph	phenyl
iB	*iso*butyl	D	*n*-decyl	Bz	benzyl
A	*n*-pentyl	L	*n*-dodecyl		
Hx	*n*-hexyl	E-H	2-ethylhexyl		

In an abbreviation of an extractant (H) is ionizable hydrogen; D, if placed immediately after (H), means the prefix di-. The subsequent letter(s) is (are) the abbreviation(s) of the organic radical(s); an apostroph after the symbol indicates that the radical is bound directly to the phosphorus atom by a C-P bond, otherwise the radical is understood to be bound to phosphorus through an oxygen atom by a C-O-P link. The letter P, closing the extractant abbreviation, means phosphorus acid. Examples: (H)DE-HP is bis(2-ethylhexyl) phosphoric acid, (H)E-HPh'P is ethylhexyl ester of phenylphosphonic acid, (H)DHp'P is di-*n*-heptyl phosphinic acid etc.
TBP, THxPO and TOPO are tri-*n*-butyl phosphate, tri-*n*-hexyl phosphine oxide and tri-*n*-octyl phosphine oxide respectively. MiBK is 4-methyl-2-pentanone (methyl *iso*butyl ketone, hexone).

I.4. SOURCES OF ERRORS IN THE DETERMINATION OF EQUILIBRIUM CONSTANTS

Before discussing the equilibrium constants reported in the literature, it is appropriate to summarize some important errors most frequently encountered in the experimental and evaluation work. The extent of avoidance of the errors in the original work is a criterion for assigning a constant to one of the categories defined in I.1. In each individual case it is necessary to regard how many and which of the errors listed below have not been avoided, before the acceptability and precision of the constant is assessed. The errors will be refered in the following chapters by their numbers only.

The sources of errors are:

1) Use of inaccurate analytical methods for the determination of the solute (distribuend); self-absorption, quenching and presence of radioactive impurities in using solutes labelled with radioactive isotopes.

2) Necessity of preconcentrating the distributed solute more than ten times before the determination; use of too many or insufficiently effective preconcentration steps.

3) Presence of strongly extracting impurities like pyrophosphate esters in extractants used in studying the distribution of metals.

4) Presence of

  a) strongly extractable organophosphorus impurities in studying the distribution of weakly extractable compounds, e.g. TBP impurities in HDBP,

  b) weakly extractable organophosphorus impurities in studying the distribution of strongly extractable compounds, e.g. mono-2-ethylhexyl phosphoric acid impurities in (H)DE-HP.

5) Presence of strong molecular complex forming impurities like alcohols in the diluent used for a study of the distribution of a metal or an extractant.

6) Side reactions

  a) in the aqueous phase, e.g. hydrolysis of the metal extracted, its complex formation with buffer substances or anions of the inert electrolyte (especially sulfates), redox reactions etc.

  b) in the organic phase, e.g. partial decomposition of the extractant (especially by hydrolysis with mineral acids), polymerization of metal complexes of the extractants etc.

7) Omission of measuring, or clearly presenting (numerically or graphically) one of both basic dependencies, i.e. $\log D_M = f(\log [H^+])$ and $\log D_M = f(\log \overline{C}_{dim})$ in studying the distribution of a metal and $\log D_A = f(\log [H^+])$ and $\log D_A = f(\log C_A)$ in studying the distribution of an extractant.

8) Measurement of an equilibrium between a monomer and a dimer of an extractant, or between the free extractant and its molecular complex, in a concentration range in which one of the species predominates in the organic phase; then at constant pH the experimantal points lie

  a) close to the horizontal assymptote of the $\log D_A = f(\log C_A)$ or $\log D_A = f(\log \overline{C}_B)$ dependencies (the monomer or free extractant respectively predominate),

  b) close to the ascending assymptotes of the dependencies (the dimer or molecular complex respectively predominate).

9) An analogous error in the determination of the acid dissociation constant of an extractant; then at constant C_A the experimental points lie

  a) close to the horizontal assymptote of the $\log D_A = f(\log [H^+])$ dependency (negligible degree of the acid dissociation of the extractant in the aqueous phase),

  b) close to the descending assymptote of the dependency (predominating acid dissociation).

10) Too few experimental points were measured.

11) Measurement of the concentration dependencies of D_M or D_A

  a) in a too narrow pH range, b) in a too narrow C_A range.

12) Strong scattering of the experimental points.

13) The constancy of invariable values, i.e. of $\overline{C}_A$ in measuring the dependency of D_M or D_A on pH, and of pH in measuring the dependencies of D_M on $\overline{C}_{dim}$ and D_A on C_A, is not guaranteed.

14) The slope of the $\log D_M = f(\log [H^+])$ dependency strongly deviates from an integral value or the slope of the $\log D_M = f(\log \overline{C}_{dim})$ dependency strongly deviates from an integral or a half-integral value.

15) The log D_A = f(log $[H^+]$) and log D_A = f(log C_A or $\overline{C}_B$) dependencies or log D_M = f(log $[H^+]$) and log D_M = f(log $\overline{C}_{dim}$) dependencies are not mutually consistent.

16) The equilibrium concentration of the substance distributed is measured in one phase only and the concentration in the opposite phase is calculated from the difference; this must be avoided especially in systems in which phase volumes can be changed during the equilibration or the substance distributed can be lost to slightly soluble compounds adsorbed on the phase interface or vessel walls.

17) A glass electrode is calibrated with buffer solutions having a known hydrogen ion activity at a very low ionic strength, and is used at a higher ionic strength for the measurement of a value which is said to be the hydrogen ion concentration.

18) No activity coefficients are introduced while varying the concentration of a mineral acid in the region above ~2M.

19) The ionic strength is not kept constant over the whole $[H^+]$ range studied in measuring the log D_M (or D_A) = f(log $[H^+]$) dependencies.

20) The acidity constant of an extractant valid at a given ionic strength is used for the calculation of values of K_2, K_D or an adduct formation constants from distribution data obtained at a different ionic strength of the aqueous phase.

21) The log D_M = f(log $\overline{C}_{dim}$) dependency is measured in a $\overline{C}_{A,i}$ region in which the extractant is

a) present predominantly in the aqueous phase, or

b) essentially monomerized in the organic phase;

then the calculation of the concentration of the extractant dimer in the organic phase may be strongly influenced by the accuracy of the K_a, K_D and K_2 values of the extractant.

22) The log D_A = f(log C_A or $\overline{C}_B$) and log D_M = f(log $\overline{C}_{A,i}$) dependencies are measured at such extractant or molecular complexant concentrations at which the results are distorted, and the assumption that $\overline{C}_{A,i} = 2\overline{C}_{dim}$ is not justified, because of deviations from ideality due either to specific interactions with unknown equilibrium constants or nonspecific interactions or both of them. The specific interactions may be partial trimerization of the extractant which otherwise is predominantly dimeric over a broad concentration range or simultaneous formation of two or more self-associates of an extractant, which in no concentration range exists in the form of a single, predominating oligomer in nonpolar diluents. Errors from this source must be considered as not avoided, if the prevailably dimeric state of an extractant containing ethereal oxygen atoms or bulky substituents is documented for a very narrow $\overline{C}_A$ range or even a single $\overline{C}_A$ value.

23) Subjective errors are made in the graphical evaluation of results by curve fitting.

It should be mentioned that in some systems a simply expressed equilibrium constant (neglecting errors from the sources 6a and 22 occurring under the conditions of the work) surprisingly well describes the distribution of a solute as a function of the analytical concentrations of reaction components. Such formal constants, although they do not express the actual stoichiometry of distribution reactions and are not applicable to an elucidation of the chemistry of the corresponding two-phase systems, may be useful in practice for predicting D_M values under conditions not differing from those specified in the original paper.

It could be objected that some of the error sources, as listed above, are trivial and need not be mentioned explicitly. However, it will be seen that even quite elementary mistakes have been made in some of the work published. Moreover, the list of important error sources may be helpful for a user of distribution data who is acquainted with the general chemistry of solvent extraction but is not quite experienced in the particular field of acidic organophosphorus extractants; it can guide him in assessing equilibrium constants not mentioned here.

I.5. PRESENTATION OF CRITICALLY EVALUATED VALUES

Recommended and tentative equilibrium constants are numerically presented in tables. For unacceptable values the reader is referred to the original paper. Important: if $K_{u.z}$, $K_{v.u.z}$ etc. values, as given in the tables, are compared with those in the original sources, the units in which the extractant concentration is included in the definition of the constant must be noticed! In this paper it is the concentration of the dimeric extractant, while elsewhere it is sometimes the analytical concentration of the extractant, because $\overline{C}_{dim} = 0.5\overline{C}_A$ is valid in most cases within the experimental error.

The categories of equilibrium constants (see Paragraph I.1) are denoted as follows: R - recommended, A - tentatively acceptable and N - not acceptable. The symbol (r) closely following a reference denotes a paper from which data were taken for a numerical evaluation or reevaluation, as done in the course of this assessment work; equilibrium constants were taken directly from references given in the tables without any additional symbol. Methods of the determination of equilibrium constants: distr - distribution measurements, pot - potentiometric titration, cond - conductometric measurements, soly - solubility measurements, kin - kinetic measurements, iex - solid-liquid ion exchange and spphm - spectrophotometry. The symbol (orig) substitutes for a numerical value which is not acceptable, hence is not included in the Tables, but can be found in the original source.

Data in the tables are first ordered according to extractants, with aryl derivatives following alkylated compounds, in the sequence phosphoric acid diesters, phosphonic acid monoesters, phosphinic acids, and within each group in the sequence of increasing molecular weight. Data on the extraction of metals with an extractant are ordered according to increasing valence of the metals and, within the lanthanide(III) and actinide(III) groups, according to increasing atomic number. For each metal first recommended equilibrium constants are given, followed by tentatively accepted and unacceptable values; within each category the data are sequenced according to diluents, approximately in the order of decreasing extraction efficiency.

II. EQUILIBRIA INVOLVING THE EXTRACTANTS

II.1. GENERAL CONSIDERATIONS

The over-all distribution of organophosphorus acids between two immiscible liquid phases is a balance of a number of individual equilibria such as the acid dissociation in the aqueous phase, partition of monomeric species between the phases, self-association (mostly dimerization) in the organic phase, adduct formation, etc. The individual equilibria are characterized by the equilibrium constants K_a, K_D and K_2, defined in paragraph I.2. Concentration equilibrium constants have mostly been determined at a constant ionic strength in the aqueous phase, almost exclusively by measuring D_A as a function of $[H^+]$, $\overline{C}_{A,i}$, $\overline{C}_B$, etc. The calculation of the equilibrium constants from the distribution data has been reviewed elsewhere (71K) and need not be described here. Conductometric measurements and potentiometric titrations have been used in a few cases for the determination of the acid dissociation constant. The following correlations (71K) helped to judge the plausibility of the equilibrium constants reported:

1) The acid strength of di-n-alkyl phosphoric acids decreases with increasing length of the alkyl chain.
2) At invariant R the acid strength decreases in the sequence $(RO)_2POOH$ > $(RO)(R)POOH$ > $(R)_2POOH$.
3) The partition coefficients of monomers of di-n-alkyl phosphoric acids increase with the alkyl chain length (by a factor of ~4 per methylene group.
4) The self-association constants of acidic organophosphates usually decrease and the partition coefficient of their monomers usually increase in the diluent sequence aliphatic hydrocarbons, alicyclic hydrocarbons, carbon tetrachloride, toluene, chlorobenzene, benzene, ketones, alcohols.

The following equilibria cannot be assessed because of lack of general information:

1) Self-association and partition of diacidic organophosphorus compounds which tend to form very large oligomers in the organic phase (71K,76K),
2) self-association of acidic organophosphorus compounds in the aqueous phase which seems to be strongly influenced by the nature and concentration of electrolytes contributing to the ionic strength (69K,71K), and
3) self-association of monoacidic organophosphorus compounds higher than dimerization in the organic phase.

II.2. DI-n-ALKYL PHOSPHORIC ACIDS

Equilibrium constants characterizing the behavior of (H)DBP in two-liquid-phase systems have already been critically evaluated (74M). Thus only recent data on (H)DBP will be mentioned here.

II.2.1. ACID DISSOCIATION IN THE AQUEOUS PHASE

A survey of the data is given in Table II-1.

TABLE II-1. Acid dissociation constants of di-n-alkyl phosphoric acids at 20°C (65U,70U,77N) and 25°C (other references); see explanation in I.5

Acid	-Log constant (method)	I	Category (error source no.)	Note	Ref.
(H)DEP	0.73±0.05(distr)	1.0	R	c	64D
(H)DEP	0.85±0.1(distr)	0.1	A(9b)	c	64D
(H)DEP	0.95±0.05(cond)	~0	R	d	09H(r),17D(r)
(H)DEP	(orig) (distr)	0.1	N(?)	c	64D
(H)DEP, (H)DPP, (H)DAP, (H)DHxP	(orig) (pot)	~0	N(?)	d	43K,72L,74G
(H)DAP	0.93±0.05(distr)	1.0	A	-	69K
(H)DHxP	1.04±0.05(distr)	1.0	A	-	69K
(H)DOP	1.48±0.05(distr)	1.0	A	-	68K
(H)DHxP, (H)DOP	(orig) (distr)	0.1	N(1,2,15,17)	a,b,f	70U
(H)DHxP, (H)DOP	(orig) (distr)	0.1	N(1,2,17)	a,b,f	65U
Bis(butoxyethyl) phosphoric acid	(orig) (distr)	2.0	N(?)	e	77N

Notes:

a) The organophosphoric acid has been preconcentrated by extraction into carbon tetrachloride, decomposed (probably by evaporation with perchloric acid) and determined spectrophotometrically (probably as heteropoly blue).

b) There is no mutual consistency between the data given on the same acids in (65U) and (70U).

c) Only the log $D_A = f(\log [H^+])$ dependency obtained with 2-methyl-4-pentanol diluent is acceptable. There is an unexpected effect of the ionic strength at $[H^+] > 0.1$ g-ion dm^{-3} in the distribution measurements with MiBK diluent.

d) The acidity constants determined conductometrically and potentiometrically are valid for electrolyte concentrations of ~0.02M and can be considered as thermodynamic values. There is a striking discrepancy between the K_a^o values determined by different methods: potentiometric titration (43K,65P,72L,74G) yields a K_a^o value lower by a factor of 2 to 4 than the conductometric method (09H,17D) and distribution measurements with an approximative recalculation for I = 0 (57D,64D,69K). In agreement with the previous criticism (74M) the K_a^o values from the potentiometric studies are considered here to be too low. They would suggest single ion activity coefficients of ~0.3 for anions of (H)DEP and (H)DBP and this is in contradiction with data on comparable monobasic anions (37K). The error of the potentiometric method, which obviously is systematic in the determination of the dissociation constant of rather strong acids, cannot be found in analyzing the description of the experimental work in the original papers. The use of the conductometric method is limited to lower di-n-alkyl phosphoric acids; higher acids at their limited aqueous solubility are fully dissociated in their aqueous saturated solutions.

e) No details are given on the measurement of D_A and the evaluation of the results.

f) Error source no. 17: the measured pH values are probably lower by 0.1 to 0.2 units than the negative logarithms of the actual H^+ concentrations (77V).

II.2.2. PARTITION OF MONOMERIC SPECIES BETWEEN TWO LIQUID PHASES AND DIMERIZATION IN THE ORGANIC PHASE

A survey of the data is given in Table II-2. Notes:

a) The notes a) and f) in II.2.1 are valid here for (65U,70U).

b) (H)DE^{32}P containing ~1% highly extractable radioactive impurities has been used in (64D). Since mostly low D_A have been measured, ~50% of the radioactivity found in the organic phase has belonged to the impurities and the accuracy of the D_A values is correspondingly reduced.

c) See note c) in II.2.1.

d) In the radiometric measurement of high D_A values with (H)DHx^{32}P and (H)DO^{32}P (68K,69K), the distortion of the results by radioactive monoester impurities (error source 4b, see I.4) has been avoided. An aliquot of the equilibrium aqueous phase has been slightly acidified and shaken with CCl_4, so that the impurities were left in the aqueous aliquot, and samples for the radioactivity measurements of ^{32}P have been taken from the CCl_4 extract containing the diester only. In (70U) the preconcentration of the diester by extraction into CCl_4 from the equilibrium aqueous phase has lowered the accuracy of the D_A determination, but removed monoester impurities from the aqueous samples.

e) The K_D and K_2 values are apparent, because they include a molecular association of (H)DBP with TBP. For the reevaluation the value of pK_a^o = 1.17 was taken, as recommended for pure water (74M).

f) K_2 is too low and K_D is too high. This is the most usual distortion of the results in the determination of the constant in systems with nonpolar diluents, due most probably to errors from the source no. 5 (see I.4).

g) K_2 is too high and K_D is too low; the error source is difficult to estimate.

h) See note e) in II.2.1.

The more recently published K_D and K_2 values for (H)DBP in the system 0.1M HCl/toluene (76B) agree within the error limits given with the equilibrium constants recommended in (74M).

TABLE II-2. Partition coefficients and dimerization constants of di-*n*-alkyl phosphoric acids as determined by distribution measurements at an undefined room temperature (60I,67Kd,72L), 20°C (65U,70U,77N) and 25°C (other references); see explanation in I.5.

Diluent	log K_D	log K_2	I	Category (error source no.)	Note	Ref.
Diethyl phosphoric acid						
Chloroform	-2.05±0.1	4.45±0.05	0.1, 1.0	R(1,2,4a)	a,b	64D,70U
Nitrobenzene	-2.14±0.05	3.61±0.05	1.0	A(4a)	b	64D
Propyl ether	-1.75±0.05	2.19±0.05	1.0	A(4a)	b	64D
n-Hexane, *n*-octane	-5.1±0.15	7.3±0.15	1.0	A(1,2)	a	70U(r)
MiBK	(orig)	-	0.1, 1.0	N(?)	c	64D
Di-n-butyl phosphoric acid						
20% TBP in kerosene	0.94±0.05	0.85±0.1	~0	A	e	60I(r)
Di-n-pentyl phosphoric acid						
CCl_4	0.38±0.04	5.84±0.08	1.0	A	-	69K
Toluene	0.69±0.04	5.32±0.08	1.0	A	-	69K
Chloroform	1.78±0.04	4.25±0.08	1.0	A	-	69K
Butyl ether	1.39±0.04	2.75±0.08	1.0	A	-	69K
MiBK	2.64±0.04	1.27±0.08	1.0	A	-	69K
Heptane, cyclohexane	(orig)	(orig)	1.0	N(5?)	f	69K
Toluene	(orig)	(orig)	1.0	N(1)	f	67Kd
Bis(butoxyethyl) phosphoric acid						
Benzene	(orig)	(orig)	2.0	N(?)	h	77N
Di-n-hexyl phosphoric acid						
Chloroform	2.90±0.04	4.35±0.08	0.1, 1.0	R(1,2)	a,d	69K,70U(r)
Aliphatic	0.5±0.2	6.1±0.2	0.1	A(1,2,17)	a,d	70U(r)
Cyclohexane	0.85±0.04	6.26±0.08	1.0	A	d	69K
CCl_4	1.66±0.04	5.62±0.08	1.0	A	d	69K
Toluene	2.04±0.04	5.09±0.08	1.0	A	d	69K

continued

TABLE II-2 (continued)

Diluent	log K_D	log K_2	I	Category (error source no.)	Note	Ref.
Chloroform	2.90±0.04	4.35±0.08	1.0	A	d	69K
Butyl ether	2.63±0.04	2.48±0.08	1.0	A	d	69K
MiBK	3.68±0.04	1.27±0.08	1.0	A	d	69K
n-Heptane	(orig)	(orig)	0.1	N(5?)	d,f	69K
n-Octane	(orig)	(orig)	0.1	N(1,2,15,17)	a,b,d,f	65U
Di-n-octyl phosphoric acid						
n-Octane	3.7±0.2	3.5±0.2	0.1	R(1,2,17)	a	65U(r)
n-Heptane	3.98±0.04	3.48±0.08	1.0	R	d	68K
Cyclohexane	4.19±0.04	3.47±0.08	1.0	A	d	68K
Benzene	4.90±0.04	3.13±0.08	1.0	A	d	68K
Toluene	4.78±0.04	3.21±0.08	1.0	A	d	68K
Chlorobenzene	4.56±0.04	3.19±0.08	1.0	A	d	68K
Chloroform	5.37±0.04	2.36±0.08	1.0	A	d	68K
Butyl ether	4.78±0.04	2.39±0.08	1.0	A	d	68K
Nitrobenzene	4.34±0.04	2.70±0.08	1.0	A	d	68K
MiBK	5.82±	-0.2±0.2	1.0	A	d	68K
Aliphatic, chloroform	(orig)	(orig)	0.1	N(1,2,17)	a,b,d,g	70U
Di-n-alkyl phosphoric acids (alkyl = pentyl to decyl)						
Benzene	(orig)	(orig)	~0	N(2,8b,16)	-	72L

II.2.3. ADDUCT FORMATION WITH NEUTRAL ORGANOPHOSPHATES IN THE ORGANIC PHASE

Equilibrium constants of the adduct formation of (H)DHxP and (H)DOP with TBP and TOPO in aliphatic diluents as given in (70U) are not acceptable because of the error sources 8b, 10, 20 (K_a is not properly known at I = 0.1) and 22 (see I.4). The authors claim the complex HA.B to be formed; simultaneous formation of HA.B and HA.2B would better interprete the data, but cannot be proved with only for to five points in each log D_A = f(log $\overline{C}_B$) dependency.

As for the adduct formation between (H)DBP and TBP, the acceptable value of log $Q_{(1)}$ = 0.4±0.1 can be introduced into Table IV-1 in (74M), page 24; the value was calculated from recently published data (76B).

II.3. BIS(2-ETHYLHEXYL) PHOSPHORIC ACID

The previous assessment of equilibrium constants of reactions involving (H)-DE-HP (74M) can now be completed: the determination of constants taken for (74M) from (71L) has more recently been described in detail (72La) and can be discussed here.

II.3.1. ACID DISSOCIATION IN THE AQUEOUS PHASE, PARTITION OF MONOMERIC SPECIES BETWEEN TWO LIQUID PHASES AND DIMERIZATION IN THE ORGANIC PHASE

A survey of the data is given in Table II-3.

TABLE II-3. Equilibrium constants of some reactions involving (H)DE-HP, as determined by distribution measurements at 20°C (63U,70U), 25°C (72La) and 25° to 50°C (69S); see explanation in I.5

Diluent	$-\log K_a$	$\log K_D$	$\log K_2$	I	Category (error source no.)	Note	Ref.
n-Octane	1.25±0.15	3.3±0.15	4.8±0.15	0.1	A(1,2,17)	a,e	70U(r)
Chloroform	-	4.8±0.15	4.3±0.15	0.1	A(1,2,17)	a,e	70U
n-Octane	(orig)	(orig)	(orig)	0.1	N(1,2,15,17)	a	63U
n-Decane	(orig)	-	-	0.1	N(4b)	b	69S
Toluene	(orig)	(orig)	(orig)	0.1	N(4b?,6a?)	c,d	72La

Notes:

a) See notes a) and f) in II.2.1 and note d) in II.2.2.

b) The experimental points of the dependency $\log D_A = f(\log [H^+])$ do not lie on a curve of the type $-\log y = -\log (1+x)$.

c) Supposing the acid dissociation to be the only reaction in the aqueous phase, two mutually inconsistent $\log D_A = f(\log [H^+])$ dependencies can be constructed from the data: one of them, valid at $-\log [H^+] = 1.0$ to 2.2, implies $pK_a = 1.35$ and the another, valid at $-\log [H^+] = 3.6$ to 5.7, gives $pK_a = 4.3$. To overcome the discrepancy, two additional reactions in the aqueous phase are supposed in the original work: dimerization with an unreasonably high equilibrium constant criticized in (74M) and with K_D being unexpectedly higher for the monomeric than the dimeric species, and formation of a species H_2A^+ extractable as $HA.HClO_4$. Further data are needed for confirming these reactions and excluding a possible complexation of (H)DE-HP species by the buffer substances used at $-\log [H^+] > 2$ (sulfanilic acid and Na_2HPO_4).

d) No significant change of D_A with C_A is obvious at $\bar{C}_{A,i} = 6 \times 10^{-5}$ to 5×10^{-4}F. The D_A values of (H)DE-HP are lower than in the analogous system with aliphatic diluents and this contradicts the known correlations (see II.1). Further data are needed for the confirmation of the effectiveness of removing weakly extractable impurities from the (H)DE-$H^{32}P$ preparation used in the original work. Measures for avoiding an effect of impurities, such as described in note d) in II.2.2, should be taken.

e) The measurements have been made at $\overline{C}_{A,i} < 0.01F$ and deviations from ideality, due to partial trimerization of (H)DE-HP in the organic phase or nonspecific interactions, can be expected not to exceed 3% (59B).

II.3.2. ADDUCT FORMATION IN THE ORGANIC PHASE

The unsuitability of the results given in (70U) for the calculation of equilibrium constants of the adduct formation of (H)DE-HP with TBP and TOPO can be substantiated as in II.2.3. The impossibility of assessing the data on the adduct formation with tri-n-octyl amine (72La) is explained in the second part of note d) in II.3.1. Equilibrium constants given in (75R) for the formation of adducts with TBP, chloroform, methyl hexyl ketone and octanol are not acceptable because of the error source no. 22 and those of the adduct formation with CCl_4 and benzene have no physical significance because here the interaction with (H)DE-HP has predominantly a nonspecific nature.

II.3.3. COMPLEX FORMATION WITH NITRIC ACID

The apparent equilibrium constants of the extraction of nitric acid in the form of the complex $(HA)_2.2H_2O.HNO_3$ into neat extractant and its 0.1F and 0.2F solutions in kerosene and CCl_4 respectively have been presented in (72R). The constants, which include thermodynamic activities of water and aqueous nitric acid, exhibit a good invariancy over the range of 2.5 to 8.5M HNO_3 in the aqueous phase. In spite of this, they cannot be accepted beacuse in their determination the water activity and extractant concentration have not been varied at a constant nitric acid acitivity and the composition of the complex extracted cannot be considered to be proved. The constants are not consistent with the activity coefiicients of (H)DE-HP given on the mole fraction scale in (73R,73Ra): no common equilibrium constant for all three solvents is obtained in applying the activity coefficients to the constants given in (72R).

II.4. DIARYL AND DIBENZYL PHOSPHORIC ACIDS

II.4.1. ACID DISSOCIATION IN THE AQUEOUS PHASE

A survey of the data is given in Table II-4.

TABLE II-4. Acid dissociation constants of diaryl and dibenzyl phosphoric acids as determined by potentiometric titration (65P,72L,74G) and distribution measurements (other references) at an unspecified room temperature (72L), 25°C (67C,74G) and 20°C (other refences); see explanation in I.5

R in $(RO)_2POOH$	pK_a	I	Category (error source no.)	Note	Ref.
Benzyl	0.60±0.03	1.0	R	a	63K(r),67C(r)
p-Cresyl	0.34±0.08	1.0	R	a	63K(r),65Pa(r)
p-Chlorophenyl	0.20±0.1	1.0	A(16,23)	-	63K
ß-Naphtyl	0.74±0.1	1.0	A(16,23)	-	63K
Phenyl	0.26±0.1	1.0	A(16,23)	-	63K
p-Chlorophenyl, phenyl, p-cresyl, benzyl, ß-naphtyl	(orig)	0.1	N(9b,16,23)	-	63K
Phenyl, p-cresyl	(orig)	~0	N(?)	b	65P,72L,74G

Notes:

a) Error sources 16 and 23 not avoided in (63K).

b) The potentiometric titration yields lowered K_a^o values (see note d) in II.2.1). There are considerable differences between K_a^o values reported by different authors. See also the second part of note a) in II.5.1 which applies to the determination of K_a^o of (H)DPhP as made in (65P).

II.4.2. PARTITION OF MONOMERIC SPECIES BETWEEN TWO LIQUID PHASES AND DIMERIZATION IN THE ORGANIC PHASE

A survey of the data is given in Table II-5. Notes:

a) Calculation of K_D is not justified, because K_a is reliably known only for I = 1.0.

b) Contrary to the conclusion of the original authors, at >1 g-ion H^+ dm^{-3} the K_2 value is dependent on the nitric acid concentration in the aqueous phase and, thus, includes equilibrium constants of a complexation of (H)DpCP with nitric acid. Original constants in (65Pa) are not acceptable.

c) The average degree of the self-association of (H)DC-PP in CCl_4 seems to be higher than two.

d) In the region of higher $\overline{C}_A$ the aqueous H^+ concentration is influenced by (H)DBzP distributed to the aqueous phase and thus not constant.

e) The accepted accuracy of the constants was estimated not from the scattering of the experimental points, but with regard to the unspecified temperature.

f) The ionic strength is not clearly specified for the data given in Fig. 1 in (63K).

g) No log D_A = f(log C_A) dependency is presented with chloroform diluent at I = 1.0; without it the log D_A = f(log $[H^+]$) dependency tabulated in (67C) cannot be evaluated.

II.4.3. ADDUCT FORMATION IN THE ORGANIC PHASE

Equilibrium constants of adduct formation of (H)DpCP in CCl_4, as presented in (66K), are not acceptable. At low concentrations of molecular complexants, D_A of (H)DpCP tends to an assymptotic value which is considerably higher that expected from data obtained in the absence of the complexants. Moreover, the error source no. 22 has not been avoided in the experiments with chloroform and <u>iso</u>propyl ether as molecular complexants; no conclusions are possible on the composition of adducts formed with octyl an benzyl alcohols, because the degree of self-association of the alcohols in CCl_4 is not known.

TABLE II-5. Equilibrium constants of reactions involving diaryl and dibenzyl phosphoric acids as determined by distribution measurements at 20°C (63K,65Pa), 25°C (67C) and an unspecified room temperature (66K); see explanations in I.5

Diluent	log K_D	log K_2	I	Category (error source no.)	Note	Ref.
Bis(p-cresyl) phosphoric acid						
Chloroform	-	4.01±0.04	0.1	R	a,b	65Pa(r),63K(r)
Chloroform	0.78±0.07	3.86±0.05	1.0	A	b	65Pa(r)
Benzene	-	4.19±0.05	0.1	A	a,b	65Pa(r)
Benzene	0.44±0.05	4.06±0.05	1.0	A	b	65Pa(r)
Benzene	-	3.98±0.05	5	A	a,b	65Pa(r)
CCl_4	-	4.94±0.07	0.1	A	a,b	65Pa(r)
CCl_4	-	4.69±0.03	5	A	a,b	65Pa(r)
Dibenzyl phosphoric acid						
Benzene	-0.09±0.05	5.56±0.05	1.0	A	-	67C(r)
Nitrobenzene	1.22±0.05	3.09±0.05	1.0	A	-	67C(r)
Toluene	-	5.3±0.15	0.01	A	a	67C
Benzene	-	4.9±0.15	0.01	A	a	67C
Nitrobenzene	-	3.3±0.15	0.01	A	a	67C
Chloroform	(orig)	-	1.0	N(7)	g	67C
CCl_4	-	(orig)	0.01	N(12)	a	67C
MiBK, butyl acetate	-	(orig)	0.01	N(13)	a,d	67C
Chloroform	-	(orig)	?	N(7)	a,f	63K
Bis(chlorophenyl) phosphoric acid						
Isopropyl ether	-	1.2±0.1	0.1	A	a,e	66K(r)
Kerosene	-	4.8±0.1	0.1	A	a,e	66K
Benzene	-	4.2±0.1	0.1	A	a,e	66K
MiBK	-	0.9±0.1	0.1	A	a,e	66K
CCl_4	-	(orig)	0.1	N	a,c	66K
Chloroform	-	(orig)	?	N(7)	a,f	63K
Diphenyl and dinaphtyl phosphoric acids						
Chloroform	-	(orig)	?	N(7)	a,f	63K

II.5. MONOESTERS OF PHOSPHONIC ACIDS; PHOSPHINIC ACIDS

II.5.1. ACID DISSOCIATION IN THE AQUEOUS PHASE, PARTITION OF MONOMERIC SPECIES BETWEEN TWO LIQUID PHASES AND DIMERIZATION IN THE ORGANIC PHASE

A survey of the data is given in Table II-6. Notes:

a) For rather weak acids both the potentiometric titration (53C,72L) and the conductometric measurements (64K) yield the same pK_a^o value (contrary to stronger acids, see II.2.1). Regarding the fact that even weak organophosphorus acids are partially dissociated in their saturated aqueous solutions, the term Y in the equation $pK_a = pH + \log Y$ must not simply be $[HA][A^-]^{-1}$, as taken in (53C), but has to be $(C_A-\underline{a}C_A-[H^+])(C_A+[H^+])^{-1}$, as taken in (72L); $\underline{a}$ is the number of moles of NaOH added per mole of the organophosphorus acid. The results from (53C) were correspondingly recalculated.

b) Results of experiments with (H)E-HPh'P have led the authors of (78E) to conclude that K_a and K_2 values, if determined by the distribution method, depend on the constant $\overline{C}_{A,i}$ and pH values, at which the dependencies $\log D_A = f(\log [H^+])$ and $\log D_A = f(\log C_A)$ respectively are measured. Starting from the general equation for D_A, as reviewed e.g. in (71K), it can easily be shown that this is not true provided the $\overline{C}_A$ value does not significantly change with $[H^+]$ (high D_A values are measured) and the acid dissociation and dimerization are the predominant reactions in the aqueous and organic phases respectively. The former condition is fulfilled for the majority of the results presented in (78E) and side reactions, like extraction of (H)E-HPh'P in the form of its sodium salt or self-association in the aqueous phase, can practically be excluded at $pH < 4$. The substantial misleading circumstance has most probably been the measurement of very high D_A values (up to 1600) based on an analytical procedure unsuitable for the purpose, namely preconcentration of (H)E-HPh'P in aqueous and organic samples by evaporation, decomposition to phosphoric acid by an acid treatment and determination of total phosphorus as phosphomolybdic acid. Moreover, error source no. 4b has not been avoided. Thus the high D_A in (78E) can hardly be free from a considerable negative error, and this suffices to explain why K_a and K_2 apparently depend on the conditions of the measurement of the corresponding D_A dependencies. Consequently, the conclusion of the authors of (78E) is not justified until it is convincingly supported by data obtained in a system with well measurable distribution ratios.

c) The constants are mutually comparable within 0.03 logarithmic units. A lower absolute accuracy must be assigned to them, because the temperature is not specified in the original source.

d) The $\log D_A = f(\log [H^+])$ dependency exhibits a maximum which has plausibly been interpreted in the original paper by complex formation between (H)E-HPh'P and nitric acid. However, pK_a values have been calculated under the erroneous assumption that in the maximum of the dependency the concentrations of the species A^- and H_2A^+ are negligible in comparison with that

TABLE II-6. Equilibrium constants of reactions involving phosphonic acid monoesters and phosphinic acids as determined by potentiometric titration (53C,72L) and conductometric (64K) or distribution (other references) measurements; see explanation in I.5. rt - Unspecified room temperature

Diluent	pK_a	log K_D	log K_2	t^oC	I	Category (error source no.)	Note	Ref.
Di-n-butyl phosphinic acid								
-	3.39±0.05	-	-	20-25	~0	R	a	53C, 64K,72L
-	3.3±0.1	-	-	20	1.0	A	-	65K
Di-n-pentyl phosphinic acid								
-	3.52±0.1	-	-	rt	~0	A	c	72L
Di-n-hexyl phosphinic acid								
-	3.55±0.1	-	-	rt	~0	A	c	72L
2-Ethylhexyl phenylphosphonic acid								
(Decane)	1.1±0.15	-	-	2	<0.4	A(12,17,19)	d	74A(r)
(Decane)	1.35±0.15	-	-	10	<0.4	A(12,17,19)	d	74A(r)
(Decane)	1.6±0.15	-	-	20	<0.4	A(12,17,19)	d	74A(r)
(Decane)	1.5±0.15	-	-	27	<0.4	A(12,17,19)	d	74A(r)
(Decane)	1.8±0.15	-	-	30	<0.4	A(12,17,19)	d	74A(r)
(Decane)	2.0±0.15	-	-	40	<0.4	A(12,17,19)	d	74A(r)
(Decane)	1.9±0.15	-	-	50	<0.4	A(12,17,19)	d	74A(r)
-	(orig)	-	-	?	~0	N	f	74Ea
Benzene	-	-	(orig)	rt	0.5	N(1,2,17?)	b	78E
Benzene	(orig)	-	(orig)	25	<0.4	N(17,19,20)	e,h	75A,76Ba
Di-n-octyl phosphinic acid								
Xylene	-	(orig)	(orig)	20	<4	N(?)	i	68M
n-Octyl phenylphosphonic acid								
Benzene,cyclohexane,octane	-	(orig)	(orig)	20	2.0	N	j	75N
Diphenyl phosphinic, phenyl phenylphosphonic and p-cresyl p-cresylphosphonic acids								
Chloroform	(orig)	(orig)	(orig)	20	?	N(7)	g	65K

of HA. Surprisingly, the incorrectly calculated pK_a values give a smooth straight line if plotted vs. 1/T and $\Delta H = -21.3$ kJ mol^{-1} as well as $\Delta S = -103$ J K^{-1} mol^{-1} are the values found for the thermodynamic functions of the acid dissociation of (H)E-HPh'P. The pK_a values obtained by reevaluation are acceptable as a mere semiquantitative illustration of the temperature effect. The plot of pK_a vs. 1/T is of course scattered and a rough estimation yields $\Delta H \sim -36$ kJ mol^{-1} and $\Delta S \sim -150$ J K^{-1} mol^{-1}.
e) The log $D_A = f(\log [H^+])$ dependency deviates at $[H^+] < 0.01$ g-ion dm^{-3} from the theoretical slope -1 to a lower value (see Fig. 1 in (75A)).
f) The original source is not available (cited in (74E,78E)).
g) No information is given on the composition of the aqueous phase.
h) The two log $D_A = f(\log \overline{C}_A)$ dependencies given in (76Ba) for 0.4M $HClO_4$ and pH 3.02 are inconsistent: either D_A values at pH 3.02 should be ten times lower or pH is to be 2.02 instead of 3.02. The reevaluation done with $pK_a = 1.5$ yielded in both cases log $K_2 = 1.6$. This value, as well as log $K_2 = 2.6$ reported in (75A), does not agree with isopiestic results (61F), according to which (H)E-HPh'P is fully dimerized in benzene even at a concentration of 0.0088F. Calculation of K_D is not justified (see the error sources indicated).
i) The shape of the log $D_A = f(\log C_A)$ dependency corresponds to trimerization of (H)DHp'P in the organic phase without any intermediate dimerization step, but the data are interpreted by dimerization of (H)DHp'P. The determination of K_2 in the aqueous phase is irrelevant, because at the value given the fraction of (H)DHp'P dimerized in its saturated aqueous solution would be ~0.05%.

j) The K_D - K_2 pairs do not follow the correlation 4 in II.1.

II.5.2. COMPLEX FORMATION WITH NITRIC ACID

The reactions governing the extraction of nitric acid with (H)DHp'P in xylene have been suggested to be $H^+ + NO_3^- + \overline{(HA)_2} = \overline{(HA)_2.HNO_3}$ at an aqueous HNO_3 concentration of 2M and $H^+ + NO_3^- + \overline{HA} = \overline{HA.HNO_3}$ at 8M HNO_3 (68M). This interpretation is not convincing and the equilibrium constants are not acceptable, because neither the dimeric nature of (H)DHp'P in xylene in equilibirium with 2M HNO_3 (see note i) in II.5.1) nor the predominancy of monomeric (H)DHp'P in xylene in equilibrium with 8M HNO_3 have clearly been demonstrated.

(H)E-HPh'P forms in aqueous solutions of perchloric acid a species formulated as H_2A^+ (74A); the equilibrium constant of the reaction cannot be accepted, because in its calculation the authors have neglected possible variations of activity coefficients of (H)E-HPh'P species with considerable changes of the concentration of perchloric acid.

III. EQUILIBRIA INVOLVING METALS

III.1. GENERAL CONSIDERATIONS

Only ion exchange extraction reactions are assessed in this chapter. A critical evaluation of equilibrium constants of solvation reactions, proceeding at high acidities of the aqueous phase, would exceed the scope of this work. The over-all ion exchange reactions at moderate hydrogen ion concentrations in the aqueous phase proceed in the extraction of mono-, di- and trivalent cations mostly without any participation of inorganic anions and can generally be written as

$$M^{z+} + u\overline{(HA)_2} = \overline{MA_z.(2u-z)HA} + zH^+, \tag{1}$$

where $u \geqslant z$ is more usual than $u < z$. In the extraction of tetravalent cations the participation of mineral acid anions in the ion exchange reaction is more frequent and the reaction equation has the form

$$M^{4+} + vX^- + u\overline{(HA)_2} = \overline{MX_vA_{4-v}.(2u+v-4)HA} + (4-v)H^+ \tag{2}$$

with $u < 4$ being usual and X^- representing NO_3^-, ClO_4^- or Cl^-. In practice, concentration equilibrium constants of the reactions are measured in the presence of inert electrolytes in the aqueous phase. The constants, defined in I.2 and denoted $K_{u,z}$ and $K_{v,u,z}$ for the reactions (1) and (2) respectively, make visible by the number of indices the type of the reaction which they characterize. The indices display the number of particles reacting with an M^{z+} ion and the number of hydrogen ions released; consequently, they also give the composition of the complex extracted, which is uncharged. The values of $K_{u,z}$ and $K_{v,u,z}$ can be directly calculated from distribution data; the equilibrium concentration of the dimeric extractant in the organic phase, if not practically equal to $0.5\overline{C}_{A,i}$, can be easily calculated provided K_a, K_D and K_2 are known. The calculation is little affected by uncertainties of the three constants, if a predominating fraction of the extractant is present in the organic phase and is dimeric; this is mostly the case.

Some authors have attempted to characterize partial two-phase equilibria like

$$M^{z+} + zA^- + xHA = \overline{MA_z.xHA} \tag{3}$$

or

$$M^{z+} + zA^- + x\overline{HA} = \overline{MA_z.xHA}. \tag{4}$$

Equilibrium constants of the reactions (3) and (4), K_3 and K_4 respectively, are related to $K_{u,z}$; since $u = (x+z)/2$,

$$K_3 = K_{u,z}K_D^{2u}K_2^{u}K_a^{-z} \quad \text{and} \quad K_4 = K_{u,z}K_D^{z}K_2^{u}K_a^{-z}.$$

It is clearly seen that the accuracy of K_3 and K_4 is very sensitive to the quality of K_a, K_D and K_2 and will thus not be assessed here. If the error limits of K_a, K_D and K_2 are known, the reader can himself estimate the possible statistical deviation of log K_3 and log K_4; he will see that it may often exceed one logarithmic unit and can hardly be smaller than 0.3 logarithmic units with M^{2+} and 0.5 logarithmic units with M^{3+}. It must be pointed out here that in the chemical literature the statistical deviations of log K_3, log K_4 and analogous constants are those calculated from the statistics of the metal distribution data (mostly from the mere scattering of the D_M values measured,without taking into account possible uncertainties of pH measurement) and do not include statistical deviations of K_a, K_D and K_2.

The assessment of the plausibility of equilibrium constants was assisted by regarding the following general correlations, which are qualitatively well documented in the literature:

1) The extraction ability of an organophosphorus acid is strongly dependent on the nature of the diluent and decreases in the order aliphatic diluents > cyclohexane > ethers > CCl_4 > xylene > toluene > chlorobenzene > benzene > $CHCl_3$ > nitrobenzene > alcohols.

2) Within the lanthanide(III) and actinide(III) series the extractability of M^{3+} increases with the atomic number.

3) The extracting power of monoacidic organophosphorus compounds decreases at invariable R in the order $(RO)_2POOH$ $(RO)(R)POOH$ $(R)_2POOH$ in the extraction of lanthanides(III) and actinides(III) and in the inverse order in the extraction of uranium(VI).

4) The length of the alkyl chain in the molecule of a di-n-alkyl phosphoric acid does not significantly influence the extracting power, but branching reduces it.

It must strongly be emphasized that the validity of each $K_{u,z}$ and $K_{v,u,z}$ value, as reported for a given metal, extractant and diluent, is limited to a certain composition of the aqueous phase and to certain concentration ranges of hydrogen ions and the extractant (and, of course, to a certain temperature). Application of the equilibrium constants outside the concentration ranges in which they have been determined should be avoided and, if done all the same, certain aspects discussed below must be regarded.

The nature and concentration of an inert electrolyte present in the aqueous phase influences $K_{u,z}$ and $K_{v,u,z}$ even if its ions do not directly participate in the extraction reaction. The reasons are:

First, the complexation of the metal extracted even by anions such as nitrate and chloride cannot be neglected. It would be reasonable to present distribution data primarily on systems with a virtually noncomplexing aqueous phase containing perchlorate anions only (in general studies, of course, not in applied investigations of e.g. the recovery of metals from leach liquors). Data on systems with a weakly complexing aqueous phase could then be gained, with some loss of accuracy, by recalculation. However, data on systems involving perchlorates are not very frequent and numerous authors have studied the distribution of metals with chloride, nitrate or sulfate aqueous phases. It is pointed out that equilibrium constants, both taken directly from original papers or obtained by recalculation of original data, will be rendered here as valid for the aqueous phase used in the original work. No attempt will be made here to recalculate them for a non-complexing aqueous phase, because a search for relaible complexity constants of metal chloride, nitrate and sulfate complexes in aqueous solutions would essentially exceed the scope of the assessment work. Use of stability constants will only be made in comparing the plausibility of values of an equilibrium constant reported by different authors for the same organic phase but various aqueous phases.

Second, the partition of extractant species between the phases and, consequently, the equilibrium concentration of extractant dimers in the organic phase depend on the ionic medium in the aqueous phase; this is important especially for extractants with a higher aqueous solubility, e.g. (H)DBP.

The upper limit of the pH range, in which an equilibrium constant is valid, is determined by the hydrolysis of the metal extracted and by the fact that cations of the inert electrolyte, mostly Na^+, can at higher pH also be extracted and so lower the concentration of free extractant in the organic phase. The latter aspect must be born in mind in applying $K_{u,z}$ values of the extraction of weakly extractable metals (alkaline earth elements, bivalent transition metals etc.) with high molecular weight extractants like (H)DE-HP. The application of equilibrium constants below the pH range studied in the original work may be incorrect because of a possible contribution of the solvation mechanism to the metal distribution equilibrium. This is important especially in the extraction of tetravalent metals.

The concentration range of the extractant in the organic phase, in which a $K_{u,z}$ or $K_{v,u,z}$ value has been determined, is also important. Above the upper extractant concentration limit, u in the reaction (1) or (2) may become higher and a D_M value calculated from the constant given is lower than the actual value; on the other side, u can remain constant but the extractant may not behave ideally and a higher D_M value is obtained from the constant. Below the extractant concentration limit studied, u in the reaction (1) or (2) may become lower and an erroneously low D_M value is calculated from the constant; moreover, the simplifying assumtion that $\overline{C}_{A,i} = 2\overline{C}_{dim}$ may be false because of a pronounced monomerization of the extractant or transfer of it to the aqueous phase at low $\overline{C}_{A,i}$.

Experience shows that the experimental slopes of the linear dependencies $\log D_M = f(\log [H^+])$ and $\log D_M = f(\log \overline{C}_{dim})$ are in most cases lower than the expected integer or half-integer values by 5 to 10%. The error limits of equilibrium constants of the reactions (1) and (2) are determined more by this systematic error than by statistical factors like the scattering of experimental points. Consequently, the accuracy of an equilibrium constant outside the concentration ranges studied is correspondingly lower than within it, even if none of the additional factors, as mentioned above, plays any role. The relative accuracy of equilibrium constants obtained under analogous conditions for chemically similar elements (adjacent lanthanides(III) or actinides(III) etc.) and, consequently, separation factors calculated thereof may be much better than the absolute accuracy, because similar elements can be expected to exhibit similar deviations from the expected ideal behavior.

Original data were in many cases reevaluated for this chapter. If K_a, K_D and K_2 values were needed for the calculation of $\overline{C}_{dim}$, those recomme or tentatively accepted in the previous chapter and (74M) were taken.

III.2. DI-n-ALKYL PHOSPHORIC ACIDS

III.2.1. EXTRACTION OF URANIUM(VI) AND BERYLLIUM(II)

A survey of the data is given in Table III-1.

TABLE III-1. Data on the extraction of U(VI) and Be(II) with di-n-alkyl phosphoric acids at an unspecified room temperature (50S,61Ha,73Rb), 20°C (61H,62Sb), 22°C (62Sa,70M) and 25°C (59D,60Da,68L); see explanation in I.5

Diluent Aqueous phase	log $K_{2,2}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
System: U(VI)/Di-n-butyl phosphoric acid					
CCl_4 0.1M H_2SO_4	3.46±0.1	3×10^{-4} to 0.12 0.133	R(7,21a)	a,b	68L,60Da
Hexane 0.1M H_2SO_4	3.96±0.1	0.001 to 0.26 0.133	A(7,21a)	b,c	68L
Chloroform 1M (Na,H)ClO_4	3.5±0.1	0.001 to 0.05 0.1 to 0.9	A	-	59D(r)
MiBK 1M (Na,H)ClO_4	4.7±0.15	0.005 to 0.5 0.1	A(7,21b)	b	59D(r)
Butyl ether 2M HNO_3	5.4±0.15	0.0024 to 0.01 2.0	A(7)	b	50S(r)
Benzene Dilute HNO_3	(orig)	-	N(14,15,19)	-	62Sa,62Sb
Toluene Dilute HNO_3	(orig)	-	N(14,15,19)	-	61H
System: U(VI)/Di-n-pentyl phosphoric acid					
Toluene Dilute HNO_3	(orig)	-	N(14,15,19)	-	62Sa
Butyl ether Dilute HNO_3	(orig)	-	N(7,21b)	d	50S

continued

TABLE III-2 (continued)

Diluent Aqueous Phase	log $K_{2,2}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$g-ion dm^{-3}	Category (error source no.)	Note	Ref.
System: U(VI)/Di-n-heptyl phosphoric acid					
Xylene Dilute HNO_3	(orig)	-	N(10)	-	73Rb
System: U(VI)/Di-n-octyl phosphoric acid					
Heptane 1M (Na,H)Cl	3.90±0.05	0.02 to 0.3 0.06 to 1.0	A		70M
Benzene 1M (Na,H)Cl	4.90±0.05	0.02 to 0.3 0.06 to 1.0	A	-	70M
Butyl ether Dilute HNO_3	(orig)	-	N(7,21b)	d	50S
Systems: U(VI)/Di-n-propyl, diisobutyl and diphenyl phosphoric acids					
Butyl ether Dilute HNO_3	(orig)	-	N(7,21b)	d	50S
Systems: Be(II)/Di-n-butyl, di-n-octyl and di-n-decyl phosphoric acids					
Toluene Dilute HNO_3	(orig)	-	N(7,10,11b)	-	61Ha

Notes:

a) Data from (60Da) have been reevaluated in (68L).

b) Omission of measuring the log $D_M = f(\log [H^+])$ dependency (error source no. 7) is no significant insufficiency here, beacuse u = 2 is well documented in the literature. However, it limits the validity of $K_{2,2}$ to a single concentration of a mineral acid.

c)Higher self-association of (H)DBP than dimerization in the organic phase has been taken into account in the calculation of $\overline{C}_{dim}$.

d) Distribution data have been given neither numerically nor clearly graphically in the original source, and could not be reevaluated in this work.

The results of an extensive experimental study and a sophisticated computer evaluation of U(VI) distribution data in a system invloving (H)DBP extractant, TBP and TOPO synergists and hexane and CCl_4 diluents (68L) show that a number of mixed complexes of U(VI) can be formed in the organic phase and that the previous interpretations (60Da,61Sb,62Sa64H) are too simple. An assessment of equilibrium constants of reactions proceeding in such very complex systems may only be possible when additional results from independent sources become available.

III.2.2. EXTRACTION OF LANTHANIDES(III) AND ACTINIDES(III)

A survey of the data is given in Table III-2.

TABLE III-2. Data on the extraction of lanthanides(III) and actinides(III) with di-n-alkyl phosphoric acids at an unspecified room temperature (61Sa, 62S), 20°C (61S,63Z,66K,74V), 22° or 23°C (60P,66Ka,67Kc,70M,73Z) and 25°C (60D,62D); see explanation in I.5

M	Diluent Aq. phase	u	log $K_{u,3}$	Ranges of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Extractant: Di-n-butyl phosphoric acid							
La	Butyl ether 0.1M $HClO_4$	3	1.31±0.02	0.013-0.05 0.1	A(7)	a	62D(r)
La	Toluene 1M $(Na,H)NO_3$	3	-0.80±0.1	0.005-0.2 0.0025-0.06	A	c	66Ka
La	CCl_4 Dilute HNO_3	3	(orig)	-	N(7,11b,19)	-	61Sa
Ce	Butyl ether 0.1M $HClO_4$	3	2.0±0.1	0.02-0.05 0.1	A(7)	a	62D(r)
Ce	Toluene 1M $(Na,H)NO_3$	3	-0.26±0.08	0.005-0.2 0.005-0.06	A	c	66Ka
Ce	Benzene Dilute HNO_3	3	(orig)	-	N(14,19)	-	61S
Pr	Butyl ether 0.1M $HClO_4$	3	2.05±0.1	0.013-0.05 0.1	A(7)	a	62D(r)
Pr	CCl_4 Dilute HNO_3	3	(orig)	-	N(7,11b,19)	-	61Sa,62S
Nd	CCl_4 Dilute HNO_3	3	(orig)	-	N(7,11b,19)	-	62S
Pm	Butyl ether 0.1M $HClO_4$	3	2.43±0.05	0.01-0.04 0.1	A(7)	a	62D(r)
Pm	Toluene 1M $(Na,H)NO_3$	3	0.5±0.1	0.005-0.05 0.05-0.3	A	c	66Ka
Sm	Butyl ether 0.1M $HClO_4$	3	2.81±0.03	0.006-0.04 0.1	A(7)	a	62D(r)
Sm	Toluene 1M $(Na,H)NO_3$	3	1.03±0.08	0.005-0.05 0.05-0.3	A	c	66Ka
Eu	Butyl ether 0.1M $HClO_4$	3	3.1±0.1	0.006-0.05 0.1	A(7)	a	62D(r)

continued

TABLE III-2 (continued)

M	Diluent Aq. phase	u	log $K_{u,3}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Eu	Toluene 1M $(Na,H)NO_3$	3	1.25±0.08	0.005-0.05 0.01-0.3	A	c	66Ka
Eu	Hexane 0.1M HNO_3	3	4.0±0.2	0.01-0.1 0.1	A(7)	a	60D(r)
Eu	CCl_4 0.1M HNO_3	3	2.95±0.15	0.005-0.1 0.1	A(7)	a	60D(r)
Eu	Chloroform 0.1M HNO_3	3	1.03±0.07	0.02-0.5 0.1	A(7)	a	60D(r)
Eu	MiBK 0.1M HNO_3	3	0.35±0.1	0.08-0.5 0.1	A(7)	a	60D(r)
Eu	Benzene Dilute HNO_3	3	(orig)	-	N(14,19)	-	61S
Eu	Propyl ether 0.1M HNO_3	3	(orig)	-	N(12)	-	60D
Eu	CCl_4, CH_2Cl_2 1M $(Na,H)NO_3$	3	(orig)	-	N	e	73Z
Eu	Xylene,benzene 1M $(Na,H)NO_3$	3	(orig)	-	N	e	73Z
Eu	Chlorobenzene 1M $(Na,H)NO_3$	3	(orig)	-	N	e	73Z
Gd	Butyl ether 0.1M $HClO_4$	3	3.4±0.1	0.0025-0.04 0.1	A(7)	a	62D(r)
Tb	Butyl ether 0.1M $HClO_4$	3	4.1±0.1	0.0025-0.04 0.1	A(7)	a	62D(r)
Tb	Toluene 1M $(Na,H)NO_3$	3	2.50±0.08	0.005-0.05 0.05-0.5	A	c	66Ka
Tb	Chloroform 1M $HClO_4$	3	(orig)	-	N(7)	-	66Kc
Dy	Toluene 1M $(Na,H)NO_3$	3	3.01±0.08	0.005-0.05 0.03-0.3	A	c	66Ka
Ho	Butyl ether 0.1M $HClO_4$	3	5.0±0.1	0.0025-0.05 0.1	A(7)	a	62D(r)
Ho	Toluene 1M $(Na,H)NO_3$	3	3.37±0.08	0.005-0.05 0.05-1.0	A	c	66Ka
Er	Toluene 1M $(Na,H)NO_3$	3	3.77±0.08	0.005-0.05 0.1-1.0	A	c	66Ka

continued

TABLE III-2 (continued)

M	Diluent Aq. phase	u	log $K_{u,3}$	Ranges of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Tm	Butyl ether 0.1M $HClO_4$	3	6.0±0.2	0.001-0.03 0.1	A(7)	a	62D(r)
Tm	Toluene 1M $(Na,H)NO_3$	3	4.36±0.08	0.005-0.05 0.2-1.0	A	c	66Ka
Tm	Chloroform 1M $HClO_4$	3	(orig)	-	N(7)	-	66Kc
Yb	Toluene 1M $(Na,H)NO_3$	3	4.8±0.1	0.005-0.05 0.2-1.0	A	c	66Ka
Yb	CCl_4 Dilute HNO_3	3	(orig)	-	N(7,11b,19)	-	62S
Lu	Butyl ether 0.1M $HClO_4$	3	6.8±0.2	0.0016-0.025 0.1	A(7)	a	62D(r)
Lu	Toluene 1M $(Na,H)NO_3$	3	5.3±0.1	0.005-0.05 0.2-1.0	A	c	66Ka
Y	Butyl ether 0.1M $HClO_4$	3	5.1±0.1	0.0014-0.04 0.1	A(7)	a	62D(r)
Y	Toluene 1M $(Na,H)NO_3$	3	3.7±0.1	0.005-0.05 0.2-1.0	A	c	66Ka
Y	Chloroform HNO_3,$HClO_4$	3	3.2±0.1	0.003-0.1 0.1-1.0	R(19)	-	57D(r),66Kc
Y	Benzene Dilute HNO_3	3	(orig)	-	N(14,19)	-	61S
U	Benzene 0.2M (Na,H)Cl	3	0.15±0.2	0.05-0.5 0.025-0.2	A(15)	b	70S(r)
Am	Butyl ether 0.1M $HClO_4$	3	1.90±0.08	0.01-0.4 0.1	A(7)	a	62D(r)
Am	Hexane 0.1M HNO_3	3	2.8±0.1	0.01-0.1 0.1	A(7)	a	60D(r)
Am	CCl_4 0.1M HNO_3	3	1.4±0.1	0.02-0.2 0.1	A(7)	a	60D(r)
Am	Propyl ether 0.1M HNO_3	3	0.85±0.07	0.02-0.2 0.1	A(7)	a	60D(r)
Am	Chloroform 0.1M HNO_3	3	-0.35±0.05	0.05-0.5 0.1	A(7)	a	60D(r)
Am	MiBK 0.1M HNO_3	3	-0.6±0.1	0.08-0.5 0.1	A(7)	a	60D(r)

continued

TABLE III-2 (continued)

M	Diluent Aq. phase	u	log $K_{u,3}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Am	Benzene Dilute HNO_3	3	(orig)	-	N(19,22)	-	63Z
Cm	Butyl ether 0.1M $HClO_4$	3	1.91±0.06	0.01-0.4 0.1	A(7)	a	62D(r)
Extractant: Di-n-pentyl phosphoric acid							
La	Toluene 1M $(Na,H)NO_3$	3	-0.6±0.1	0.01-0.2 0.0025-0.06	A	-	66Ka
Ce	Toluene 1M $(Na,H)NO_3$	3	-0.15±0.1	0.01-0.2 0.0025-0.05	A	-	66Ka
Pm	Toluene 1M $(Na,H)NO_3$	3	0.36±0.08	0.005-0.05 0.005-0.1	A	-	66Ka
Sm	Toluene 1M $(Na,H)NO_3$	3	1.12±0.08	0.005-0.05 0.05-0.3	A	-	66Ka
Eu	Toluene 1M $(Na,H)NO_3$	3	1.3±0.1	0.005-0.05 0.05-0.3	A	-	66Ka
Tb	Toluene 1M $(Na,H)NO_3$	3	2.3±0.1	0.005-0.05 0.05-0.5	A	-	66Ka
Dy	Toluene 1M $(Na,H)NO_3$	3	2.86±0.08	0.005-0.05 0.05-0.5	A	-	66Ka
Ho	Toluene 1M $(Na,H)NO_3$	3	2.87±0.06	0.005-0.05 0.05-1.0	A	-	66Ka
Er	Toluene 1M $(Na,H)NO_3$	3	3.67±0.06	0.005-0.05 0.1-1.0	A	-	66Ka
Tm	Toluene 1M $(Na,H)NO_3$	3	4.26±0.06	0.005-0.05 0.2-1.0	A	-	66Ka
Yb	Toluene 1M $(Na,H)NO_3$	3	4.71±0.06	0.005-0.05 0.2-1.0	A	-	66Ka
Lu	Toluene 1M $(Na,H)NO_3$	3	5.12±0.06	0.005-0.05 0.2-1.0	A	-	66Ka
Y	Toluene 1M $(Na,H)NO_3$	3	3.59±0.06	0.005-0.05 0.1-1.0	A	-	66Ka
Y	Benzene Dilute HNO_3	3	(orig)	-	N(11a,11b,12)	-	60P

continued

TABLE III-2 (continued)

M	Diluent Aq. phase	u	log $K_{u,3}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Extractant: Diisopentyl phosphoric acid							
La	Toluene 1M $(Na,H)NO_3$	3	-1.15±0.08	0.01-0.2 0.0025-0.04	A	-	66Ka
Ce	Toluene 1M $(Na,H)NO_3$	3	-0.61±0.08	0.01-0.2 0.0025-0.02	A	-	66Ka
Pm	Toluene 1M $(Na,H)NO_3$	3	0.10±0.08	0.01-0.2 0.03-0.3	A	-	66Ka
Sm	Toluene 1M $(Na,H)NO_3$	3	0.64±0.06	0.02-0.06 0.02-0.2	A	-	66Ka
Eu	Toluene 1M $(Na,H)NO_3$	3	1.02±0.06	0.005-0.05 0.01-0.3	A	-	66Ka
Tb	Toluene 1M $(Na,H)NO_3$	3	2.29±0.06	0.005-0.05 0.05-0.5	A	-	66Ka
Dy	Toluene 1M $(Na,H)NO_3$	3	2.69±0.08	0.005-0.05 0.03-0.3	A	-	66Ka
Ho	Toluene 1M $(Na,H)NO_3$	3	3.01±0.08	0.005-0.05 0.05-1.0	A	-	66Ka
Er	Toluene 1M $(Na,H)NO_3$	3	3.51±0.08	0.005-0.05 0.1-1.0	A	-	66Ka
Tm	Toluene 1M $(Na,H)NO_3$	3	4.10±0.08	0.005-0.05 0.2-1.0	A	-	66Ka
Yb	Toluene 1M $(Na,H)NO_3$	3	4.53±0.08	0.005-0.05 0.2-1.0	A	-	66Ka
Lu	Toluene 1M $(Na,H)NO_3$	3	4.76±0.08	$5x10^{-4}$-0.05 0.2-1.0	A	-	66Ka
Y	Toluene 1M $(Na,H)NO_3$	3	3.46±0.06	0.005-0.05 0.2-1.0	A	-	66Ka
Extractant: Di-n-octyl phosphoric acid							
La	Toluene 1M $(Na,H)NO_3$	3	-0.61±0.08	0.01-0.2 0.0025-0.04	A	-	66Ka
Ce	Heptane 1M $(Na,H)Cl$	2.5	2.05±0.06	0.02-0.3 0.06-1.0	A	-	70M
Ce	Toluene 1M $(Na,H)NO_3$	3	-0.03±0.08	0.01-0.2 0.0025-0.02	A	-	66Ka

continued

TABLE III-2 (continued)

M	Diluent Aq. phase	u	log $K_{u,3}$	Ranges of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Ce	Benzene 1M (Na,H)Cl	3	-0.10±0.06	0.02-0.3 0.06-1.0	A	-	70M
Pm	Heptane 1M (Na,H)Cl	2.5	2.35±0.06	0.02-0.3 0.06-1.0	A	-	70M
Pm	Toluene 1M (Na,H)NO_3	3	0.47±0.06	0.01-0.2 0.03-0.3	A	-	66Ka
Pm	Benzene 1M (Na,H)Cl	3	0.38±0.06	0.02-0.3 0.06-1.0	A	-	70M
Sm	Toluene 1M (Na,H)NO_3	3	1.00±0.06	0.02-0.3 0.02-0.2	A	-	66Ka
Eu	Heptane 1M (Na,H)Cl	2.5	2.75±0.06	0.02-0.3 0.06-1.0	A	-	70M
Eu	Heptane 1M (Na,H)NO_3	2.5	2.98±0.06	0.005-0.05 0.05-1.0	A	f	67Kc
Eu	Isooctane 1M (Na,H)NO_3	2.5	2.81±0.08	0.005-0.05 0.05-1.0	A	g	67Kc
Eu	Cyclohexane 1M (Na,H)NO_3	2.5	2.55±0.08	0.005-0.05 0.05-1.0	A	-	67Kc
Eu	Butyl ether 1M (Na,H)NO_3	3	2.14±0.08	0.005-0.05 0.05-0.5	A	-	67Kc
Eu	CCl_4 1M (Na,H)NO_3	3	(orig)	-	N(22)	i	67Kc
Eu	*p*-Xylene 1M (Na,H)NO_3	3	1.48±0.08	0.005-0.05 0.05-0.5	A	-	67Kc
Eu	*o*-Xylene 1M (Na,H)NO_3	3	1.43±0.08	0.005-0.05 0.05-0.5	A	-	67Kc
Eu	Bromoform 1M (Na,H)NO_3	3	(orig)	-	N(22)	i	67Kc
Eu	Toluene 1M (Na,H)NO_3	3	1.20±0.08	0.005-0.05 0.02-0.3	A	-	66Ka,67Kc
Eu	Chlorobenzene 1M (Na,H)NO_3	3	1.20±0.08	0.005-0.05 0.01-0.2	A	-	67Kc
Eu	Benzene 1M (Na,H)Cl	3	1.20±0.06	0.02-0.3 0.06-1.0	A	-	70M
Eu	Benzene 1M (Na,H)NO_3	3	1.13±0.08	0.005-0.05 0.01-0.2	A	-	67Kc

continued

TABLE III-2 (continued)

M	Diluent Aq. phase	u	log $K_{u,3}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Eu	CH_2Cl_2 1M $(Na,H)NO_3$	3	0.92±0.08	0.01-0.2 0.02-0.3	A	-	67Kc
Eu	Chloroform 1M $(Na,H)NO_3$	3	0.25±0.08	0.01-0.2 0.01-0.2	A	-	67Kc
Eu	Nitrobenzene 1M $(Na,H)NO_3$	2.5	0.89±0.06	0.02-0.2 0.02-0.3	A	-	67Kc
Eu	MiBK 1M $(Na,H)NO_3$	2	(orig)	-	N	h	67Kc
Tb	Heptane 1M $(Na,H)NO_3$	2.5	3.88±0.08	0.005-0.05 0.1-1.0	A	f	67Kc
Tb	*Iso*octane 1M $(Na,H)NO_3$	2.5	3.74±0.08	0.005-0.05 0.1-1.0	A	g	67Kc
Tb	Cyclohexane 1M $(Na,H)NO_3$	2.5	3.46±0.08	0.005-0.05 0.1-1.0	A	-	67Kc
Tb	Butyl ether 1M $(Na,H)NO_3$	3	3.10±0.08	0.005-0.05 0.1-1.0	A	-	67Kc
Tb	CCl_4, $CHBr_3$ 1M $(Na,H)NO_3$	3	(orig)	-	N(22)	i	67Kc
Tb	*p*-Xylene 1M $(Na,H)NO_3$	3	2.60±0.08	0.005-0.05 0.1-1.0	A	-	67Kc
Tb	*o*-Xylene 1M $(Na,H)NO_3$	3	2.55±0.08	0.005-0.05 0.1-1.0	A	-	67Kc
Tb	Toluene 1M $(Na,H)NO_3$	3	2.39±0.08	0.005-0.05 0.1-1.0	A	-	66Ka,67Kc
Tb	Benzene 1M $(Na,H)NO_3$	3	2.11±0.08	0.005-0.05 0.05-0.5	A	-	67Kc
Tb	Chlorobenzene 1M $(Na,H)NO_3$	3	2.25±0.08	0.005-0.05 0.05-0.5	A	-	67Kc
Tb	CH_2Cl_2 1M $(Na,H)NO_3$	3	2.00±0.08	0.005-0.05 0.02-0.3	A	-	67Kc
Tb	Chloroform 1M $(Na,H)NO_3$	3	1.25±0.08	0.005-0.05 0.01-0.3	A	-	67Kc
Tb	Nitrobenzene 1M $(Na,H)NO_3$	2.5	1.90±0.08	0.005-0.05 0.01-0.3	A	-	67Kc
Tb	MiBK 1M $(Na,H)NO_3$	2	(orig)	-	N	h	67Kc

continued

TABLE III-2 (continued)

M	Diluent Aq. phase	u	log $K_{u,3}$	Range of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Dy	Toluene 1M $(Na,H)NO_3$	3	2.98±0.08	0.005-0.05 0.03-0.3	A	-	66Ka
Ho	Toluene 1M $(Na,H)NO_3$	3	3.32±0.08	0.005-0.05 0.05-1.0	A	-	66Ka
Er	Toluene 1M $(Na,H)NO_3$	3	3.74±0.08	0.005-0.05 0.1-1.0	A	-	66Ka
Tm	Heptane 1M (Na,H)Cl	2.5	5.45±0.06	0.02-0.3 0.06-1.0	A	-	70M
Tm	Toluene 1M $(Na,H)NO_3$	3	4.34±0.08	0.005-0.05 0.1-1.0	A	-	66Ka
Tm	Benzene 1M (Na,H)Cl	3	3.90±0.06	0.02-0.3 0.06-1.0	A	-	70M
Yb	Toluene 1M $(Na,H)NO_3$	3	4.76±0.08	0.005-0.05 0.2-1.0	A	-	66Ka
Lu	Toluene 1M $(Na,H)NO_3$	3	5.08±0.08	0.005-0.05 0.2-1.0	A	-	66Ka
Y	Heptane 1M (Na,H)Cl	2.5	4.75±0.06	0.02-0.3 0.06-1.0	A	-	70M
Y	Toluene 1M $(Na,H)NO_3$	3	3.67±0.08	0.005-0.05 0.1-1.0	A	-	66Ka
Y	Benzene 1M (Na,H)Cl	3	3.20±0.08	0.02-0.3 0.06-1.0	A	-	70M
Am,Cm	Heptane 1M (Na,H)Cl	2.5	2.05±0.06	0.02-0.3 0.06-1.0	A	-	70M
Am,Cm	Benzene 1M(Na,H)Cl	3	-0.10±0.06	0.02-0.3 0.06-1.0	A	-	70M

System involving M = Cm, Bk or Cf and (H)DAP, (H)DHpP, (H)DNP or (H)DLP

M	Diluent Aq. phase	u	log $K_{u,3}$	Range	Category	Note	Ref.
M	Decane Dilute HNO_3	3	(orig)	-	N(7,19)	d	74V

Notes:

a) See note b) in III.2.1 (u = 3 is well established here).

b) There are no indications of a distorting effect of U(IV) which could eventually be present in a small amount.

c) The difference between $\overline{C}_{A,i}$ and $2\overline{C}_{dim}$ due to the aqueous solubility of (H)DBP has been neglected and, thus, the log $K_{3,3}$ values are systematically

low by approximately 0.05 logarithmic unit.
d) A value of u = 3 has been assumed without confirming it by the measurement of the log $D_M = f(\log \overline{C}_{dim})$ dependency (it should be remembered that u = 2.5 has been found (66Ka,70M) in systems involving an aliphatic diluent and an extractant with long alkyl groups, namely (H)DOP). At least some of the $K_{3,3}$ values given for different ionic strengths have been calculated from one single D_M value. The authors also have made an extrapolation of the $K_{3,3}$ values to I = 0 in order to determine 'effective' equilibrium constants of the extraction reaction; the extrapolation is hardly justified because under the conditons of the work it is extremely sensitive to subjective errors.
e) A rough reevaluation of the data indicates that in contradiction to what is said in the original paper no correction has been made for the distribution of (H)DBP between the phases and, moreover, log D_M has been plotted vs. log $\overline{C}_{A,i}$ and not log $\overline{C}_{dim}$.
f) The equilibrium constant is also valid for an analogous system involving dodecane diluent.
g) The <u>iso</u>octane diluent has been 2,2,4-trimethylpentane.
h) The equilibrium constant is obviously ${}^{m}K_{4,3}$, but a clear definition is missing in the original paper.
i) The extractant has been reported (68K) to form higher self-associates than dimers in CCl_4 and bromoform.

In comparing $K_{3,3}$ values reported for different ionic media, the effect of complexation of lanthanides(III) by nitrate and chloride ions was roughly estimated in taking the corresponding stability constants from (62P,67K, 69Mb).

III.2.3. EXTRACTION OF BISMUTH(III)

A part of the data given in (74Y) is tentatively acceptable (see Table III-3), in spite of the error sources indicated and the unspecified temperature, but within correspondingly large statistical deviations. The reasons for the acceptability are the obviously good reproducibility of the experimental work and the obedience of the correlations 1 and 4 listed in III.1.

Notes:
a) See note c) in III.2.2.
b) See note i) in III.2.2.

III.2.4. EXTRACTION OF THORIUM(IV), PLUTONIUM(IV) AND HAFNIUM(IV)

A survey of the data is given in Table III-4. Notes:

a) D_M has not been measured as a function of the H^+ and NO_3^- concentrations and, consequently, the reaction stoichiometry is not properly proven.
b) <u>sec</u>-Hexanol is 4-methyl-2-pentanol.
c) Different Pu(IV) complexes have been found to be extracted in two analo-

Table III-3. Equilibrium constants of the extraction of Bi(III) from 1.0M (Na,H)ClO_4 at $[H^+]$ = 0.4 to 1 g-ion dm^{-3} and 20° to 25°C (74Y); see explanation in I.5

Diluent	u	log $K_{u,3}$	Range of $\overline{C}_{A,i}$ F	Category (error source no.)	Note
Extractant: Di-n-butyl phosphoric acid					
Octane, heptane, hexane, cyclohexane, CCl_4	2.5,3	(orig)	-	N(16,21a)	-
Butyl ether	3	3.3±0.1	0.06-0.2	A(16)	a
Xylene	3	2.85±0.1	0.1-0.3	A(16)	a
Bromoform	3	2.8±0.1	0.1-0.4	A(16)	a
Toluene	3	2.6±0.1	0.12-0.4	A(16)	a
Benzene	3	2.4±0.1	0.2-0.5	A(16)	a
Chlorobenzene	3	2.6±0.1	0.1-0.3	A(16)	a
Chloroform	3	1.8±0.1	0.2-0.7	A(16)	-
Extractant: Di-n-octyl phosphoric acid					
Octane, heptane, hexane	2.5	4.4±0.15	0.015-0.06	A(14,16)	-
Cyclohexane	2.5	4.1±0.15	0.025-0.1	A(16)	-
CCl_4, bromoform	3	(orig)	-	N(16,22)	b
Butyl ether	3	3.8±0.1	0.06-0.16	A(16)	-
Xylene	3	3.25±0.1	0.08-0.16	A(16)	-
Toluene	3	3.0±0.1	0.1-0.3	A(16)	-
Benzene	3	2.8±0.1	0.16-0.4	A(16)	-
Chlorobenzene	3	2.9±0.1	0.12-0.4	A(16)	-
Chloroform	3	2.2±0.1	0.2-0.7	A(16)	-

gous systems, namely $Pu(NO_3)_3A.HA$ in extraction from 6M (Li,H)NO_3 (59S), and $Pu(NO_3)_2A_2.2HA$ in extraction from 6M (Na,H)NO_3 (63D). In both papers the data are well documented and the error is probably to be sought in the starting material: Pu(IV) has been depolymerized in the stock solution in (63D), while no measure of such kind is mentioned in (59S).

d) Reactions with v,u = 1,2 and 1,2.5 have been found to proceed simultaneously in the extraction from 1M HNO_3. The determination of the composition of the complex extracted from 6M (Na,H)NO_3 is not fully justified: an error from the source 21a may become very considerable, because K_D and K_2 of (H)DBP in the system depends significantly on the hydrogen ion con-

TABLE III-4. Data on the extraction of Th(IV), Pu(IV) and Hf(IV) with di-*n*-alkyl phosphoric acids at an unspecified room temperature (66Kb,67Ka), 19° to 22°C (59S,63Sa,67N,68N,76H) and 25°C (63D,64Da,71L,71La). If u and v are not given numerically, see the corresponding note. An asterisk denotes a numerical value of ${}^{m}K_{v,u,4}$, otherwise $K_{v,u,4}$ is given. See explanation in I.5

M	Diluent Aq. phase	v,u	log $K_{v,u,4}$	Range of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Extractant: Di-n-butyl phosphoric acid							
Th	Chloroform 1M $(Na,H)ClO_4$	1,2.5	6.65±0.15	0.0001-0.03 0.1-1.0	A	-	64Da(r)
Th	Chloroform 1M (Na,H)Cl	0,3	6.85±0.1	0.002-0.06 0.2-1.0	A	-	64Da(r)
Th	Chloroform 1M $(Na,H)NO_3$	1,2.5	(orig)	-	N(7)	-	64Da
Th	Hexane 1M HCl, HNO_3	1,2.5	(orig)	-	N(7,12,21a)	-	64Da
Th	*sec*-Hexanol 1M $(Na,H)NO_3$	1,4	4.2±0.1*	0.1-0.4 0.14-1.0	A	b	64Da(r)
Th	*sec*-Hexanol 1M $(Na,H)NO_3$	2,2	2.0±0.1*	0.004-0.06 0.14-1.0	A	b	64Da(r)
Th	CCl_4 0.95M HNO_3	0,3	(orig)	-	N(7,21a)	a	63Sa
Pu	Benzene $(Na,Li,H)NO_3$	diff.	(orig)	-	N	c	59S,63D
Pu	CCl_4 $(Na,H)NO_3$	diff.	(orig)	-	N(12,21a)	d	67Ka
Pu	CCl_4 1M HNO_3	-	(orig)	-	N(7)	e	66Kb
Hf	2-Ethylhexanol 2M $(Li,H)ClO_4$	0,4	8.8±0.1*	0.014-0.05 1.0-2.0	A	-	76H
Hf	2-Ethylhexanol 3.5M $HClO_4$	0,4	9.0±0.1*	0.016-0.06 3.5	A	-	76H
Hf	2-Ethylhexanol 2M (Na,H)Cl	0,4	(orig)	-	N	f	76H
Hf	Hexane $(Na,H)HSO_4$	diff.	(orig)	-	N(21a)	g	71L,71La
Hf	Different Dil. HCl,$HClO_4$	1,2.5	(orig)	-	N(21a)	h	67N,68N

continued

TABLE III-4 (continued)

M	Diluent Aq. phase	v,u	log $K_{u,v,4}$	Range of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Extractant: Di-n-pentyl phosphoric acid							
Hf	Toluene Dil. HCl,$HClO_4$	1,2.5	(orig)	-	N(21b)	h	67N,68N
Extractant: Di-n-octyl phosphoric acid							
Hf	Octane Dil. HCl,$HClO_4$	1,1.5	(orig)	-	N(21b)	h	67N,68N

centration (67Kb).

e) The distribution of Pu(IV) has been studied in the presence of the THxPO (= B) synergist. The equilibrium constant has not been clearly defined and the composition of the complex extracted, namely $Pu(NO_3)_2A_2B$, has not been properly proven.

f) The ${}^{m}K_{0,4,4}$ value includes a term expressing the formation of Hf(IV) chlorocomplexes in the aqueous phase with stability constants valid at I = 3; however, the distribution of Hf(IV) has been measured at I = 2.

g) A K_D value of (H)DBP valid in a system involving 0.1M H_2SO_4 has been taken, i.e. the only one known for a sulfate containing system, but in the distribution measurements with Hf(IV) the aqueous phase has been 0.5 or 1M (Na,H)HSO_4. This can play a significant role in a system in which the error source 21a can hardly be avoided. Four species, namely $\overline{HfA_4}$, $\overline{HfA_4.HA}$, $\overline{Hf(SO_4)A_2.2HA}$ and $\overline{Hf(SO_4)A_2.3HA}$, are suggested to be formed in the organic phase containing the (H)DBP extractant alone (71L) and even six species in the presence of TOPO (71La); the plausibility of the reported composition of the species, and thus the justification of the definition of the equlibrium constants, cannot be assessed until additional data from independent sources become available.

h) The distribution measurements with Hf(IV) have been made in systems involving 2M mineral acids, but in the evaluation of the results K_2 and K_D values of the extractants valid at significantly lower H^+ concentrations have been taken.

III.3. DIALKYL PHOSPHORIC ACIDS WITH BRANCHED ALKYL CHAINS; BIS(ALKOXYALKYL)PHOSPHORIC ACIDS

III.3.1. BIS(2-ETHYLHEXYL) PHOSPHORIC ACID

(H)DE-HP has been shown to exhibit nonideal behavior in aliphatic diluents at $\overline{C}_A > 0.05F$ (59B,60B,71Ka). This has been ascribed to partial trimerization in the organic phase (60B,71Ka) or to possible nonspecific interactions (59B). In spite of these deviations from ideality, linear log D_M = f(log $\overline{C}_{A,i}$) dependencies (implying that $\overline{C}_{dim} = 0.5\overline{C}_{A,i}$) have been observed by some other authors (see Table III-5) at much higher (H)DE-HP concentrations in alkane diluents; since the cause of the nonideality has not been definitively clarified, equilibrium constants gained from those data must be considered as subject to an error resulting from the source 22 and are not acceptable.

III.3.1.1. EXTRACTION OF ALKALI METALS AND OF SILVER(I)

A survey of the data is given in Table III-5.

TABLE III-5. Data on the extraction of Na(I), Rb(I), Cs(I), Ag(I), Cu(II), Cd(II), Zn(II), Mn(II), Co(II) and Ni(II) at an unspecified room temperature (67D,70Sa,72Lb,72S,72Sa), 22°C (70Sb,73S,74Gb), 25°C (69B,69Ka) and 30° to 70°C (74S). An asterisk denotes a numerical value of ${}^mK_{u,z}$, otherwise $K_{u,z}$ is given. Notes a) to c) - see III.3.1.1, other notes - see III.3.1.3. See also explanation in I.5

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Na	Benzene 0.5M $(Na,H)NO_3$	2	-4.26±0.04	0.1-0.5 0.0006-0.03	R	a	69Ka
Na	Benzene 0.1M $(Li,H)ClO_4$	2	-4.3±0.1	0.3-1.0 0.01-0.1	A(7)	b,c	72Lb
Na	Benzene 0.01M HCl	2	-4.6±0.1	0.1-1.0 0.01	A(7)	b,c	67D(r)
Na	CCl_4 0.1M $(Li,H)ClO_4$	2	-3.5±0.1	0.3-1.0 0.01-0.1	A(7)	b,c	72Lb
Na	Xylene 0.1M $(Li,H)ClO_4$	2	-3.8±0.1	0.3-1.0 0.01-0.1	A	b	72Lb
Na	Octanol 0.1M $(Li,H)ClO_4$	1	-3.55±0.1*	0.3-1.0 0.01-0.1	A(7)	b,c	72Lb

continued

TABLE III-5 (continued)

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Na	Decane 0.1M $(Li,H)ClO_4$	2	(orig)	-	N(22)	-	72Lb
Na	Decane 0.1M $(Li,H)NO_3$	2	(orig)	-	N(22)	-	74S
Rb	CCl_4 0.1M $(Li,H)ClO_4$	2	-3.65±0.1	0.3-1.0 0.01-0.1	A(7)	b,c	72Lb
Rb	Xylene 0.1M $(Li,H)ClO_4$	2	-4.1±0.1	0.3-1.0 0.01-0.1	A	b	72Lb
Rb	Octanol 0.1M $(Li,H)ClO_4$	2	-3.6±0.1*	0.3-1.0 0.01-0.1	A(7)	b,c	72Lb
Rb	Decane 0.1M $(Li,H)ClO_4$	2	(orig)	-	N(22)	-	72Lb
Cs	CCl_4 0.1M $(Li,H)ClO_4$	2	-3.85±0.1	0.3-1.0 0.01-0.1	A(7)	b,c	72Lb
Cs	Benzene 0.1M $(Li,H)ClO_4$	2	-4.3±0.1	0.3-1.0 0.01-0.05	A	b	72Lb
Cs	Benzene 0.01M HCl	2	-4.5±0.1	0.4-1.0 0.01	A(7)	b,c	67D(r)
Cs	Octanol 0.1M $(Li,H)ClO_4$	2	-3.7±0.1*	0.3-1.0 0.01-0.1	A(7)	b,c	72Lb
Cs	Decane 0.1M $(Li,H)ClO_4$	2	(orig)	-	N(22)	-	72Lb
Ag	Decane $(Li,H)(NO_3,ClO_4)$	1.5	(orig)	-	N(22)	-	70Sb
Cu	Benzene 0.5M $(Na,H)NO_3$	2	-3.39±0.05	0.01-0.5 0.004-0.25	A	-	69Ka
Cu	Dodecane 1M $(Na,H)NO_3$	2	-3.1±0.1	0.003-0.03 0.003-0.1	A	-	74Gb(r)
Cu	Kerosene $\leq$0.2M $Cu(SO_4)_2$	2	(orig)	-	N(7,10,14,22)	-	69B
Cd	Dodecane 1M $(Na,H)NO_3$	2.5	-1.65±0.1	0.005-0.03 0.003-0.1	A	-	74Gb(r)
Zn	CCl_4 0.1M $(Li,H)ClO_4$	2	-0.19±0.1	0.15-0.7 0.01-0.1	A(7)	d,e,f	72Sa
Zn	Xylene 0.1M $(Li,H)ClO_4$	2	-0.22±0.1	0.15-0.7 0.01-0.1	A(7)	d,e,f	72Sa

continued

TABLE III-5 (continued)

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Zn	Benzene 0.1M $(Li,H)ClO_4$	2	-0.30±0.1	0.15-0.7 0.01-0.1	A(7)	d,e,f	72Sa
Zn	Chloroform 0.1M $(Li,H)ClO_4$	2	-0.60±0.1	0.15-0.7 0.01-0.1	A(7)	d,e,f	72Sa
Zn	<u>n</u>-Alkanes 0.1M $(Li,H)NO_3$	1.5	(orig)	-	N(22)	g	72Sa
Mn	CCl_4 0.1M $(Li,H)ClO_4$	2.5	-2.91±0.1	0.1-0.6 0.01-0.1	A	d,e	72S
Mn	Xylene 0.1M $(Li,H)ClO_4$	2.5	-3.22±0.1	0.1-0.6 0.01-0.1	A	d,e	72S
Mn	Benzene 0.1M $(Li,H)ClO_4$	2.5	-3.48±0.1	0.1-0.6 0.01-0.1	A(7)	d,e,f	72S
Mn	Chloroform 0.1M $(Li,H)ClO_4$	2.5	-3.80±0.1	0.1-0.6 0.01-0.1	A(7)	d,e,f	72S
Mn	<u>n</u>-Alkanes 0.1M $(Li,H)ClO_4$	2	(orig)	-	N(22)	g	72S
Ni	CCl_4 0.05M $(Li,H)NO_3$	2	-6.24±0.04	0.45-1.1 0.001-0.01	A(7)	d,f	73S
Ni	Benzene 0.05M $(Li,H)NO_3$	2	-6.79±0.04	0.45-1.1 0.001-0.01	A(7)	d,f	73S
Ni	Chloroform 0.05M $(Li,H)NO_3$	2	-6.90±0.04	0.45-1.1 0.001-0.01	A(7)	d,f	73S
Ni	Octane 0.05M $(Li,H)NO_3$	2	(orig)	-	N(22)	-	73S
Ni	Kerosene <0.07M $Ni(SO_4)_2$	2	(orig)	-	N(7,10,14,22)	-	69B
Co	Dodecane 1M $(Na,H)NO_3$	2	-4.95±0.1	0.01-0.03 0.005-0.02	A	-	74Gb(r)
Co	Decane $(Li,H)ClO_4$	2	(orig)	-	N(22)	-	70Sa
Co	Kerosene ≤0.2M $Co(SO_4)_2$	2	(orig)	-	N(7,10,14,22)	-	69B

Notes:

a) The constant is recommended because of its consistency with results reported in (67D,72Lb); at I = 3, $K_{2,1}$ seems to be ten times lower (71M).

b) A lower accuracy was assigned to the constants here than in the original paper, because they have been calculated from results obtained at an unspecified room temperature.

c) The log D_M = f(log $[H^+]$) dependency is not presented; this is no serious omittance, because the slope of the dependency has been well documented in the literature to be -1.

III.3.1.2. EXTRACTION OF ALKALINE EARTH ELEMENTS

No attempt was made here to assess equilibrium constants reported for Ca(II), Sr(II) and Ba(II), because there is no agreement about the composition of the complexes extracted. Species ranging from $\overline{MA_2.2HA}$ to $\overline{MA_2.4HA}$ have been found to be formed in systems with different diluents (62Pb,65M, 66M,67D,68S,72Ld). The slope of the log D_M = f(log $\overline{C}_{dim}$) dependency appears to be influenced not only by the nature of the diluent, but also by the range of the (H)DE-HP concentration in the organic phase, the sodium concentration in the aqueous phase and the fraction of (H)DE-HP converted in the organic phase to a sodium salt.

III.3.1.3. EXTRACTION OF BIVALENT TRANSITION METALS

A survey of the data is given in Table III-5. Notes:

d) The $K_{u,2}$ value is acceptable exclusively at the given ionic strength adjusted by perchloric acid and lithium perchlorate or nitrate, because at $I < 0.1$ the constant is strongly dependent on I. An attempt to determine $K^o_{u,2}$ by extrapolation to zero ionic strength, as done in the original work, is not justified; the extrapolation can hardly be performed without a considerable subjective error.

e) During the experimental work the temperature has been kept constant within ±0.3°C, but has not been specified in the paper (most probably it has been 20 or 25°C). Thus an absolute inaccuracy of 0.1 logarithmic unit was assigned to the constant, but its relative accuracy with regard to other constants reported in the same paper can be as good as 0.04 logarithmic unit.

f) The log D_M = f(log $[H^+]$) dependency is missing in the paper, but this does not depreciate the plausibility of conclusions made therein. It has been proven in the literature that the dependency has a slope of -2.

g) The diluents are hexane, octane and decane.

III.3.1.4. EXTRACTION OF URANIUM(VI) AND BERYLLIUM(II)

A survey of the data is given in Table III-6.

TABLE III-6. Data on the extraction of U(VI) and Be(II) with (H)DE-HP at an unspecified room temperature (61Ha,71Ra), 20°C (64G,66U,74R), 22°C (62Pa,64M) and 25°C (58B,68A). An asterisk denotes a numerical value of ${}^{m}K_{2,2}$, otherwise $K_{2,2}$ is given. See explanation in I.5

M	Diluent Aq. phase	log $K_{2,2}$	Ranges of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
U	Hexane 2M $(Na,H)ClO_4$	4.5±0.1	0.005-0.05 1.0	A	a,b	58B
U	Isooctane 1M $HClO_4$	4.45±0.15	0.0001-0.01 1.0	A	b,c	64G
U	Octane 0.1M $(Na,H)ClO_4$	4.35±0.1	0.001-0.05 0.09	A	b,d	66U(r)
U	CCl_4 Dilute HNO_3	3.9±0.1	→0-0.2 I →0	R	e	68A,71Ra
U	Toluene 1M $(Na,H)ClO_4$	3.58±0.05	0.01-0.1 0.06-1.0	A	-	62Pa
U	Toluene 1M $(Na,H)NO_3$	3.55±0.05	0.01-0.1 0.06-1.0	A	-	62Pa
U	Toluene 1M (Na,H)Cl	3.32±0.05	0.01-0.1 0.06-1.0	A	-	62Pa
U	Decanol 0.25M HCl	0.73±0.05*	< 0.03 0.25	A	b,g,h	64M
U	Pentanol 0.25M HCl	0.42±0.05*	< 0.03 0.25	A	b,g,h	64M
U	Pentanol 0.25M HNO_3	0.73±0.05*	< 0.03 0.25	A	b,g,h	64M
U	Octane 0.1M $(Na,H)NO_3$	-	-	N	f	66U
U	Toluene UO_2Cl_2+HCl	-	-	N	i	74R
Be	Kerosene Dilute HCl	(orig)	-	N(10,19,22)	-	61Ha

Notes:

a) Only the log $K_{2,2}$ value calculated from the log $D_M = f(\log \overline{C}_{dim})$ dependency was taken for Table III-6; the log $D_M = f(\log [H^+])$ dependency has been measured at $\overline{C}_{A,i} = 0.1F$ and so an error from the source no. 22 cannot be excluded.

b) The correctness of defining the equilibrium constant of the extraction reaction as $K_{2,2}$ is doubtless, even if only data from the log $D_M = f(\log \overline{C}_{A,i})$ dependency are taken for its calculation or the H^+ dependency is not presented. The log $D_M = f(\log [H^+])$ dependency has been very well documented in the literature to have a slope of -2 in systems involving different diluents ranging from nonpolar alkanes to polar alcohols. The validity of the $K_{2,2}$ value is in such case limited to a single concentration of the mineral acid employed.

c) The $K_{2,2}$ value has been calculated from the D_M vs. $\overline{C}_{A,i}$ data. The H^+ dependency has been measured at a variable ionic strength.

d) The log $D_M = f(\log \overline{C}_{dim})$ dependency at 0.09, 0.01 and 0.001 g-ion H^+ dm^{-3} has been numerically presented in the paper. Only the first set of data was taken for reevaluation, because at the lower H^+ concentrations U(VI) can be hydrolyzed to some extent in the aqueous phase.

e) The $K_{2,2}$ value also describes the distribution of U(VI) between 0.1F (H)DE-HP in CCl_4 and 9M $(NH_4,H)NO_3$, 8M $(Na,H)NO_3$ and 6M $(Li,H)NO_3$, if activity coefficients from (71Ra) are introduced.

f) A ${}^{m}K_{2,2}$ value has been calculated from very low D_M values measured at extremely low extractant concentrations. The results are sensitive to the presence of impurities.

g) The ${}^{m}K_{2,2}$ value has been calculated from the D_M vs. $\overline{C}_{A,i}$ data, because the H^+ dependency has been measured at a different ionic strength.

h) At >0.3F (H)DE-HP the extraction reaction is $UO_2^{2+} + 4\overline{HA} = \overline{UO_2A_2.2HA} + 2H^+$ and log ${}^{m}K_{4,2}$ is 2.61±0.05 (decanol/0.25M HCl), 1.97±0.05 (pentanol/0.25M HCl) and 1.19±0.05 (pentanol/0.25M HNO_3). D_M values measured at 0.03 to 0.3F (H)DE-HP can be calculated in combining the corresponding ${}^{m}K_{2,2}$ and ${}^{m}K_{4,2}$ values.

i) The thermodynamic equilibrium constant of the hypothetic reaction $UO_2^{2+} + 2\overline{HA} = \overline{UO_2A_2} + 2H^+$ has been caculated from distribution data obtained at a loading of the organic phase ranging from about 2 to almost 100 per cent. The very important facts have been neglected that the U(VI) complex formed with (H)DE-HP is highly polymerized in the organic phase at high loadings (58B) and that the stoichiometry of the extraction reaction strongly depends on the equilibrium U(VI) concentration in the organic phase. While the species $UO_2A_2.2HA$ predominates in the organic phase at low loadings, a polymeric complex of the type $(UO_2A_2)_n$ with n being as high as 10,000 may be expected to be extracted at a loading approaching 100 per cent. The number of possible intermediate steps between the two extremities must be enormously high.

Attempts have been made to characterize by equilibrium constants the formation of mixed U(VI) complexes extracted by (H)DE-HP in the presence of neutral organophosphorus synergists like TBP or TOPO (63B,74Mb). In view of the ability of (H)DBP to form a wide variety of synergic complexes

(68L) the interpretation suggested in (63B) for systems with (H)DE-HP seems to be too simple. On the other hand, a very complex system has been studied in (74Mb). Thus no assessment of the equilibrium constants is possible until an extensive additional experimental study has been made.

III.3.1.5. EXTRACTION OF LANTHANIDES(III), ACTINIDES(III), YTTRIUM(III) AND SCANDIUM(III)

In spite of the simple solution chemistry of the title elements, the possibility of obtaining (H)DE-HP in a pure state and a generally good reproducibility of distribution measurements with (H)DE-HP, there is often a surprising disagreemnent between extraction equilibrium constants reported by different authors for the same system. There is also some disagreement considering the composition of complexes extracted into (H)DE-HP solutions in aliphatic diluents: the log $D_M = f(\log \overline{C}_{A,i})$ dependency is in some papers said to be a straight line with a slope of 2.5, indicating the extraction of species of the type $\overline{MA_3.2HA}$ (67D,76M), while other authors (60B,71Ka) believe the dependency to be curved and explain the deviation from the slope 3 (corresponding to the formation of the usual complex $\overline{MA_3.3HA}$) by partial trimerization of (H)DE-HP in the organic phase. The latter interpretation will be accepted in this work. A confirmation is yielded by reevaluation of the data on the extraction of macro amounts of yttrium(III) by (H)DE-HP in kerosene (72B) in which the concentration of free (H)DE-HP has been varied by two ways: by varying $\overline{C}_{A,i}$ at a constant, low starting aqueous concentration of Y(III) and by varying the starting aqueous Y(III) concentration at constant $\overline{C}_{A,i}$. A nonvariant equilibrium constant could only be obtained with the supposition that the complex $MA_3.3HA$ was formed.

There is a general agreement that the slope of the log $D_M = f(\log [H^+])$ dependency is -3 in systems with aliphatic, halogenated and aromatic diluents and the log $D_M = f(\log \overline{C}_{A,i})$ dependency has the slope 3 in systems with halogenated and aromatic diluents. Thus distribution data may be fully acceptable for the calculation of equilibrium constants even if the error source number 7 has not been avoided.

The consistency of data obtained by different authors with various ionic media in the aqueous phase was assessed here in using the stability constants of chloride and nitrate complexes given in (62P,67K,69Mb).

A survey of the data is given in Table III-7. Notes:
a) The $K_{3,3}$ value, either taken directly from the original paper or calculated from data presented therein, is too high in comparison with analogous acceptable values.
b) A $K_{u,3}$ value with u = 2.4 found empirically has been calculated under the arbitraty assumption that the average degree of self-association of (H)DE-HP in the organic phase is 2.5. A possible increase of the degree of self-association with increasing $\overline{C}_{A,i}$ has not been taken into account.
c) The $K_{3,3}$ value was calculated from the D_M vs. $\overline{C}_{A,i}$ data; the log D_M = f(log $[H^+]$) dependency has been measured at $\overline{C}_{A,i}$ = 0.1F and so an error

TABLE III-7. Data on the extraction of lanthanides(III), actinides(III) and Sc(III) with (H)DE-HP at an unspecified room temperature (66G,67D,69M, 71C), 20°C (64G,76Ha), 22° to 23°C (57P,57Pa,58P,59P,64M,66Ka,69Ma,71K,72B, 73Z,76M) and 25°C (63P,68E,69A,72H,75C,75D,75M,76A). An asterisk denotes a numerical value of ${}^{m}K_{3,3}$, otherwise $K_{3,3}$ is given. See explanation in I.5

M	Diluent Aq. phase	log $K_{3,3}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
La	Toluene 1M (Na,H)ClO$_4$	-2.4±0.1	0.09-0.6 0.01-1.0	R	-	58P(r),63P(r)
La	Toluene Dilute HCl	-	-	N(7,19,22)	a	57Pa
La	Benzene Dilute HNO$_3$	-	-	N(19)	a	69Ma
La	Heptane Dilute HCl	-	-	N(7)	b	76Ha
Ce	Hexane 1M (Na,H)ClO$_4$	0.6±0.1	0.03-0.05 0.1	A	c	71K(r)
Ce	Toluene Dil. HClO$_4$,HCl	-1.8±0.1	0.5-0.6 0.023-0.16	A(7,19)	-	59P(r),63P(r)
Ce	Toluene Dilute HClO$_4$	(orig)	-	N	a	75C,75D
Ce	Heptane 1M (Na,H)Cl	-	-	N	d	76M
Pr	Toluene Dilute HClO$_4$	-1.5±0.1	0.6 0.023-0.12	A(7,19)	-	63P(r)
Nd	Toluene Dilute HClO$_4$	-1.3±0.1	0.6 0.04-0.16	A(7,19)	-	63P(r)
Nd	Heptane Dilute HCl	-	-	N(7)	b	76Ha
Nd	Benzene Dilute HNO$_3$	-	-	N(19)	a	69Ma
Pm	Toluene 1M (Na,H)ClO$_4$	-0.85±0.1	0.04-0.6 0.01-1.0	R	-	58P(r),63P(r)
Pm	Toluene Dilute HCl	-1.1±0.1	0.15-0.75 0.12-0.55	A(7,19)	-	57P(r),66G(r)
Pm	Toluene 1M (Na,H)NO$_3$	-1.7±0.1	0.02-0.2 0.03-0.3	A	-	66Ka
Pm	Heptane 1M (Na,H)Cl	-	-	N	d	76M

continued

TABLE III-7 (continued)

M	Diluent Aq. phase	log $K_{3,3}$	Range of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Sm	Toluene Dilute $HClO_4$	-0.5±0.1	0.6 0.08-2.0	A(7,19)	-	63P(r)
Sm	Toluene 1M $(Na,H)NO_3$	-0.95±0.1	0.02-0.2 0.02-0.3	A	-	66Ka
Sm	Toluene 1M $LiClO_4$	(orig)	-	N	e	75M
Sm	Benzene Dilute HNO_3	-	-	N(19)	a	69Ma
Eu	Hexane 1M $(Na,H)ClO_4$	2.55±0.1	0.01-0.05 0.02	A	c	71K(r)
Eu	Toluene 0.1M $(Na,H)ClO_4$	-0.1±0.1	0.0015-1.0 0.004-0.1	R	f	63P(r),67D(r), 76A
Eu	Toluene Dilute HCl	-0.4±0.1	0.75 0.2-0.7	A(7,19)	-	57P(r),66G(r)
Eu	Toluene 1M $(Na,H)NO_3$	-0.8±0.1	0.01-0.2 0.05-0.2	A	-	66Ka
Eu	Decanol 0.025M HCl	-2.63±0.05*	0.03-0.1 0.025	A	g	64M
Eu	Heptane 1M (Na,H)Cl	-	-	N	d	76M
Eu	CCl_4 NO_3^-, Cl^-	(orig)	-	N	h	67D(r),73Z
Eu	Xylene NO_3^-, Cl^-	(orig)	-	N	i	67D(r),73Z
Eu	Toluene Dilute $HClO_4$	(orig)	-	N	a	75C,75D
Eu	Toluene 1M $LiClO_4$	(orig)	-	N	e	75M
Eu	Benzene NO_3^-, Cl^-	(orig)	-	N	h	67D(r),69Ma(r), 71C,73Z
Eu	C_6H_5Cl, CH_2Cl_2 1M $(Na,H)NO_3$	(orig)	-	N	j	73Z
Gd	Toluene Dil. HCl,$HClO_4$	-0.05±0.1	0.6-1.6 0.1-1.0	A(7,19)	-	63P(r),66G(r)
Gd	Toluene Dilute $HClO_4$	(orig)	-	N	a	75C,75D

continued

TABLE III-7 (continued)

M	Diluent Aq. phase	log $K_{3,3}$	Range of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Gd	Toluene 1M $LiClO_4$	(orig)	-	N	e	75M
Tb	Toluene Dilute $HClO_4$	0.6±0.1	0.6 0.12-1.1	A(7,19)	-	63P(r)
Tb	Toluene 1M $(Na,H)NO_3$	0.4±0.1	0.02-0.3 0.02-0.1	A	-	66Ka
Tb	Toluene Dilute HCl	(orig)	-	N(7,19)	a	66G
Tb	Toluene 1M $LiClO_4$	(orig)	-	N	e	75M
Dy	Toluene Dilute $HClO_4$	1.0±0.1	0.6 0.3-2.0	A(7,19)	-	63P(r)
Dy	Toluene 1M $(Na,H)NO_3$	0.9±0.1	0.01-0.2 0.03-0.3	A	-	66Ka
Dy	Toluene 1M $LiClO_4$	(orig)	-	N	e	75M
Ho	Toluene Dilute $HClO_4$	1.3±0.1	0.6 0.3-2.0	A(7,19)	-	63P(r)
Ho	Toluene 1M $(Na,H)NO_3$	1.25±0.1	0.01-0.2 0.03-0.3	A	-	66Ka
Er	Toluene 1M $(Na,H)NO_3$	1.75±0.1	0.005-0.05 0.03-0.3	A	-	66Ka
Tm	Toluene 1M$(Na,H)ClO_4$	2.3±0.1	0.03-0.3 0.03-1.0	A	-	58P(r)
Tm	Toluene Dilute HCl	2.1±0.1	0.15-0.75 0.15-0.55	A(19)	-	57P(r)
Tm	Toluene 1M $(Na,H)NO_3$	2.3±0.1	0.005-0.05 0.05-0.5	A	-	66Ka
Tm	Octane 0.1M $(Na,H)ClO_4$	5.6±0.1	0.0002-0.003 0.001-0.01	A	-	69M
Tm	Decanol Dilute HCl	-2.33±0.05*	0.02-0.05 0.025	A	g	64M
Tm	Octane 0.1M $(Na,H)ClO_4$	-	-	N	k	69M
Tm	Heptane 1M $(Na,H)Cl$	-	-	N	d	76M

continued

TABLE III-7 (continued)

M	Diluent Aq. phase	log $K_{3,3}$	Range of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Tm	Toluene NO_3^-, ClO_4^-	(orig)	-	N	a	69A,73Z
Tm	Toluene Dilute $HClO_4$	(orig)	-	N	a	75C,75D
Tm	Different 1M $(Na,H)NO_3$	(orig)	-	N	j,l	73Z
Yb	Toluene 1M $(Na,H)NO_3$	2.8±0.1	0.005-0.05 0.05-0.5	A	-	66Ka
Lu	Toluene 1M $(Na,H)NO_3$	2.95±0.1	0.005-0.05 0.05-0.5	A	-	66Ka
Lu	Heptane 1M $(Na,H)Cl$	-	-	N	d	76M
Y	Toluene 1M $(Na,H)ClO_4$	1.8±0.1	0.03-0.3 0.03-1.0	A	-	58P(r)
Y	Toluene Dilute HCl	1.5±0.1	0.15-0.75 0.15-0.55	A	-	57P(r)
Y	Toluene 1M $(Na,H)NO_3$	1.6±0.1	0.005-0.05 0.03-0.3	A	-	66Ka
Y	Kerosene $Y(NO_3)_3$+HNO_3	4.4±0.1	0.25-1.00 0.1-1.0	A	m	72B(r)
Y	Decanol 0.025M HCl	-2.63±0.05*	0.03-0.07 0.025	A	g	64M
Y	Heptane 1M $(Na,H)Cl$	-	-	N	d	76M
Y	Toluene Dilute $HClO_4$	-	-	N(7,8,19)	e	63P(r)
Y	Toluene 0.5M $NaClO_4$	(orig)	-	N	a	69A
Sc	Kerosene Dilute $HClO_4$	11.5±0.1	0.0012-0.011 0.6-1.8	A(19)	-	68E(r)
Sc	Toluene 1M $(Na,H)ClO_4$	8.8±0.1	0.01-0.075 0.1-1.0	A	-	58P(r)
Sc	Decanol 0.50M HCl	3.04±0.05*	0.01-0.03 0.50	A	g	64M
Am	Toluene 1M $(Na,H)ClO_4$	-1.8±0.3	0.01-1.5 0.0025-0.55	A	n	57P(r),58P(r), 66G,72H(r)

continued

TABLE III-7 (continued)

M	Diluent Aq. phase	log $K_{3,3}$	Range of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Am	Hexane 1M $(Na,H)ClO_4$	0.6±0.1	0.01-0.05 0.1	A	c	71K(r)
Am	Isooctane 0.01M $HClO_4$	0.35±0.05	0.05-0.1 0.01	A	-	64G
Am	Decanol 0.025M HCl	-2.90±0.05*	0.03-0.2 0.025	A	-	64M
Am	Heptane 1M (Na,H)Cl	-	-	N	d	76M
Am	Toluene Dilute $HClO_4$	(orig)	-	N	a	75C,75D
Cm	Toluene Dilute HCl	-1.4±0.1	1.5 0.2-0.5	A(7,19)	-	66G
Cm	Toluene Dilute $HClO_4$	(orig)	-	N	a	75C,75D
Cm	Heptane 1M (Na,H)Cl	-	-	N	d	76M
Bk	Toluene 0.13 M HCl	-0.4±0.1	0.5 0.13	A(7)	-	59P(r)
Cf	Toluene Dilute HCl	-0.15±0.1	1.5 0.4-2.0	A(7,19)	-	66G
Cf	Toluene Dilute $HClO_4$	(orig)	-	N	a	75C,75D
Fm	Toluene Dilute HCl	0.5±0.1	1.5 0.7-2.0	A(7,19)	-	66G

from the source 22 has possibly not been avoided.

d) A $K_{2.5,3}$ value has been calculated in the original work.

e) The $K_{3,3}$ value, either as directly taken from the original paper or as calculated from data presented therein, is too low in comparison with analogous acceptable values.

f) The $K_{3,3}$ value is also valid for 0.1M HCl and 0.1 to 0.5M $HClO_4$.

g) At higher extractant concentrations the extraction reaction is $M^{3+} + 6\overline{HA} = \overline{MA_3.3HA} + 3H^+$ and the log $^{m}K_{6,3}$ values are -1.51 for Eu(III) at $\overline{C}_{A,i} >$ 0.5F, 0.26 for Y(III) at $\overline{C}_{A,i} >$ 0.25F, 0.49 for Tm(III) at $\overline{C}_{A,i}$ > 0.25F and 2.67 for Sc(III) at $\overline{C}_{A,i}$ > 0.15F (all ±0.05 logarithmic units). D_M values expected in the $\overline{C}_{A,i}$ region, in which the complexes $\overline{MA_3}$ and $\overline{MA_3.3HA}$ coexist in the organic phase, can be calculated in combining the corresponding ${}^{m}K_{3,3}$ and ${}^{m}K_{6,3}$ values.

h) There are significant discrepancies between $K_{3,3}$ values either directly given in the papers or calculated from data presented therein.

i) The $K_{3,3}$ value, either directly given in the original paper or calculated from data presented therein, is lower than the corresponding constant valid for an analogous system involving toluene diluent (see criterion 1 in III.1).

j) The $K_{3,3}$ values given in the paper cannot in most cases be compared with analogous values from independent sources; those which can be compared, see notes h) and i), do not agree with data of other authors.

k) An ${}^{m}K_{3,3}$ value has been calculated from very low distribution ratios measured at extremely low extractant concentrations; the results are very sensitive to the presence of impurities.

l) The diluents are n-heptane, cyclohexane, butyl ether, CCl_4, xylene, benzene, nitrobenzene, chlorobenzene, bromoform, dichloromethane and chloroform.

m) The ionic strength ranges from 1 to 1.6.

n) The constant is also valid for 0.15 to 0.55M HCl. Although obtained by comparing data from four independent sources, it cannot be classified as recommended because of its large error limit.

III.3.1.6. EXTRACTION OF BISMUTH(III), GALLIUM(III), INDIUM(III), THALLIUM(III), CHROMIUM(III) AND IRON(III)

A survey of the data is given in Table III-8. Notes:

a) The constant have been calculated from well reproducible results, but a rather low accuracy must be assigned to them with regard to an unspecified room temperature at which the measurements have been made.

b) Complexes extracted from nitrate and perchlorate media differ in their composition. In spite of this the $K_{2.5,3}$ values are acceptable: spectral measurements show that the difference is not caused by the participation of nitrate ions in the formation of the complex in the organic phase.

c) The diluents are hexane, octane and cyclohexane. See III.3.1.

d) It is not clarified in the paper whether and how the incomplete dissociation of sulfuric acid has been regarded in the calculation of the H^+ concentration and the ionic strength.

e) The diluents are bromoform, butyl ether, butyl acetate, ethylene glycol bischloroethyl ether and nitrobenzene. There is a discrepancy in the paper: either the scale on the ordinate in Figs. 4a and 4v is wrongly marked or the composition of the complexes extracted, as given in Table 1 for the corresponding diluents, is not correct.

f) The diluents are butyl ether, ethylene glycol bischloroethyl ether, tetrabromoethane and bromoform. There is no criterion for assessing the plausibility of the equilibrium constants.

g) The diluents are heptane, octane, cyclohexane, CCl_4, toluene, benzene, chloroform, bromoform and butyl ether; an error from the source no. 22

TABLE III-8. Data on the extraction of Bi(III), Ga(III), In(III), Tl(III), Cr(III) and Fe(III) with (H)DE-HP at 20°C (71R), 25°C (60B) and an unspecified room temperature (other references); see explanation in I.5

M	Diluent Aq. phase	u	log $K_{u,3}$	Range of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Bi	CCl_4 1M $(Na,H)ClO_4$	3	2.1±0.1	0.2-0.7 0.3-1.0	A	a	70Lb
Bi	o-Xylene 1M $(Na,H)ClO_4$	3	1.7±0.1	0.3-1.0 0.3-1.0	A	a	70Lb
Bi	Toluene 1M $(Na,H)ClO_4$	3	1.45±0.1	0.3-1.1 0.3-1.0	A	a	70Lb
Bi	Benzene 1M $(Na,H)ClO_4$	3	1.2±0.1	0.4-1.1 0.3-1.0	A	a	70Lb
Bi	Chloropentane 1M $(Na,H)ClO_4$	3	1.6±0.1	0.3-1.0 0.3-1.0	A	a	70Lb
Bi	Dichlorobenzene 1M $(Na,H)ClO_4$	3	1.35±0.1	0.3-1.1 0.3-1.0	A	a	70Lb
Bi	CCl_4 1M $(Na,H)NO_3$	2.5	0.75±0.1	0.1-0.35 0.1-0.35	A	a,b	70La
Bi	o-Xylene 1M $(Na,H)NO_3$	2.5	0.4±0.1	0.15-0.5 0.1-0.35	A	a,b	70La
Bi	Toluene 1M $(Na,H)NO_3$	2.5	0.1±0.1	0.2-0.7 0.1-0.35	A	a,b	70La
Bi	Benzene 1M $(Na,H)NO_3$	2.5	-0.05±0.1	0.2-0.7 0.1-0.35	A	a,b	70La
Bi	Dichlorobenzene 1M $(Na,H)NO_3$	2.5	0.1±0.1	0.2-0.7 0.1-0.35	A	a,b	70La
Bi	Nonpolar NO_3^-,ClO_4^- (I=1)	2.5	(orig)	-	N(22)	c	70La,70Lb
Bi	Octane $(Na,H)HSO_4$	2.5	(orig)	-	N(6a,22)	d,h	72Lc
Bi	Different 1M $(Na,H)ClO_4$	-	(orig)	-	N	e	70Lb
Bi	Different 1M $(Na,H)NO_3$	2.5	(orig)	-	N	f	70La
Ga	Octane $(Na,H)HSO_4$	1.5	(orig)	-	N(6a,22)	d,h	72Lc
Ga	Different $(Na,H)HSO_4$	1.5	(orig)	-	N(6a,22)	d,g,h	73L

continued

TABLE III-8 (continued)

M	Diluent Aq. phase	u	log $K_{u,3}$	Range of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Ga	Different 2M $(Na,H)ClO_4$	1.5	(orig)	-	N(6a,22)	i,k	73L
In	Octane $(Na,H)HSO_4$	3	(orig)	-	N(6a,22)	d,h	72Lc
In	Different Dilute H_2SO_4	3	(orig)	-	N(7,14,18, 19,22)	d,h,j	67L
Tl	Octane $(Na,H)HSO_4$	3	(orig)	-	N(22)	d,h	72Lc
Tl	Different 6M $(NH_4,H)NO_3$	2	(orig)	-	N(7,14,22)	l	71R
Tl	Different $(NH_4,H)HSO_4$	3	(orig)	-	N(14,22)	d,h,l	70L
Cr	Different $(Li,H)(NO_3,ClO_4)$	2	(orig)	-	N(14)	m	71S
Fe	Octane 2M $(Na,H)ClO_4$	3	6.2±0.1	0.01-0.025 0.3-0.6	A	n	60B
Fe	Octane 2M $(Na,H)ClO_4$	2.5,3	(orig)	-	N	o	75Ba

cannot be excluded in systems involving the first three diluents.

h) The fraction of the metal existing as M^{3+} in the aqueous phase can change with varying H^+ concentration even at a constant total sulfate concentration; this has not been considered.

i) The diluents are octane, cyclohexane, CCl_4, ethylene glycol bischloroethyl ether, chlorobenzene, chloroform and butyl ether.

j) The diluents are heptane, CCl_4, butyl ether, tetrabromoethane, dichloroethane and isopentyl benzoate.

k) A reaction of $GaOH^+$ with (H)DE-HP at 0.5 to 2 g-ion H^+ dm^{-3} is supposed, but no convincing evidence is given that the mononuclear hydrolyzed species really predominates in the aqueous phase in this acidity range.

l) The diluents are heptane, octane, cyclohexane, CCl_4, toluene, benzene and chloroform, and also xylene in (70L). It is claimed that at 3 to 5 g-ion H^+ dm^{-3} Tl^{3+} reacts with (H)DE-HP and the complexes $\overline{TlA_3.3HA}$ and $\overline{TlA_3.HA}$ are extracted from the sulfate and nitrate media respectively. However, the slopes of the log $D_M = f(\log [H^+])$ dependencies shown in the paper range from -2 to -2.5 and no single dependency with a slope of -3 is presented.

m) Values of $K_{2,3}$ have been calculated for a reaction of $CrOH^+$ with (H)DE-HP in which $\overline{Cr(OH)A_2.2HA}$ is extracted. However, the actual slopes of the log $D_M = f(\log \bar{C}_{A,i})$ dependencies are 2.3 to 2.4 with aliphatic diluents, benzene and xylene, and 2.6 with chloroform. The expected slope of 2 has been approached only with CCl_4 diluent. No reasonable evidence is given for the existence of the hydrolyzed complex in the organic phase; the distribution data could also be interpreted as extraction of Cr(III) in the form of the complex $\overline{CrA_3.HA}$.

n) Equilibrium constants are also given, characterizing the extraction of macro amounts of Fe(III) in the form of polynuclear complexes. The system is very complex and the number of possible species existing in the organic phase is very high; thus the constants cannot be assessed without additional data.

o) Results from (60B) have been reevaluated in (75Ba) and coexistence of the complexes $\overline{FeA_3.3HA}$ and $\overline{FeA_3.2HA}$ in the organic phase has been suggested. The incorrect assumption has been made that the concentration ratio of the complexes is fixed even at varying $\bar{C}_{A,i}$. Actually, the ratio would have to be a function of the concentration of free (H)DE-HP.

III.3.1.7. EXTRACTION OF HAFNIUM(IV), THORIUM(IV) AND PLUTONIUM(IV)

A survey of the data is given in Table III-9.

TABLE III-9. Data on the extraction of Hf(IV), Th(IV) and Pu(IV) with (H)DE-HP at 19^o to 20^{o}C (64G,67N,68N), 22^{o}C (60Pa,64M) and 25^{o}C (71L). An asterisk denotes a numerical value of ${}^mK_{v,u,4}$, otherwise $K_{v,u,4}$ is given. See explanation in I.5

M	Diluent Aq. phase	v,u	log $K_{v,u,4}$	Range of $\bar{C}_{A,i}$ F [H$^+$] g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Hf	Toluene 1M (Na,H)X	-	-	-	N	a	71L
Hf	Octane 2M HX	1,2.5	(orig)	-	N(21b)	b	67N,68N
Th	Toluene 1M (Na,H)NO_3	1,3	6.8±0.1	0.001-0.008 0.09-1.0	A	-	60Pa(r)
Th	Decanol 0.25M HCl	0,4	2.25±0.1*	0.02-0.06 0.25	A	c	64M
Pu	Decane Dilute $HClO_4$	3,2	(orig)	-	N(6a)	d	64G

Notes:

a) X is ClO_4 or HSO_4. Equilibrium constants are given only for the reaction of Hf^{4+} with five or six monomeric HA molecules; thus they are very sensitive to possible inaccuracy of K_a, K_D and K_2 of (H)DE-HP (see more in III.1; see also note c) in II.3). In the system involving sulfates the equilibrium constants cannot be more relaible than stability constants of sulfate complexes formed by Hf(IV) in the aqueous phase. The original data on the perchlorate system could also be simply intepreted by assuming practically full dimerization of (H)DE-HP over the whole $\overline{C}_{A,i}$ range studied and the formation of one single complex in the organic phase. However, a reevaluation of the data showed that it was difficult to decide whether the formation of the complex $\overline{Hf(NO_3)A_3.3HA}$ fits them better than the formation of $\overline{HfA_4.2HA}$.

b) X is Cl or ClO_4.

c) At $\overline{C}_{A,i}$ = 0.06 to 0.5F the complex $\overline{ThA_4.2HA}$ is formed simultaneously with $\overline{ThA_4}$, log $^mK_{0,6,4}$ being 3.4±0.1. D_M values expected in this $\overline{C}_{A,i}$ range can be calculated in combining $^mK_{0,4,4}$ and $^mK_{0,6,4}$.

d) No comparable data from independent sources are available and the plausibility of the composition of the complex extracted, as suggested in the paper, cannot be assessed.

III.3.2. OTHER DIALKYL OR BIS(ALKOXYALKYL)PHOSPHORIC ACIDS

Bis(hexoxyethyl) phosphoric acid has been clearly shown to form higher self-associates than dimers in cyclohexane (65Pb) and the same phenomenon must be expected in heptane. Thus the equilibrium constants of the extraction of U(VI) by the extractant in heptane and of Eu(III) and Am(III) by the extractant in cyclohexane, as given in (67M), cannot be accepted, although they formally well describe the distribution of the metals in the respective systems. The impossibility of assessing the equilibrium constant of the extraction of Ca(II) by the extractant in heptane and benzene (67M) is caused, as in III.3.1.2, by the potential ability of Ca(II) to form different complexes in the organic phase. Nothing is known about the state of oligomerization of the extractant in MiBK, and the respective equilibrium constants of the extraction of Ca(II), U(VI), Eu(III), Tm(III) and Am(III), as given in (67M), are not acceptable either.

A predominantly dimeric nature of bis(2,6-dimethyl-4-heptyl) phosphoric acid in heptane (70Mc) and benzene (71P) has been postulated, but without being documented by any quantitative data. Thus the equilibrium constants of the extraction of U(VI), Eu(III), Lu(III), Y(III), Sc(III), Am(III) and Th(IV) by the extractant in heptane and benzene (71P) are not acceptable.

Data on the extraction with bis(butoxyethyl) phosphoric acid in benzene, as presented in (77N), are not suitable for the calculation of equilibrium constants: in the case of Hf(IV) the error source no. 7 has not been avoided and in the case of Eu(III) the distribution data have been taken for the calculation at an $[H^+]$ value at which the log D_M = f(log $[H^+]$) dependency is not linear.

Also inadequate are the numerically presented data on the extraction of La(III), Ce(III), Nd(III), Sm(III), Gd(III), Tb(III), Ho(III), Er(III), Yb(III), Y(III) and Th(IV) by (H)DiBP in kerosene from sulfuric acid solutions (63S); here errors from the sources 6a, 7, 11a, 18, 19, 21a and 22 have not been avoided.

Acceptable data are gathered in Table III-10.

TABLE III-10. Data on the extraction of U(VI), lanthanides(III) and actinides(III) by dialkyl and bis(alkoxyalkyl) phosphoric acids at 22^{o} to 23^{o}C; an asterisk denotes a numerical value of $^{m}K_{u,z}$, otherwise $K_{u,z}$ is given. See explanations in I.5

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F [H$^+$] g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Extractant: Bis(2,2-dimethylhexyl) phosphoric acid							
U	Heptane 1M (Na,H)Cl	2	4.08±0.05	0.02-0.1 0.06-1.0	A	a	70Mb
U	Benzene 1M (Na,H)Cl	2	3.30±0.05	0.02-0.3 0.06-1.0	A	a	70Mb
Ce	Heptane 1M (Na,H)Cl	2.5	-0.95±0.1	0.02-0.1 0.06-1.0	A	a	70Mb
Ce	Benzene 1M (Na,H)Cl	3	-3.1±0.1	0.02-0.3 0.012-0.25	A	a	70Mb
Pm	Heptane 1M (Na,H)Cl	2.5	-0.25±0.1	0.02-0.1 0.06-1.0	A	a	70Mb
Pm	Benzene 1M (Na,H)Cl	3	-2.15±0.05	0.02-0.3 0.012-0.25	A	a	70Mb
Eu	Heptane 1M (Na,H)Cl	2.5	0.60±0.05	0.02-0.1 0.06-1.0	A	a	70Mb
Eu	Benzene 1M (Na,H)Cl	3	-1.32±0.05	0.02-0.3 0.012-0.25	A	a	70Mb
Tm	Heptane 1M (Na,H)Cl	2.5	3.05±0.1	0.02-0.1 0.06-1.0	A	a	70Mb
Tm	Benzene 1M (Na,H)Cl	3	0.9±0.1	0.02-0.3 0.06-1.0	A	a	70Mb
Y	Heptane 1M (Na,H)Cl	2.5	2.45±0.1	0.02-0.1 0.06-1.0	A	a	70Mb
Y	Benzene 1M (Na,H)Cl	3	0.2±0.1	0.02-0.3 0.06-1.0	A	a	70Mb

continued

TABLE III-10 (continued)

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Am	Heptane 1M (Na,H)Cl	2.5	-0.95±0.1	0.02-0.1 0.06-1.0	A	a	70Mb
Am	Benzene 1M (Na,H)Cl	3	-2.8±0.1	0.02-0.3 0.012-0.25	A	a	70Mb
Cm	Heptane 1M (Na,H)Cl	2.5	-0.95±0.1	0.02-0.1 0.06-1.0	A	a	70Mb
Cm	Benzene 1M (Na,H)Cl	3	-2.6±0.1	0.02-0.3 0.012-0.25	A	a	70Mb
Extractant: Bis(butoxyethyl) phosphoric acid							
La	Toluene 1M (Na,H)NO_3	3	2.3±0.1	0.01-0.1 0.05-0.5	A	b	71Kb
Ce	Toluene 1M (Na,H)NO_3	3	2.85±0.1	0.005-0.05 0.05-0.5	A	b	71Kb
Pr	Toluene 1M (Na,H)NO_3	3	2.66±0.08	0.005-0.05 0.1-0.3	A	b	71Kb
Pm	Toluene 1M (Na,H)NO_3	3	2.95±0.1	0.005-0.05 0.1-0.3	A	b	71Kb
Sm	Toluene 1M (Na,H)NO_3	3	3.10±0.08	0.008-0.05 0.1-0.3	A	b	71Kb
Eu	Toluene 1M (Na,H)NO_3	3	3.24±0.05	0.005-0.05 0.10-0.12	A(11a)	b	71Kb
Tb	Toluene 1M (Na,H)NO_3	3	3.61±0.07	0.005-0.05 0.09-0.5	A	b	71Kb
Dy	Toluene 1M (Na,H)NO_3	3	4.16±0.07	0.005-0.05 0.2-1.0	A	b	71Kb
Ho	Toluene 1M (Na,H)NO_3	3	4.39±0.05	0.005-0.05 0.2-0.7	A	b	71Kb
Er	Toluene 1M (Na,H)NO_3	3	4.88±0.08	0.005-0.05 0.2-1.0	A	b	71Kb
Tm	Toluene 1M (Na,H)NO_3	3	5.36±0.08	0.005-0.05 0.2-0.5	A	b	71Kb
Yb	Toluene 1M (Na,H)NO_3	3	6.0±0.1	0.005-0.05 0.3-1.0	A	b	71Kb

continued

TABLE III-10 (continued)

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F H^+ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Extractant: Bis(hexoxyethyl) phosphoric acid							
U	Decanol 1M (Na,H)Cl	2	1.85±0.05*	0.02-0.05 0.06-1.0	A	c,d	67M
U	Benzene 1M (Na,H)Cl	2	5.51±0.05	0.08-0.3 0.06-1.0	A	e	67M
Eu	Decanol 1M (Na,H)Cl	3	-0.3±0.1*	0.03-0.1 0.06-0.5	A	c,f	67M
Tm	Decanol 1M (Na,H)Cl	3	-0.3±0.1*	0.01-0.05 0.06-1.0	A	c,g	67M(r)
Am	Decanol 1M (Na,H)Cl	3	-0.7±0.1*	0.03-0.1 0.06-0.3	A	c,f	67M
Am,Eu	Benzene ?	2.5	(orig)	-	N	h	67M

Notes:

a) The extractant has been shown (70Mb) to be predominantly dimeric in its 0.1F solutions in heptane and benzene. In the former the average degree of self-association is 2.2 and thus the dimeric state of the extractant can plausibly be expected only below the concentration of 0.1F.

b) The extractant can with a very good probability be supposed to be dimeric in toluene with regard to the behavior of its hexoxyethyl analogon (see note e).

c) The monomeric state of the extractant in decanol has not been documented, but can be assumed with high probability.

d) At $\overline{C}_{A,i} > 0.05$F two complexes coexist in the organic phase, namely $\overline{UO_2A_2}$ and probably $\overline{UO_2A_2.2HA}$.

e) The extractant has been found to be dimeric in benzene up to its concentration 0.25F (65Pb).

f) At $\overline{C}_{A,i} > 0.1$F two complexes coexist in the organic phase, $\overline{MA_3}$ and probably $\overline{MA_3.2HA}$.

g) Coexistence of a complex of the type $\overline{MA_3.2HA}$ with $\overline{MA_3}$ in the organic phase is rather clearly indicated at $\overline{C}_{A,i} > 0.05$F.

h) The constants are based on distribution data presented in (65Pb) and it is not clear whether they are valid for a perchlorate or a chloride medium.

III.4. DIARYL AND DIBENZYL PHOSPHORIC ACIDS

Equilibrium constants of the extraction of Ca(II), Sr(II) and Ba(II) with bis(p-1,1,3,3-tetramethylbutyl phenyl) phosphoric acid in xylene from Cl^- solutions (62Pb) cannot be assessed without additional data from independent sources, because the elements have been shown in systems involving other extractants to be able to form a variety of extracted complexes (see III.3.1.2).

The equilibrium constant of the extraction of U(VI) by bis(2,6-di*iso*propyl phenyl) phosphoric acid in benzene from a 1M (Na,H)Cl solution (78M) cannot be accepted, because the postulated predominantly dimeric state of the extractant in the organic phase has not been documented.

A survey of other data is given in Table III-11.

TABLE III-11. Data on the extraction of U(VI), lanthanides(III), Am(III), Sc(III) and Th(IV) with diaryl and dibenzyl phosphoric acids at an unspecified room temperature (70F,71Lb), 20°C (65Ka,66Kc) and 22°C (58P,60Pa,78Ma); $K_{0,u,4}$ values are given for Th(IV). See explanation in I.5

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Extractant: Bis(p-1,1,3,3-tetramethylbutyl phenyl) phosphoric acid							
U	Benzene 1M $(Na,H)NO_3$	2	4.46±0.05	0.01-0.15 0.06-1.0	A	-	78Ma
U	Benzene 1M (Na,H)Cl	2	4.29±0.05	0.01-0.15 0.06-1.0	A	-	78Ma
Pm	Toluene 1M $(Na,H)ClO_4$	3	4.4±0.1	0.005-0.09 0.12-1.0	A	-	58P(r)
Eu	Benzene 1M (Na,H)Cl	3	3.82±0.05	0.01-0.15 0.06-1.0	A	-	78Ma
Y	Toluene 1M $(Na,H)ClO_4$	3	5.6±0.1	0.0025-0.09 0.12-1.0	A	-	58P(r)
Sc	Toluene 1M $(Na,H)ClO_4$	3	12.9±0.1	0.0012-0.01 0.25-1.0	A	-	58P(r)
Am	Toluene 1M $(Na,H)ClO_4$	3	4.1±0.1	0.005-0.09 0.12-1.0	A	-	58P(r)
Am	Benzene 1M (Na,H)Cl	3	3.13±0.05	0.01-0.15 0.06-1.0	A	-	78Ma
Th	Toluene 1M $(Na,H)ClO_4$	3	11.2±0.1	0.001-0.009 0.19-1.0	A	-	60Pa(r)

continued

TABLE III-11 (continued)

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Th	Toluene 1M $(Na,H)NO_3$	3	10.3±0.1	0.001-0.009 0.19-1.0	A	-	60Pa(r)
Th	Toluene 1M (Na,H)Cl	3	10.55±0.1	0.001-0.009 0.19-1.0	A	-	60Pa(r)
Th	Benzene 1M (Na,H)Cl	3	9.9±0.1	0.001-0.02 0.06-1.0	A	-	78Ma
Extractant: Dibenzyl phosphoric acid							
U	Chloroform 1M $(Na,H)ClO_4$	2	(orig)	-	N(1,7,16)	a	65Ka
Extractant: Bis(o-cresyl) phosphoric acid							
U	Benzene 1M $(Na,H)ClO_4$	2	(orig)	-	N(7,14,16,17)	b	71Lb
Extractant: Bis(p-cresyl) phosphoric acid							
U	Benzene 1M $(Na,H)ClO_4$	2	(orig)	-	N(7,14,16,17)	b	71Lb
U	Chloroform 1M $(Na,H)ClO_4$	2	(orig)	-	N(1,7,16)	a	65Ka
Ln	Chloroform 1M $(Na,H)ClO_4$	2.5	(orig)	-	N(7)	a,c	66Kc
Y	Chloroform 1M $(Na,H)ClO_4$	2.5	4.8±0.1	0.005-0.05 0.1-1.0	A(7)	a,d	66Kc
Y	Chloroform Dilute HNO_3	2.5	4.55±0.1	0.01-0.2 0.25-1.0	A(19)	a,d,e	70F(r)
Extractant: Diphenyl phosphoric acid							
U	Chloroform 1M $(Na,H)ClO_4$	2	(orig)	-	N(1,7,16,21)	a	65Ka
Ln	Chloroform 1M $(Na,H)ClO_4$	2.5	(orig)	-	N(7)	a,f	66Kc
Extractants: Bis(p-chlorophenyl) and dinaphtyl phosphoric acids							
U	Chloroform 1M $(Na,H)ClO_4$	2	(orig)	-	N(1,7,16)	a	65Ka

continued

TABLE III-11 (continued)

M	Diluent Aq. phase	u	$\log K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Ln	Chloroform 1M $(Na,H)ClO_4$	2.5	(orig)	-	N(7)	a,f	66Kc

Notes:

a) Neither the log D_M = f(log $[H^+]$) nor the log D_M = f(log $\overline{C}_{dim}$) dependencies are directly presented.

b) The method of the determination of U(VI) is not described in the paper and an error from the source no. 1 is also possible.

c) Ln is Ce, Eu, Tb and Tm.

d) The values of $K_{2.5,3}$ are accepted because of their mutual consistency.

e) The authors have evaluated the data given in Table 2 of the paper in setting u equal to three; however, the data are better fitted with u = 2.5. The $K_{3,3}$ values given in Table 3 of the paper are fully inacceptable; they have been calculated without any clear evidence for u = 3 and are not consistent.

f) Ln is Ce, Eu, Tb, Tm and Y.

III.5. MONOESTERS OF ALKYL AND ARYLPHOSPHONIC ACIDS; PHOSPHINIC ACIDS

The predominantly dimeric state of extractants of the type $(H)R_1R_2'P$ and (H)-DR'P in nonpolar diluents has been sufficiently well documented (71K) for compounds with R being n-alkyl, 2-ethylhexyl or phenyl, i.e. no very bulky substituent. Little is known about the self-association of sterically hindered compounds. Thus an a priori assumption that di-tert-pentyl phosphinic acid is dimeric in benzene need not be justified and the equilibrium constant of the extraction of U(VI) from chloride solutions (78S) cannot be accepted. Neither acceptable is the equilibrium constant of the extraction from chloride media of U(VI) by di-tert-butyl phosphinic acid in benzene (78M), which has been said to be dimeric (74Mc) without documenting the postulation. n-Octyl and 2-ethylhexyl hydrogen phosphinic acids obviously form higher oligomers in benzene, where their average degree of self-association is 2.6 to 2.8 (66P), and the equilibrium constant reported in the paper for the extraction of U(VI), Pm(III) and Cm(III) by the extractant in benzene from a chloride medium are not acceptable. It should be noted that the constants, which in some instances have no clear physical meaning, formally well describe the distribution of the metals in the two-liquid-phase systems.

The composition of complexes formed by alkaline earth elements cannot be considered as established: (H)OPh'P has been reported to extract Sr(II) as $\overline{SrA_2.4HA}$ into xylene (62Pb), while the complex $\overline{SrA_2.3HA}$ has been found to be extracted into a similar diluent, namely toluene (71Sa). No attempt was made to assess equilibrium constants determined in systems involving Ca(II), Sr(II) and Ba(II).

Unfortunately, a great part of equilibrium constants reported for phosphonic and phosphinic extractants must be rejected; this is illustrated in Table III-12, which gives a survey of the data.

TABLE III-12. Data on the extraction of U(VI), lanthanides(III), actinides(III), Fe(III) and Zr(IV) by phosphonic and phosphinic extractants at an unspecified room temperature (72M,73Rb,74E,74Z), 20°C (65Ua), 22 to 23°C (61P,65Pc,70Ma,71Kb) and 25°C (75A,75B); see explanation in I.5

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Extractant: Pentyl methylphosphonic acid							
Zr	Xylene 2M (Li,H)NO_3	-	(orig)	-	N(21a)	a	65Ua
Extractant: n-Heptyl n-heptylphosphonic acid							
U	Xylene Dilute HNO_3	2	(orig)	-	N(10)	-	73Rb
Extractant: n-Octyl n-octylphosphonic acid							
Ce	Toluene 1M (Na,H)NO_3	2.5	-1.32±0.07	0.01-0.1 0.01-0.05	A	-	71Kb
Pr	Toluene 1M (Na,H)NO_3	2.5	-1.41±0.09	0.008-0.05 0.012-0.05	A	-	71Kb
Pm	Toluene 1M (Na,H)NO_3	2.5	-1.03±0.07	0.008-0.05 0.01-0.1	A	-	71Kb
Eu	Toluene 1M (Na,H)NO_3	2.5	-0.65±0.1	0.008-0.1 0.03-0.3	A	-	71Kb
Tb	Toluene 1M (Na,H)NO_3	2.5	0.2±0.1	0.005-0.1 0.02-0.3	A	-	71Kb
Dy	Toluene 1M (Na,H)NO_3	2.5	0.85±0.09	0.008-0.05 0.03-0.3	A	-	71Kb
Ho	Toluene 1M (Na,H)NO_3	2.5	1.15±0.1	0.01-0.05 0.05-0.5	A	-	71Kb

continued

TABLE III-12 (continued)

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Tm	Toluene 1M $(Na,H)NO_3$	2.5	1.86±0.08	0.005-0.05 0.025-0.2	A	-	71Kb
Yb	Toluene 1M $(Na,H)NO_3$	2.5	2.7±0.1	0.005-0.05 0.05-0.5	A	-	71Kb
Lu	Toluene 1M $(Na,H)NO_3$	2.5	2.90±0.08	0.005-0.05 0.1-0.5	A	-	71Kb
Extractant: n-Pentyl phenylphosphonic acid							
M	Diethylbenzene Dil. HNO_3,$HClO_4$	3	(orig)	-	N(7,19)	b,c	74Z
Extractant: Isopentyl phenylphosphonic acid							
M	Diethylbenzene Dilute $HClO_4$	3	(orig)	-	N(7,14,19)	c,d,e	74Z
M	Diethylbenzene Dilute HNO_3	3	(orig)	-	N(7,19)	c,d	74Z
Extractant: n-Octyl phenylphosphonic acid							
M	Diethylbenzene Dilute HX	3	(orig)	-	N(7,19)	c,f,g	74Z
Extractant: 2-Ethylhexyl phenylphosphonic acid							
Pm	Octane,benzene $(NH_4,H)ClO_4$	3	(orig)	-	N(14)	i	74E
Pm	Toluene (Na,H)X	3	(orig)	-	N(7)	f,h	61P
Eu	Diethylbenzene Dilute HX	3	(orig)	-	N(7,19)	c,f	74Z
Am	Octane,benzene $(NH_4,H)ClO_4$	3	(orig)	-	N(14)	i	74E
M	Diethylbenzene Dilute $HClO_4$	3	(orig)	-	N(7,19)	c,j	74Z,75B
Am	Diethylbenzene Dilute HNO_3	3	(orig)	-	N(7,19)	c	74Z
Cm	Octane,benzene $(NH_4,H)ClO_4$	3	(orig)	-	N(14)	i	74E

continued

TABLE III-12 (continued)

M	Diluent Aq. Phase	u	log $K_{u,z}$	Ranges of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Cm	Toluene (Na,H)X	3	(orig)	-	N(7)	f,h	61P
Cm	Diethylbenzene Dil. HNO_3,HCl	3	(orig)	-	N(7,19)	c	74Z
Cf	Diethylbenzene Dilute HX	-	(orig)	-	N(7,19)	k	74Z,75B
Bk	Diethylbenzene Dilute HNO_3	3	(orig)	-	N(7,19)	c	74Z
Fe	Benzene Dil.HNO_3,$HClO_4$	3	(orig)	-	N(14,19)	l	75A

Extractant: n-Decyl phenylphosphonic acid

M	Diluent Aq. Phase	u	log $K_{u,z}$	Ranges of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
M	Diethylbenzene Dilute HX	3	(orig)	-	N(7,19)	c,f,m	74Z

Extractant: Di-n-heptyl phosphinic acid

M	Diluent Aq. Phase	u	log $K_{u,z}$	Ranges of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
U	Xylene Dilute HNO_3	2	(orig)	-	N(10)	-	73Rb
La	Benzene 0.1M HCl	2.5	(orig)	-	N	n	72M
Ho	Benzene 0.1M HCl	2.5	-0.26±0.05	0.03-0.2 0.1	A(7)	o	72M
Er	Benzene 0.1M HCl	2.5	0.25±0.05	0.03-0.3 0.1	A(7)	o	72M
Tm	Benzene 0.1M HCl	2.5	0.63±0.05	0.02-0.3 0.1	A	o	72M
Yb	Benzene 0.1M HCl	2.5	1.28±0.05	0.025-0.25 0.1	A(7)	o	72M
Lu	Benzene 0.1M HCl	2.5	1.42±0.05	0.03-0.25 0.1	A(7)	o	72M
Y	Benzene 0.1M HCl	2.5	0.01±0.05	0.03-0.2 0.1	A(7)	o	72M

Extractant: Di-n-octyl phosphinic acid

M	Diluent Aq. Phase	u	log $K_{u,z}$	Ranges of $\bar{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
U	Benzene 1M (Na,H)Cl	2	4.32±0.05	0.012-0.33 0.06-1.0	A	-	65Pc

continued

TABLE III-12 (continued)

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\bar{C}_{A,i}$ F $[H^+]$g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Ce	Benzene 1M (Na,H)Cl	2.5	-4.49±0.05	0.025-0.4 0.014-0.2	A	o	65Pc
Eu	Benzene 1M (Na,H)Cl	2.5	-2.38±0.05	0.03-0.4 0.016-0.25	A	o	65Pc
Tm	Benzene 1M (Na,H)Cl	2.5	0.11±0.05	0.03-0.4 0.06-1.0	A	o	65Pc
Yb	Benzene 1M (Na,H)Cl	2.5	0.67±0.05	0.03-0.4 0.06-1.0	A	o	65Pc
Y	Benzene 1M (Na,H)Cl	2.5	-0.50±0.05	0.03-0.4 0.06-1.0	A	o	65Pc
Am	Benzene 1M (Na,H)Cl	2.5	-4.17±0.05	0.03-0.4 0.016-0.25	A	-	65Pc
Cm	Benzene 1M (Na,H)Cl	2.5	-3.93±0.05	0.03-0.4 0.016-0.2	A	-	65Pc

Extractant: n-Octyl phenyl phosphinic acid

U	Benzene 1M (Na,H)Cl	2	4.3±0.1	0.02-0.3 0.06-1.0	A	-	70Ma
Ce	Benzene 1M (Na,H)Cl	2.5	-1.25±0.1	0.02-0.3 0.06-1.0	A	-	70Ma
Pm	Benzene 1M (Na,H)Cl	2.5	-0.4±0.1	0.02-0.3 0.06-1.0	A	-	70Ma
Eu	Benzene 1M (Na,H)Cl	2.5	0.45±0.1	0.02-0.3 0.06-1.0	A	-	70Ma
Tm	Benzene 1M (Na,H)Cl	2.5	3.09±0.05	0.02-0.3 0.06-1.0	A	-	70Ma
Y	Benzene 1M (Na,H)Cl	2.5	2.35±0.1	0.02-0.3 0.06-1.0	A	-	70Ma
Am	Benzene 1M (Na,H)Cl	2.5	-1.05±0.05	0.02-0.3 0.06-1.0	A	-	70Ma
Cm	Benzene 1M (Na,H)Cl	2.5	-0.80±0.05	0.02-0.3 0.06-1.0	A	-	70Ma

Extractant: Cyclooctyl phenyl phosphinic acid

U	Benzene 1M (Na,H)Cl	2	4.78±0.05	0.02-0.3 0.06-1.0	A	-	70Ma

continued

TABLE III-12 (continued)

M	Diluent Aq. phase	u	log $K_{u,z}$	Ranges of $\overline{C}_{A,i}$ F $[H^+]$ g-ion dm^{-3}	Category (error source no.)	Note	Ref.
Ce	Benzene 1M (Na,H)Cl	2.5	-1.65±0.1	0.02-0.3 0.03-0.5	A	-	70Ma
Pm	Benzene 1M (Na,H)Cl	2.5	-0.65±0.1	0.02-0.3 0.06-1.0	A	-	70Ma
Eu	Benzene 1M (Na,H)Cl	2.5	0.35±0.1	0.02-0.3 0.06-1.0	A	-	70Ma
Tm	Benzene 1M (Na,H)Cl	2.5	2.53±0.08	0.02-0.3 0.06-1.0	A	-	70Ma
Y	Benzene 1M (Na,H)Cl	2.5	2.05±0.05	0.02-0.3 0.06-1.0	A	-	70Ma
Am	Benzene 1M (Na,H)Cl	2.5	-1.35±0.05	0.02-0.3 0.06-1.0	A	-	70Ma
Cm	Benzene 1M (Na,H)Cl	2.5	-1.21±0.05	0.02-0.3 0.06-1.0	A	-	70Ma

Notes:

a) The extraction reaction has been interpreted as $ZrOA^+ + \overline{HA} = \overline{ZrOA_2} + H^+$, but the predominance of neither the species $ZrOA^+$ in the aqueous phase nor the monomer $\overline{HA}$ in the organic phase has been proven.

b) M is Eu, Cm and Cf.

c) With some exceptions, neither the log D_M = f(log $[H^+]$) nor the log D_M = dependencies are directly presented in (74Z).

d) M is Pm, Eu, Am, Cm and Cf.

e) The log D_M = f(log $\overline{C}_{A,i}$) dependencies, as presented for Eu and Am, imply u = 2.5 rather than u = 3.

f) X is ClO_4, Cl and NO_3.

g) M is Pm, Am, Cm and Cf.

h) The log D_M = f(log $[H^+]$) dependencies have been measured with 1M (Na,H)X as the aqueous phase, while 0.125M HX has been used in measuring the log D_M vs. log $\overline{C}_{A,i}$ dependencies. The $K_{3,3}$ values are influenced by the ionic strength even in the systems involving the noncomplexing perchlorate aqueous phases. For an unambigous characterization of the ionic strength effect it would be appropriate to measure both the H^+ and the $\overline{C}_{A,i}$ dependencies at each of the two I values.

i) $K_{3,3}$ values are not given directly in the paper, but can easily be calculated from the numerically presented distribution data.

j) M = Am and Cm. The formation of two complexes in the organic phase, namely $\overline{MA_3.HA}$ and $\overline{MA_3.2HA}$, has been suggested in (75B) in contradiction to (74Z) where the single complex $\overline{MA_3.3HA}$ is said to be extracted. Error source no. 22 has possibly not been avoided in (75B). The log $D_M = f(\log \overline{C}_{A,i})$ dependency is shown in neither paper and is mentioned in the text only. More precise and relaible data, obtained at a constant ionic strength and clearly presented, are needed for determining the composition of the complexes extracted.

k) X is ClO_4 in (74Z,75B) and also Cl and NO_3 in (74Z). The complex present in the organic phase is contradictorily said to be $\overline{CfA_3.HA}$ (75B) and $\overline{CfA_3.3HA}$ (74Z). The unacceptability of the $K_{u,3}$ values given in the papers can be reasoned as in the preceding note.

l) No evidence is given whether equilibrium has been attained after the shaking time of 30 min, as maintained in the work (as mentioned in (60B), the extraction of Fe(III) may be rather slow). The log $D_M = f(\log \overline{C}_{A,i})$ dependency has a slope which depends on the mineral acid concentration in the aqueous phase and cannot be used directly for calculating $K_{3,3}$. The concentration of dimeric extractant in the organic phase, as caculated in the work, is based on a wrong K_2 value of the extractant (see note h in II.5.1).

m) M = Pm, Eu, Am, Cm and Cf.

n) The constant appears to be too high. It lies above the extrapolated line of log $K_{2.5,3}$ vs. the atomic number of lanthanides(III), as constructed from the data on other rare earth elements given in the paper. The atomic number dependency has been shown to be practically linear for all lanthanides(III) in an analogous system involving (H)DO'P instead of (H)DHp'P (65Pc).

o) There is a good consistency between the results given in (65Pc,72M): The plots of log $K_{2.5,3}$ vs. the atomic number of the lanthanides(III) are practically parallel and the $K_{2.5,3}$ values themselves, after a correction for the formation of MCl^{2+} in the aqueous phase (62P), are almost the same both with (H)DHp'P and (H)DO'P. It appears that the alkyl chain length in the extractant molecule does not significantly influence the extraction ability of phosphonic acids; a similar phenomenon has been observed in di-_n_-alkyl phosphoric acids (66Ka).

IV. COMPLEX FORMATION IN HOMOGENOUS SOLUTIONS

IV.1. AQUEOUS SOLUTIONS

A survey of the data is given in Table IV-1. Notes:

a) The kinetic method is based on measuring the oxidation rate of iodides by hydrogen peroxide, as catalyzed by $ThOH^{3+}$ ions. The complexation of lanthanides(III) by the organophosphate anions has been estimated indirectly, from a shift of the complex formation equilibrium of Th(IV), and the concentration of free $ThOH^{3+}$ ions has been calculated by subtracting two values which differ by a factor of one to two. Thus, the statistical error of the difference may be large. Also considerable systematic errors may occur, caused e.g. by the catalytic activity of impurities and the lanthanides(III) themselves. On the other hand, the presence of the acetate buffer does not distort the results, because relative, and not absolute concentrations of metals bound to the organophosphate ligands are acquired in the measurements. The inaccuracy of the stability constant of the complex $Th(OH)A^{2+}$ (note c) must be included in the inaccuracy of the stability constants of the lanthanide(III) complexes, but this has not been done in the original papers. Some other possible error sources should be mentioned, like imperfect constancy of pH in a set of experiments, or incomplete adequacy of calculating activity coefficients in the presence of acetate ions (note e). To summarize, the accuracy of the log β_1 values gathered in Table IV-1 can be estimated as ±0.2 logarithmic unit and can in no instance be better than ±0.1 logarithmic unit. In spite of the above limitations, the constants are tentatively acceptable, because their consistency within the lanthanide(III) series or, in the frame of work made by a team of authors, within a homologous series of organophosphate ligands may be somewhat better (similar errors can be expected in analogous experiments with chemically similar elements or compounds). Moreover, dependencies of the constants on the lanthanide(III) atomic number (65S, 71Ma,72G,72Gb) and the number of carbon atoms in the organophosphate molecule (74Gc) as well as correlations with Taft and Kabachnik substituent constants (66S,74Ga) give each a reasonable picture.

b) Also log β_2 = 4.15 has been found by the spectrophotometric method. Both log β_1 and log β_2 are acceptable within ±0.1 logarithmic unit.

c) The species reacting with A^- is $ThOH^{3+}$ and the stability constant is defined as $\beta_1 = [Th(OH)A^{2+}][ThOH^{3+}]^{-1}[A^-]^{-1}$. The constant has a limited significance for solvent extraction systems which have been studied at $[H^+]$ = 0.1 to 1 g-ion dm^{-3}, where the hydrolysis of Th(IV) may be neglected.

d) Solubility measurements exhibit a rather low reproducibility. This is illustrated by the fact that a comparison of published solubility data (64S,65Sa,65Sb,66Sa), all valid for 25°C, did not make it possible to find a better value of the solubility product of La(III) dibutyl phosphate than log S = -9.5±0.4. From this point of view, the very good agreement between the β_1 values of lanthanides(III) calculated from kinetic (65S) and solubility (66Sa) data is surprising. Of the β_1 values based on solubility measurements only those are acceptable, which can be compared

TABLE IV-1. Data on the complex formation of U(VI), lanthanides(III) and Th(IV) with anions of monoacidic organophosphates in aqueous solutions at at 20°C (61S,69U) and 25°C (other references); see explanation in I.5

M	$\log \beta_1$	Medium	Method, ref.	Category	Note
Ligand: Dimethyl phosphate					
La	0.7	Acetate buffer, I→0	kin (66S)	A	a,e
Nd	0.85	Acetate buffer, I→0	kin (66S)	A	a,e
Yb	1.45	Acetate buffer, I→0	kin (66S)	A	a,e
Ligand: Diethyl phosphate					
U	2.45	1M $NaClO_4$	iex, spphm (69U)	A	b
La	1.25	Acetate buffer, I=0.021	kin (71Ma)	A	a
La	1.8	Acetate buffer, I→0	kin (66S)	A	a,e
Nd	2.0	Acetate buffer, I→0	kin (66S)	A	a,e
Pr	1.4	Acetate buffer, I=0.021	kin (71Ma)	A	a
Sm	1.7	Acetate buffer, I=0.021	kin (71Ma)	A	a
Gd	1.75	Acetate buffer, I=0.021	kin (71Ma)	A	a
Dy	2.0	Acetate buffer, I=0.021	kin (71Ma)	A	a
Er	2.1	Acetate buffer, I=0.021	kin (71Ma)	A	a
Yb	2.2	Acetate buffer, I=0.021	kin (71Ma)	A	a
Yb	2.8	Acetate buffer, I→0	kin (66S)	A	a,e
Lu	2.35	Acetate buffer, I=0.021	kin (71Ma)	A	a
Th	4.55	Acetate buffer, I=0.021	kin (71Ma)	A	a,c
Th	4.7	Acetate buffer, I→0	kin (66S)	A	a,c,e
Ligand: Di-n-propyl phosphate					
La	1.9	Acetate buffer, I→0	kin (66S)	A	a,e
Yb	3.1	Acetate buffer, I→0	kin (66S)	A	a,e
Th	4.8	Acetate buffer, I→0	kin (66S7	A	a,c,e
Ligand: Di-n-butyl phosphate					
La	1.9	(Acetate buffer), I→0	kin (65S) soly (64S,65Sb,66Sa)	R	a,d,e
La	1.6	Acetate buffer, I=0.02	kin (74Gc)	A	a
La	(orig)	I ⩽ 0.082	soly (65Sa)	N	d,f
Ce	(orig)	Dilute HNO_3	distr (61S)	N	g

continued

TABLE IV-1 (continued)

M	log β_1	Medium	Method, ref.	Category	Note
Pr	2.2	(Acetate buffer), I→0	kin (65S) soly (66Sa)	A	a,d,e
Nd	2.3	(Acetate buffer), I→0	kin (65S) soly (66Sa)	A	a,d,e
Sm	2.5	Acetate buffer, I→0	kin (65S)	A	a,e
Eu	2.6	Acetate buffer, I→0	kin (65S)	A	a,e
Gd	2.7	(Acetate buffer), I→0	kin (65S) soly (66Sa)	A	a,d,e
Tb	2.8	(Acetate buffer), I→0	kin (65S) soly (66Sa)	A	a,d,e
Ho	3.0	Acetate buffer, I→0	kin (65S)	A	a,e
Er	3.1	Acetate buffer, I→0	kin (65S)	A	a,e
Yb	3.5	(Acetate buffer), I→0	kin (65S) soly (66Sa)	A	a,d,e
Yb	3.0	Acetate buffer, I=0.02	kin (74Gc)	A	a
Yb	(orig)	Dilute HNO_3	distr (61S)	N	g
Lu	3.0	Acetate buffer, I=0.02	kin (74Gc)	A	a
Th	5.05	Acetate buffer, I→0	kin (65S)	A	a,c,e
Th	4.55	Acetate buffer, I=0.02	kin (74Gc)	A	a,c
Ligand: Di-n-pentyl phosphate					
La	2.5	Acetate buffer, I→0	kin (66S)	A	a,e
Nd	2.7	Acetate buffer, I→0	kin (66S)	A	a,e
Yb	3.8	Acetate buffer, I→0	kin (66S)	A	a,e
Th	5.4	Acetate buffer, I→0	kin (66S)	A	a,c,e
Ligand: Di-n-hexyl phosphate					
La	2.8	Acetate buffer, I=0.023	kin (72G)	A	a
Ce	3.0	Acetate buffer, I=0.023	kin (72G)	A	a
Pr	3.1	Acetate buffer, I=0.023	kin (72G)	A	a
Nd	3.2	Acetate buffer, I=0.023	kin (72G)	A	a
Sm	3.4	Acetate buffer, I=0.023	kin (72G)	A	a
Eu	3.5	Acetate buffer, I=0.023	kin (72G)	A	a
Gd	3.6	Acetate buffer, I=0.023	kin (72G)	A	a
Tb	3.7	Acetate buffer, I=0.023	kin (72G)	A	a

continued

TABLE IV-1 (continued)

M	log β_1	Medium	Method, ref.	Category	Note
Dy	3.8	Acetate buffer, I=0.023	kin (72G)	A	a
Ho	3.9	Acetate buffer, I=0.023	kin (72G)	A	a
Er	4.0	Acetate buffer, I=0.023	kin (72G)	A	a
Tm	4.1	Acetate buffer, I=0.023	kin (72G)	A	a
Yb	4.2	Acetate buffer, I=0.023	kin (72G)	A	a
Lu	4.4	Acetate buffer, I=0.023	kin (72G)	A	a
Y	4.0	Acetate buffer, I=0.023	kin (72G)	A	a
Th	5.5	Acetate buffer, I=0.020	kin (72G)	A	a,c
Ligand: Di-n-octyl phosphate					
La	4.3	Acetate buffer, I=0.02	kin (74Gc)	A	a
Nd	4.6	Acetate buffer, I=0.02	kin (74Gc)	A	a
Yb	5.5	Acetate buffer, I=0.02	kin (74Gc)	A	a
Th	6.0	Acetate buffer, I=0.02	kin (74Gc)	A	a,c
Ligand: Bis(2-ethylhexyl) phosphate					
La	4.4	Acetate buffer, I=0.022	kin (72Gb)	A	a
Ce	5.55	Acetate buffer, I=0.022	kin (72Gb)	A	a
Pr	4.6	Acetate buffer, I=0.022	kin (72Gb)	A	a
Nd	4.65	Acetate buffer, I=0.022	kin (72Gb)	A	a
Sm	4.9	Acetate buffer, I=0.022	kin (72Gb)	A	a
Eu	4.9	Acetate buffer, I=0.022	kin (72Gb)	A	a
Gd	5.0	Acetate buffer, I=0.022	kin (72Gb)	A	a
Tb	5.1	Acetate buffer, I=0.022	kin (72Gb)	A	a
Dy	5.2	Acetate buffer, I=0.022	kin (72Gb)	A	a
Ho	5.3	Acetate buffer, I=0.022	kin (72Gb)	A	a
Er	5.4	Acetate buffer, I=0.022	kin (72Gb)	A	a
Tm	5.45	Acetate buffer, I=0.022	kin (72Gb)	A	a
Yb	5.55	Acetate buffer, I=0.022	kin (72Gb)	A	a
Lu	5.7	Acetate buffer, I=0.022	kin (72Gb)	A	a
Th	6.45	Acetate buffer, I=0.020	kin (72Gb)	A	a,c

continued

TABLE IV-1 (continued)

M	log β_1	Medium	Method, ref.	Category	Note
Ligand: Di-n-decyl phosphate					
M	(orig)	Acetate buffer, I=0.02	kin (74Gc)	N	a,h
Ligand: Diphenyl phosphate					
La	1.8	Acetate buffer, I=0.02	kin (74Gc)	A	a
Nd	2.1	Acetate buffer, I=0.02	kin (74Gc)	A	a
Gd	2.4	Acetate buffer, I=0.02	kin (74Gc)	A	a
Yb	2.9	Acetate buffer, I=0.02	kin (74Gc)	A	a
Lu	3.0	Acetate buffer, I=0.02	kin (74Gc)	A	a
Th	4.2	Acetate buffer, I=0.02	kin (74Gc)	A	a,c
Ligand: Di-p-cresyl phosphate					
La	2.8	Acetate buffer, I=0.02	kin (74Gc)	A	a
Nd	3.05	Acetate buffer, I=0.02	kin (74Gc)	A	a
Eu	3.25	Acetate buffer, I=0.02	kin (74Gc)	A	a
Gd	3.3	Acetate buffer, I=0.02	kin (74Gc)	A	a
Tb	3.5	Acetate buffer, I=0.02	kin (74Gc)	A	a
Ho	3.6	Acetate buffer, I=0.02	kin (74Gc)	A	a
Yb	3.8	Acetate buffer, I=0.02	kin (74Gc)	A	a
Lu	3.9	Acetate buffer, I=0.02	kin (74Gc)	A	a
Th	5.1	Acetate buffer, I=0.02	kin (74Gc)	A	a,c
Ligand: Di-n-pentyl phosphinate					
La	2.05	Acetate buffer, I=0.023	kin (72Ga)	A	a
Ce	2.15	Acetate buffer, I=0.023	kin (72Ga)	A	a
Pr	2.25	Acetate buffer, I=0.023	kin (72Ga)	A	a
Nd	2.3	Acetate buffer, I=0.023	kin (72Ga)	A	a
Sm	2.6	Acetate buffer, I=0.023	kin (72Ga)	A	a
Eu	2.7	Acetate buffer, I=0.023	kin (72Ga)	A	a
Gd	2.9	Acetate buffer, I=0.023	kin (72Ga)	A	a
Tb	2.95	Acetate buffer, I=0.023	kin (72Ga)	A	a
Dy	3.1	Acetate buffer, I=0.023	kin (72Ga)	A	a
Ho	3.15	Acetate buffer, I=0.023	kin (72Ga)	A	a
Er	3.2	Acetate buffer, I=0.023	kin (72Ga)	A	a

continued

TABLE IV-1 (continued)

M	log β_1	Medium	Method, ref.	Category	Note
Tm	3.4	Acetate buffer, I=0.023	kin (72Ga)	A	a
Yb	3.4	Acetate buffer, I=0.023	kin (72Ga)	A	a
Lu	3.6	Acetate buffer, I=0.023	kin (72Ga)	A	a
Y	3.2	Acetate buffer, I=0.023	kin (72Ga)	A	a
Th	5.1	Acetate buffer, I=0.020	kin (72Ga)	A	a,c

Ligand: Diisopentyl phosphinate

M	log β_1	Medium	Method, ref.	Category	Note
La	1.9	Acetate buffer, I=0.023	kin (72Ga)	A	a
Nd	2.25	Acetate buffer, I=0.023	kin (72Ga)	A	a
Sm	2.4	Acetate buffer, I=0.023	kin (72Ga)	A	a
Eu	2.6	Acetate buffer, I=0.023	kin (72Ga)	A	a
Gd	2.75	Acetate buffer, I=0.023	kin (72Ga)	A	a
Tb	2.8	Acetate buffer, I=0.023	kin (72Ga)	A	a
Ho	3.0	Acetate buffer, I=0.023	kin (72Ga)	A	a
Yb	3.4	Acetate buffer, I=0.023	kin (72Ga)	A	a
Lu	3.6	Acetate buffer, I=0.023	kin (72Ga)	A	a
Y	3.1	Acetate buffer, I=0.023	kin (72Ga)	A	a
Th	5.05	Acetate buffer, I=0.020	kin (72Ga)	A	a,c

Ligand: Di-n-heptyl phosphinate

M	log β_1	Medium	Method, ref.	Category	Note
La	3.1	Acetate buffer, I=0.023	kin (72Ga)	A	a
Ce	3.2	Acetate buffer, I=0.023	kin (72Ga)	A	a
Pr	3.35	Acetate buffer, I=0.023	kin (72Ga)	A	a
Nd	3.4	Acetate buffer, I=0.023	kin (72Ga)	A	a
Sm	3.65	Acetate buffer, I=0.023	kin (72Ga)	A	a
Eu	3.8	Acetate buffer, I=0.023	kin (72Ga)	A	a
Gd	4.0	Acetate buffer, I=0.023	kin (72Ga)	A	a
Tb	4.1	Acetate buffer, I=0.023	kin (72Ga)	A	a
Dy	4.1	Acetate buffer, I=0.023	kin (72Ga)	A	a
Ho	4.25	Acetate buffer, I=0.023	kin (72Ga)	A	a
Er	4.45	Acetate buffer, I=0.023	kin (72Ga)	A	a
Tm	4.55	Acetate buffer, I=0.023	kin (72Ga)	A	a
Yb	4.7	Acetate buffer, I=0.023	kin (72Ga)	A	a
Lu	4.85	Acetate buffer, I=0.023	kin (72Ga)	A	a

continued

TABLE IV-1 (continued)

M	$\log \beta_1$	Medium	Method, ref.	Category	Note
Y	4.4	Acetate buffer, I=0.023	kin (72Ga)	A	a
Th	5.75	Acetate buffer, I=0.020	kin (72Ga)	A	a,c
Ligand: Di-n-octyl phosphinate					
La	3.7	Acetate buffer, I=0.023	kin (72Ga)	A	a
Ce	3.9	Acetate buffer, I=0.023	kin (72Ga)	A	a
Pr	3.9	Acetate buffer, I=0.023	kin (72Ga)	A	a
Nd	4.0	Acetate buffer, I=0.023	kin (72Ga)	A	a
Sm	4.2	Acetate buffer, I=0.023	kin (72Ga)	A	a
Eu	4.4	Acetate buffer, I=0.023	kin (72Ga)	A	a
Gd	4.5	Acetate buffer, I=0.023	kin (72Ga)	A	a
Tb	4.5	Acetate buffer, I=0.023	kin (72Ga)	A	a
Dy	4.6	Acetate buffer, I=0.023	kin (72Ga)	A	a
Ho	4.75	Acetate buffer, I=0.023	kin (72Ga)	A	a
Er	4.8	Acetate buffer, I=0.023	kin (72Ga)	A	a
Tm	5.0	Acetate buffer, I=0.023	kin (72Ga)	A	a
Yb	5.05	Acetate buffer, I=0.023	kin (72Ga)	A	a
Lu	5.25	Acetate buffer, I=0.023	kin (72Ga)	A	a
Y	4.8	Acetate buffer, I=0.023	kin (72Ga)	A	a
Th	6.0	Acetate buffer, I=0.020	kin (72Ga)	A	a,c
Ligand: Bis(2-ethylhexyl) phosphinate					
La	3.9	Acetate buffer, I=0.02	kin (74Gc)	A	a
Nd	4.3	Acetate buffer, I=0.02	kin (74Gc)	A	a
Lu	5.2	Acetate buffer, I=0.02	kin (74Gc)	A	a
Th	6.0	Acetate buffer, I=0.02	kin (74Gc)	A	a,c
Ligand: Di-sec-nonyl phosphinate					
La	3.65	Acetate buffer, I=0.023	kin (72Ga)	A	a
Nd	3.9	Acetate buffer, I=0.023	kin (72Ga)	A	a
Sm	4.1	Acetate buffer, I=0.023	kin (72Ga)	A	a
Eu	4.2	Acetate buffer, I=0.023	kin (72Ga)	A	a
Gd	4.3	Acetate buffer, I=0.023	kin (72Ga)	A	a
Tb	4.4	Acetate buffer, I=0.023	kin (72Ga)	A	a

continued

TABLE IV-1 (continued)

M	log β_1	Medium	Method, ref.	Category	Note
Ho	4.6	Acetate buffer, I=0.023	kin (72Ga)	A	a
Yb	4.8	Acetate buffer, I=0.023	kin (72Ga)	A	a
Lu	5.0	Acetate buffer, I=0.023	kin (72Ga)	A	a
Y	4.65	Acetate buffer, I=0.023	kin (72Ga)	A	a
Th	5.8	Acetate buffer, I=0.020	kin (72Ga)	A	a,c
Ligand: Octyl phenyl phosphinate					
La	3.5	Acetate buffer, I=0.02	kin (74Gc)	A	a
Nd	3.85	Acetate buffer, I=0.02	kin (74Gc)	A	a
Lu	4.7	Acetate buffer, I=0.02	kin (74Gc)	A	a
Th	5.6	Acetate buffer, I=0.02	kin (74Gc)	A	a,c
Ligand: 2-Ethylhexyl phenyl phosphinate					
La	3.55	Acetate buffer, I=0.02	kin (74Gc)	A	a
Nd	3.9	Acetate buffer, I=0.02	kin (74Gc)	A	a
Lu	4.8	Acetate buffer, I=0.02	kin (74Gc)	A	a
Th	5.6	Acetate buffer, I=0.02	kin (74Gc)	A	a,c

with constants determined by the kinetic method.

e) The measurements have been made at an ionic strength of ~0.02 produced by the acetate buffer; the β_1 values have been recalculated to a zero ionic strength and represent thermodynamic stability constants.

f) β_2 and β_3 are also reported. All three constants have been determined by an inaccurate graphical method from merely six experimental points.

g) The slope of the log $D_M = f(\log \overline{c}_{A,i})$ dependency has been found to have a slope of 2.1 instead of the expected value of 3 and this has been ascribed to the existence of the species MA^{2+} in the aqueous phase. In such case the dependency would have to be curved, because the concentration ratio of M^{3+} and MA^{2+} depends on the ligand concentration in the system. No deviation of the log $D_M = f(\log \overline{c}_{A,i})$ dependency from the slope 3 is mentioned in the numerous papers dealing with the extraction of lanthanides(III) by (H)DBP under conditions similar to (61S).

h) M = La, Nd, Sm, Eu, Gd, Tb, Ho, Yb, Lu and Th. The trend of the stability of metal complexes increasing with the number of carbon atoms in the molecule of the di-*n*-alkyl phosphate ligand is not followed in the case of the anion of (H)DNP and the plausibility of the β_1 values cannot be assessed.

IV.2. SOLUTIONS IN ORGANIC DILUENTS

Equilibria involving lanthanides(III) have been studied exclusively by the solubility method in solid-liquid systems. The solid phase has been a compound MA_3 formed by a lanthanide(III) with the anion of a diester of phosphoric acid and the liquid phase has been a solution of the respective diester in a nonpolar diluent. Data are available on systems involving Nd(III), (H)DBP or (H)DOP and benzene (63Ka), Yb(III), (H)DBP or (H)DOP and benzene (63Ka), Yb(III), (H)DBP and CCl_4 (61K,62S,63Ka) and Ce(III) or Y(III), (H)DpCP and chloroform (72F,72Fa). The logarithmic plot of the solubility vs. the equilibrium concentration of the acidic organophosphate is in each case a straight line with a slope of 1.5 and the reaction in the solution has been written as $\overline{MA_3} + 1.5\overline{(HA)_2} = \overline{MA_3.3HA}$. The corresponding equilibrium constants $K_{s,1.5}$ have been calculated for all of the above systems. Although the results of the solubility experiments appear to be well reproducible, there are two reasons why the $K_{s,1.5}$ values cannot be accepted: First, no direct evidence (like results of chemical analysis) has been given that the composition of the solid phase remains unchanged during the contanct with the liquid phase and, second, the concentration of M(III) in the resulting solution is rather high and the complexes formed can polymerize. An enhanced viscosity of the equilibrium liquid phase, observed in experiments with Nd(III) and dialkyl phosphoric acids in CCl_4 (63Ka) and data on the extraction with (H)DpCP in (70F) clearly show that the polymerization cannot be excluded.

A spectrophotometric study has been made of the reaction of the Pu(IV) solvate $Pu(NO_3)_4.2B$ (B = TBP) with (H)DBP in Sintine and CCl_4 (76S). The reaction has been postulated to be

$$\overline{Pu(NO_3)_4.2B} + 2\overline{HA} = \overline{Pu(NO_3)_4.2HA} + 2\overline{B},$$

but nothing more has been proved than the over-all reaction stoichiometry, i.e. that a molecule of the solvate reacts with one (H)DBP dimer or two (H)DBP monomers. No evidence has been given which would allow one to exclude other interpretations, e.g. the reaction

$$\overline{Pu(NO_3)_4.2B} + 2\overline{HA} = \overline{Pu(NO_3)_2A_2} + \overline{2B.HNO_3}$$

which is possible as well. The experimental results clearly indicate that the (H)DBP containing complex is polymerized, but this has not been taken into account in the definition of the equilibrium constant of the reaction suggested. The constant, which of course is fully unacceptable, is presented in a confusing way: there is no consistency between the values given in Table 2 of the original paper and the text, and a simple recalculation of the experimental data, presented numerically in the paper, gives again a quite different value.

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