SOLVENT EXTRACTION OF INORGANIC SPECIES

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I. INTRODUCTION

The field of solvent extraction of inorganic species has been reviewed by Diamond and Tuck (77) up to the end of 1958. At about the same time, Martin and Holt (252) published a short review, while earlier, Morrison and Freiser (281) stressed in particular the analytical applications. Earlier reviews, like those of Irving (166) and Kuznetsov (222), are now out of date, however, the latter gives references to lesser known Russian work. For readers of Russian, Fomin's recent book (103) is a very good summary, particularly of Russian work.

The present review covers the literature up to the beginning of 1962, putting particular emphasis on work published since the review by Diamond and Tuck (77). It is restricted to systems involving the distribution of inorganic species between aqueous solutions and (practically) immiscible organic solvents. The important systems involving organic chelating agents like acetylacetone, dithizone, hydroxyquinolines, *etc.*, are not included in this review, since they have been covered adequately previously (281), and no radically new developments in this field have occurred recently. However, some of the theoretical considerations involved are treated with the other material for the sake of completeness. The discussion is limited to equilibrium conditions at constant temperature and relates the distribution coefficients to the chemical nature and the concentrations of the reagents and species involved.

Analytical and preparative separations, instrumental design, flow sheets for multiple contact or counter-current extraction, *etc.*, are outside the scope of this review.

The usual abbreviations are used for organic radicals such as Me for methyl, Oc for octyl, *etc.* Others, for example, TBP for tri-*n*-butyl phosphate, are explained when first encountered in the text. The symbols listed are used

A^-, B^-	simple ligands
G	salting agent
M^{m+}	metal ion
S	solvating solvent
X^-	anion of chelating ligand
C_i	total concentration of i
D_i	distribution coefficient of i
F	correction function
h	hydration number
I	ionic strength
K	equilibrium constant
m_i	molality of i
N_i	mole fraction of i
q	solvation number
r	crystal radius of ion
R	surface density of water in first coördination sphere
S	salting out parameter
V_i	molar volume of i
y_i	molar activity coefficient of i
z	charge

Z	atomic number
α	number of bound water molecule per mole
β	over-all complex formation constant
δ	Harned's law coefficient
θ	fraction ionized
(i)	concentration of i, usually on molar scale

For all symbols suffix "or" denotes the organic phase and no suffix, the aqueous phase.

II. General Considerations

A. CLASSIFICATION OF EXTRACTION SYSTEMS

Extraction systems may be classified according to the reactions involved and the nature of the solute–solvent interaction. However, it must be borne in mind that there are gradual transitions from one mode of behavior to another.

A. The distribution of neutral covalent molecules like ruthenium tetroxide (251), iodine (14) or mercury halides (239) between aqueous solutions and inert solvents such as hydrocarbons constitutes one class of behavior, *i.e.*, physical distribution based on relative solubilities. Some compounds, like germanium and arsenic chlorides (45), show this kind of behavior, in addition to extracting as halo-acids.

B. The class of halo-metallic acid extraction involves anionic complexes of metals with ligands, mainly halide anions. These are extracted as acids, the protons of which are solvated by solvating solvents, containing as donor atoms mainly oxygen. Usually it is not possible to assign a definite solvation number for the proton (or oxonium ion). Examples are the extraction of indium bromide by ether (78) or of protactinium chloride (56) by hexone (MeCO*i*Bu). Some compounds, *e.g.*, molybdenum(VI) chloride, MoO_2Cl_2, exhibit this behavior, along with direct solvation of the metal as discussed below (339).

C. An important class of extraction systems consists of extraction by the solvating solvent directly solvating the metallic cation. It is usually possible to assign a definite solvation number, which is the difference between the number of anionic ligands needed to make the complex neutral and the coördination number of the metal. Often, secondary solvation occurs as well. The solvents of systems belonging to class B are also in this class, but in addition there are also very strongly solvating solvents like tri-*n*-butyl phosphate (TBP), which are more strongly basic than ethers or ketones. These will be considered separately below. Examples of these extraction systems are the extraction of cobalt perchlorate by octanol (278), and of uranyl nitrate by TBP (245).

Some of the more basic extractants, such as trialkylphosphine oxides, approach the behavior of another class of extractants, the strongly basic nitrogen-containing reagents, class F.

D. Liquid cation exchangers, which are organic acids, mainly acidic phosphorus esters, dissolved in diluents, are another important class. They extract metals by forming complexes with them and are usually further solvated by additional molecules of ester, as for example the extraction of lanthanides by dibutylphosphoric acid forming $Ln(Bu_2PO_4,HBu_2PO_4)_3$ (83). At high acidities, acid dissociation of the esters is repressed, and they may then act as solvating solvents, like TBP (class C). In many, but not all cases, the acid phosphorus esters behave like chelating agents, when a metal displaces the acid hydrogen and forms a chelate ring with two oxygen atoms connected to the phosphorus.

E. The class of chelate extraction, where metals are complexed by reagents satisfying simultaneously the charge neutralization and coördination number requirements, yielding compounds much more soluble in inert organic solvents than in water, is outside the scope of this review. These chelates usually do not require further solvation, although in some cases, such as with 2-thenoyltrifluoroacetone (TTA), this can bring about much higher distribution coefficients (169).

F. In extraction by strongly basic reagents, the solvent, usually diluted by an inert diluent, is attached so strongly to protons that stable onium species are formed, like trialkylammonium cations. These extract anionic metal complexes by ion pair formation rather than by direct solvation. Since the anion attached to the ammonium cation may be exchanged for others, or for complex metal anions, these solvents are often called liquid anion exchangers, resembling the resin exchangers in many of their properties. An example is the extraction of uranyl sulfate by triisooctylamine (TIOA) from sulfuric acid forming $(iOc_3NH)_4UO_2(SO_4)_2$ (96). Quaternary amines extract by a similar mechanism, but are effective also in non-acid solutions.

G. A final class of extraction system includes ion pairs formed by large cations and anions, which as with the chelates do not require further solvation, and behave in inert solvents as if they were covalent molecules, bringing us back to class A. Examples are tetraphenylarsonium perrhenate (406) and cesium tetraphenylborate (98). A similarity to extraction by amines is also evident, particularly to the behavior of quaternary amines, discussed under class F.

B. DEPENDENCE OF THE DISTRIBUTION COEFFICIENTS ON CONCENTRATION

The extraction of a solute from an aqueous solution is expressed by the distribution coefficient D. This quantity is independent of the concentration of the solute only in the ideal case of complete immiscibility of the phases and non-existence of either interactions between the solute and the solvent or dissociation or association reactions (Nernst's law). It is then called the thermodynamic partition constant. It is equal to the ratio of solubilities of the solute in the two phases, provided that the reactions enumerated above do not occur at the saturation point. These conditions are never attained in practice.

Some systems, however, do approach this behavior, and extraction isotherms, *i.e.*, plots of the concentration in the organic phase *vs.* the concentration in the aqueous phase, may have a linear portion near zero concentration, the slope being the distribution coefficient. At higher concentrations, interactions with the organic solvent occur and it may become saturated, the isotherm flattening out. In such cases, the distribution coefficients may depend on the relative volumes of the phases. This may be avoided by working at very low concentrations of the solute, *e.g.*, with radioactive tracers, although then difficulties because of adsorption on walls of vessels or reactions with impurities may occur. Generally, however, distribution coefficients are independent of the volume ratios.

In the general case the distribution coefficients depend on the concentration of the distributing solute and on the composition of the phases. Changes in the distribution coefficients are due on the one hand to chemical reactions involving the solute, and on the other to non-specific interactions with the solvents or other solutes. The chemical reactions can be described in terms of the stoichiometry and equilibrium constants involved and obey the mass action law. Often they are sufficient to describe the gross behavior of the distribution coefficients. However, non-stoichiometric effects of other solutes, generally considered as salting in or out, and effects of solvent interactions, generally considered as non-ideality and described in terms of activity coefficients, play a major role and can obscure the simple picture of dependency on the stoichiometric effects.

1. Mass Action Law Effects

For some extraction systems there is only one species of the metal in the organic phase, and the distribution coefficients may be directly interpreted in terms of equilibria in the aqueous phase. Here belong not only the chelate extraction systems and cases of simple molecular distribution, but also cases where interaction in the organic phase is practically complete, as when there are very large equilibrium constants for dissociation, self-association or association with the solvent reactions. Rydberg (333, 335) and Dyrssen (91), applying the mass action law, derived the pertinent equations and showed how equilibrium constants may be calculated from the data. These or similar equations have been widely used to describe chelate extraction systems, *e.g.*, those of TTA (319), or general applications in analysis (297).

When a chelate MX_m is the only species in the organic phase, obtained by the reactions

$$M^{m+} + mHX_{\text{or}} \rightleftarrows MX_{m\ \text{or}} + mH^+;\ K_m \qquad (1)$$

then all reactions of M^{m+} in the aqueous phase with chelate ligands forming $M_{Xx}{}^{m-x}$, and with other ligands A, B,... (including hydrolytic species where the ligand may be either OH^- or $-H^+$) can be studied by measuring the distribution coefficients as a function of ligand concentration, using (in the case of mononuclear complexes)

$$D = K_m(HX)^m(X)^{-m}/\sum_{x,a,b,\ldots=0}^{N} \beta_{x,a,b,\ldots}(X)^x(A)^a(B)^b\ldots \qquad (2)$$

Partial differentiation of log D with respect to the concentration of the ligands will give the average ligand numbers, provided activity coefficients are kept constant. In the case of the chelating ligand itself, the difference between m and the ligand number is obtained. The predominant species in both phases are thus known as a function of concentration. Treatment of the data by graphical means or least squares computing (335) yields the equilibrium constants for all reactions.

Job's method of continuous variations requires the study of a property of a system at constant total concentration of two reactants as function of composition. Since the concentration of a solute in the organic phase is proportional to that of the species of the same composition in the aqueous phase, the distribution coefficient can act as this property (104, 110, 172, 389). The general drawbacks and errors involved in the method are of course also present here (104, 172).

In general, several species of the solute exist in the organic phase. In extraction systems belonging to classes B, C, D and E there are dissociation reactions of ion pairs and association reactions with solvating solvents, among others, to be considered. Irving and Rossotti (174) presented general equations for class B systems that take only some of these reactions into account. In particular, changes in the distribution coefficients with metal concentration could be subject to different interpretations. An increase of D with the metal concentration is often ascribed to polymerization in the organic phase (174, 226), whereas self-salting-out may also be an important cause at higher concentrations. Decrease of D with increasing metal concentration was thought in the past to be due to polymerization in the aqueous phase, but this is not always the case. Thus the dissociation of halo-metallic acids in the organic phase causes complications that are discussed by Poskanzer (317), Saldick (339) and Diamond and Tuck (77). The equations presented by these authors relate the distribution coefficients to the concentrations of the distributing metal, of acid and of the halide ion. Assuming in a typical case the reactions

$$\mathrm{M}^{3+} + 4\mathrm{A}^- + \mathrm{H}^+ \rightleftarrows \mathrm{H}^+_{\mathrm{or}} + \mathrm{MA}_4{}^-{}_{\mathrm{or}} \quad (K_\mathrm{M}) \tag{3}$$

$$\mathrm{H}^+ + \mathrm{A}^- \rightleftarrows \mathrm{H}^+_{\mathrm{or}} + A^-_{\mathrm{or}} \quad (K_\mathrm{A}) \tag{4}$$

and

$$\mathrm{H}^+_{\mathrm{or}} + \mathrm{MA}_4{}^-{}_{\mathrm{or}} \rightleftarrows \mathrm{HMA}_{4\,\mathrm{or}} \quad (\mathrm{K}_{\mathrm{HM}}) \tag{5}$$

to be the only important reactions that involve the solvent phase (with the equilibrium constants in parentheses), then the distribution coefficient for M is

$$D = K_\mathrm{M}\beta_{4,0,0,\ldots}[(\mathrm{H})K_{\mathrm{HM}} + \{K_\mathrm{A}(\mathrm{H})(\mathrm{A}) + K_\mathrm{M}(\mathrm{H})(\mathrm{MA}_4{}^-)\}^{-1/2}]/\Sigma\beta_{a,b\ldots}(\mathrm{A})^{a-4}(\mathrm{B})^b\ldots \tag{6}$$

seen to be a complicated function of the concentration of H^+, A^- and of the metal M itself. Depending on the relative magnitude of K_A, K_M and K_{HM} and on the concentrations, various limiting cases can be derived by neglecting certain terms, where a simpler dependence should be observed.

For class C and D systems, where the organic species is solvated, it is often possible to determine the solvation number and identify the extracted species, when, in addition to the effects of the ligand, the dependence on solvent concentration is also considered. It is customary to identify the slope of a logarithmic plot of the distribution coefficient *vs.* the solvent concentration in the diluent with the solvation number. This is true only in the range where ideal behavior is followed as Hesford and McKay (153) have shown, *i.e.*, in very dilute solutions of both metal (*e.g.*, tracer) and solvent. The effect of saturating the solvent by the metal, thus decreasing the concentration of free solvent, must be considered at higher metal concentrations. This method may also be used to determine the solvation number at, or near to, saturation. This solvation number need not be identical with that obtained at low concentrations. The effect of competition for the solvent between the metal and the acid, usually present at high concentration, need also be considered when interpreting the distribution data.

The equations become rather complicated in the general case, but with tracer metal M^{m+} extracted from the acid HA as the solvated species $\mathrm{MA}_m\mathrm{S}_n$ and the acid extracted as $(\mathrm{HA})_q\mathrm{S}_p$, then, for the metal

$$D = \mathrm{K}_n(\mathrm{A})^m C_{\mathrm{S\,or}}{}^n/(1 - p\,\mathrm{K}_p(\mathrm{A})^{2q}(\mathrm{S})_{\mathrm{or}}{}^{p-1})\left(\sum_{a,b=0}^{N} \beta_{a,b}(\mathrm{A})^a(\mathrm{B})^b\right) \tag{7}$$

where K_n and K_p are the equilibrium constants for the extraction of M and A, respectively, C_{Sor} is the total concentration of the solvent in the organic phase, and complexes involving ligands B... are assumed not to be extracted. The first term in the denominator corrects for the solvent bound to the acid. Activity coefficients are assumed to remain constant and are included in the equilibrium constants. Partial differentiation with respect to C_{Sor} will give the solvation number n only when $p = 1$ or at $K_p(\mathrm{A})^{2q} << 1$.

2. Non-stoichiometric Concentration Effects

The above general equations apply only where non-stoichiometric effects are negligible, or activity coefficients are practically constant. Unfortunately, such conditions are only seldom encountered, since most extraction systems require moderate to high concentrations of ligands and solvents for measurable extraction.

Activity coefficients for the mixed components of the solvent extraction systems are difficult to determine. It is possible to determine the activity coefficients for a solvent in a diluent, *e.g.*, by cryoscopy or vapor pressure measurements (48) on the diluent and application of the Gibbs–Duhem equation. They can be expressed in different ways as a function of the concentration of the solvent, *e.g.*, $y_{\mathrm{Sor}} = 1 - 0.24(\mathrm{S})^{0.48}$ for TTA (319), $\log y_{\mathrm{Sor}} = 0.3(1 - (\mathrm{S}))^2$ (330) and $\log y_{\mathrm{Sor}} = -1.0(\mathrm{S})$ (153), for TBP in kerosene. The disagreement between the last two expressions shows the unsatisfactory position with regard to the activity coefficients even for a thoroughly studied solvent such as TBP. The situation becomes even worse when it becomes necessary to consider the activity coefficients in the presence of extracted acids and salts. As a first approximation it is often assumed that the activity coefficients of all (non-dissociated) species in the organic phase vary in a similar manner (245), *i.e.*, as $\log y_{\mathrm{or}} = k(\mathrm{S})$ where k is a "salting out" constant, often large and negative (153). However, there exists neither theory nor an experimental approach to the general solution of this problem.

Systems without diluents, belonging to class C, where appreciable concentrations of salts in the organic solvent occur, also have been studied, in particular with reference to the extraction of uranyl nitrate. Equations for the activities of uranyl nitrate, water and solvent for both phases were derived by McKay and coworkers (116, 117, 121, 177, 261, 264).

In some systems, complications occur because of self-association of the solvent, which may depend on the presence of extracted species. For instance, some long chain amines were found to form micellar aggregates of (practically) constant activity, independent of concentration (see section IIIF).

In general it is safest to work at low concentration and to test the system on a case where the expected ideal behavior is known. Deviations should then be ascribed to non-ideality, *i.e.*, activity coefficients should be calculated, and applied to the systems which are under study. Illustrations of this procedure are given below in the sections devoted to the various extraction systems.

In the aqueous phase there are similar problems. The activity coefficients of electrolytes in mixtures are not well known, in particular for the high concentrations usually involved. With chelate extraction systems it is often possible to provide a constant ionic medium which keeps activity coefficients approximately constant. With other systems this is seldom possible. Indeed, the perchlorate often added to provide the ionic medium, under the assumption that it does not form complexes with metals, has been shown to participate in extraction by TBP and other solvents (191, 324). Similarly, perchloric acid has been found to interfere seriously in halo-metallic acid extractions (77), since it provides extra hydrogen ions in the organic phase that show the common ion effect; hence it cannot be used to provide an inert constant ionic medium.

In the extraction of metal complexes by class B, C or E solvents, the electrolyte which provides the ligand usually is present in much higher concentrations than the metal. It acts both as a complexant, and as a salting-out agent. A satisfactory solution for the problem of salting out has not yet been found. Expressions by Debye (73) in terms of electrical effects, and by McDevit and Long (258) in terms of internal pressures, explain some of the observed effects. The reduction of water activity, or the dehydration of the metal to be complexed by highly hydrated cations, is probably also an important effect.

Two Russian workers have proposed semi-empirical treatments that permit the evaluation of the salting-out effect. Adamskii (2) describes the effect in terms of the parameter S

$$S_{UG} = \frac{\alpha_U C_U + \alpha_G C_G}{(1000 - C_U \bar{V}_U - C_G \bar{V}_G)/18 + I_U + I_G} \qquad (8)$$

where C is the molarity, α the number or bound water molecules per mole (obtained from the value at saturation), $\bar{V}$ the molar volume, and I the contribution to the ionic strength for the distributing salt U (in this case uranium), and the salting agent G. Adamskii found that the distribution coefficients of uranyl nitrate between oxygenated solvents and aqueous nitrate solutions depend only on S, but not otherwise on the nature or concentration of the salting agents. If the relationship $D = \mathrm{f}(S)$ is known for a given solvent, $D = \mathrm{f}(S, C_G)$ can be calculated, knowing α_G and $\bar{V}_G$, which are given in the tables. Although the data presented (2) certainly conform to this treatment, the physical significance of S, the ratio of the concentration of bound water to the sum of the ionic strength and the number of moles of water in the solution, is obscure. However, the treatment correctly predicts the increase of salting efficiency of G with its water binding power, α_G, and its (hydrated) molar volume, $\bar{V}_G$.

Another approach is that of Solovkin (386), who has found the relation $\log D = \text{const.} + 3 \log R_e'$, for the extraction of uranium by diisoamyl methyl phosphonate (DAMP), where $R_e' = m_B z_B R'$, m is the molality and z the charge of the cation of the salting agent, and R' is Samoilov's "surface density of water in first coördination sphere," $R' = n/4\pi(r + 1.38)^2$, where n is the coordination number, and $r + 1.38$ is the modified crystal radius of the cation in Ångströms. This density is also connected with Harned's law coefficient, $\delta_G = 0.424 - 6.9R'$, giving the activity coefficient of the extracted salt in the presence of the salting agent, $\log y_U = \log y_U^0 - \delta_G I_G$. The reason for the relationship found between δ_G and R' is not clear, but it holds for many mono-, di- and trivalent nitrates. Again, the third power dependence of D on R' has not been explained, so that, in spite of R' having physical significance and allowing the successful correlation of the distribution data, it does not provide a sound general theoretical basis to the salting-out effect.

The salting-out effect is most frequently described by the Setchenov equation

$$\log y_U = k_{UG} C_G \qquad (9)$$

Where y_U is the activity coefficient of a non-electrolyte U, C_G is the molar concentration of salt, and k_{UG} is a salting coefficient specific for U and G. Often, the activity coefficient of an extractable electrolyte at low concentration can be described similarly when another electrolyte is present at a high concentration.

These considerations have been applied quite often to the extracting of inorganic species, without, however, being based on any fundamental theory which describes quantitatively the extraction behavior. It is easiest to show the validity of the Setchenov equation in the case of the extraction of neutral molecules, where reactions other than salting out are negligible, as in the case of the mercury halides (239). However, even with neutral molecules care must be exercised, as in the case of ruthenium tetroxide. The extraction of this compound from nitric acid was described both in terms of salting in (contrary to salting-out by sodium nitrate), and of formation of an inextractable protonated species by the action of the acid (251). Later experiments (370) showed that the latter explanation is not correct.

In the case of extraction of metal complexes, the effects of complex formation and salting out cannot be separated. It is generally agreed that the order of efficiency as a salting agent increases with the ionic potentials, the hydration number and the activity coefficients at high concentrations. Data for chlorides (76) and nitrates (177, 343, 419, 458) exemplify these relationships. The order, however, may be different for different extraction systems, and in particular with multivalent cations, the relative importance of the anion, acting as ligand, and of the cation, acting as a dehydrating agent, may be unclear, and it is difficult to decide whether salts should be compared at equal molarities or normalities (246).

In the case of tracer concentrations of a metal salt its concentration has a negligible effect on the activity coefficient of the electrolyte supplying the ligand, present at macro concentration, and the quantity has practically the same value as in pure solutions. The activity coefficient of the metal salt likewise is not influenced by its own concentration, but depends on that of the macro electrolyte. It is then often assumed that the ratio of activity coefficients of the various complexes formed by a metal with a given ligand is independent of the concentration of the ligand over a certain range. Further, the activity of the ligand is best described by the product of its concentration and the mean activity coefficient of the ligand electrolyte. Mass action law expressions using these assumptions have been found to fit the experimental data well in spectrophotometric (33), anion exchange (256) and solvent extraction (317) measurements.

The dependence of the distribution coefficients on the nature and concentration of so-called "inert diluents" has been studied only recently and is described later in the section on mixed solvents.

III. EXTRACTION SYSTEMS

A. NEUTRAL MOLECULES (CLASS A)

There is a small class of inorganic substances which can be extracted from aqueous solutions by inert solvents such as aliphatic and aromatic hydrocarbons, carbon tetrachloride, *etc.*, *i.e.*, without strong solvation. Some of them can enter into equilibria with other species in the aqueous phase, and the extraction behavior can then give information on these equilibria.

The extractability of the mercury(II) halides by inert solvents is well known and has been reviewed recently by Marcus (239), who also studied the salting-out behavior and the equilibria that the neutral halides undergo in the aqueous phase, *i.e.*, dissociation, and association with additional ligands (240). The distribution method was shown to be capable of giving equilibrium constants as accurate as those obtained potentiometrically, and they were consistent with those of different workers (282, 345). In connection with these studies, the ligand distribution method was revived, in that Marcus used the distribution of radioactive iodide to study the mixed bromo-iodo complexes (242) while Scaife and Tyrrell (345) measured the distribution of bromine to determine the concentration of free bromide ion *via* the reactions $Br^- + Br_2 \rightleftarrows Br_3^-$ and $Br_2(aq) \rightleftarrows Br_2(or)$ in a way similar to that used over fifty years ago by Dawson (72) in the analogous mercury–iodide systems. The mixed neutral complexes were studied by Marcus (241), who noticed different equilibrium constants in the two phases (benzene and aqueous 0.5 molar sodium perchlorate) for the reactions $HgA_2 + HgB_2 \rightleftarrows 2HgAB$, although only neutral molecules are involved. The polarity of the mixed complex HgAB may account for the different stabilities in the two environments (247). In the extraction of mercury(II) chloride by ketones and alcohols, D depends on the ratio oxygen atoms/carbon atoms, but not on the nature of the aliphatic chains (223).

The formation of interhalogen compounds of the type XY can be studied by measuring the distribution of species X_2, Y_2 and XY between two phases. Thus the formation of iodine cyanide (224) and of astatine halides (14) was studied by measuring the distribution of the species ICN between heptane, and of AtBr and AtI between carbon tetrachloride and aqueous phases. The distributions of iodine (14, 224, 447) and of ICl, IBr and Br_2 (14) also have been measured.

Both in the cases of mercury halides and halogens, pseudo-halogens such as thiocyanate and cyanide act qualitatively as halogens, but show much poorer extraction. Table I compares the extractability of these substances.

TABLE I

log D(C_6H_6–0.5 M $NaClO_4$)		log D(CCl_4–water)	
$Hg(CNS)_2$	−2.2	AtBr	−1.40
$HgCl_2$	−0.96	ICN	−1.23 (heptane)
HgClBr	− .42	ICl	−0.47
$HgBr_2$	.51	IBr	.63
HgICl	.28	IAt	.74
HgIBr	.79	Br_2	1.43
HgI_2	1.77	I_2	1.55 (heptane)
		I_2	1.93

Other halides that are extractable by non-solvating solvents are those of germanium, arsenic(III) and antimony(III). These elements are present as hydrolyzed species in dilute acid solutions, but germanium and arsenic show considerable extractability above about 6 M hydrochloric acid. Germanium reaches D values of the order of 1000, and arsenic of the order of 100. The species extracted seem to be $AsCl_3$ and $GeCl_4$ (45, 97, 348). Arsenic tribromide (43) and pentabromide (393) are extracted from hydrobromic acid, and both AsI_3 (45) and SbI_3 (325) from hydriodic acid. At higher concentrations of chloride, anionic, non-extractable species are formed, and the distribution coefficients show a maximum around 11 M hydrochloric acid. Arsenic(V) is not extractable under similar conditions (97) and the extraction of mercury(II) is negligible, because of the formation of anionic $HgCl_4^{2-}$ in concentrated hydrochloric acid. The possibilities for specific separations of mercury, arsenic and germanium from all other elements in chloride solutions by extraction with inert solvents are obvious.

The extraction of ruthenium and osmium tetroxides has received some attention recently. Previously assumed polymerization of osmium tetroxide in the organic phase has not been confirmed, and the results may be explained otherwise (77, 159). In alkaline solutions, ruthenium and osmium tetroxide probably take on hydroxide ions (or equivalently protons dissociate from hydrate water, although hydration has not been proved) and since the anions are not extractable, the distribution coefficients decrease (251, 344). In acid solutions, the decrease in the distribution coefficients has been attributed to basic properties of ruthenium tetroxide (a hydroxide ion dissociating from the hydrate water; 251, 252), along with a salting-out effect. However, the basic properties could not be confirmed by other experiments (370) and the salting-in effect must be more important than previously thought.

B. HALO-METALLIC ACIDS (CLASS B)

In the past few years considerable work has been done on the extraction of halo-metallic acids, and lately the quantitative relationships between the distribution coefficients and the concentrations of reagents have been clarified. An excellent analysis of these systems has been given by Diamond and Tuck (77). Since then little material of high significance has appeared, although a few papers are worthy of notice.

It is now generally accepted that in the extraction of, *e.g.*, iron(III) by ethers, the organic species is solvated $HFeCl_4$. Contrary to the suggestion of Morrison and Freiser (281), there is no primary solvation of the iron, which is tetrahedrally surrounded by chloride ions and apparently is saturated. This has been verified again recently by paramagnetic resonance (151). The hydration and solvation which have been observed are thus limited to the proton and to secondary solvation. Solvation by dibutyl ether was shown (114) to involve three molecules of ether, by studying the change of the distribution coefficient with the concentration of ether in carbon tetrachloride or benzene. The primary species may be $[O(HO(C_4H_9)_2)_3]^+ FeCl_4$, further solvated by water and ether (111), but species where the proton is primarily solvated by water only (225) have also been proposed. In low dielectric constant solvents, the primary species may aggregate by dipole interactions of the ion pairs, and may associate with ion paired hydrochloric acid. However, the excess hydrochloric acid extracted from iron-containing solutions over that extracted from pure hydrochloric acid may also be due to salting out by the iron. In high dielectric constant solvents, dissociation of both the hydrochloric and the chloroferric acids occur, and common ion effects, as described by Saldick (339), Poskanzer (317) and Diamond and Tuck (77) are possible. Maxima in extraction curves may be due to mutual solubility of the ether and the water phases in the presence of high concentrations of the halogen acids (349). This solubility changes considerably the activities of all species in each phase; hence the simple equations derived by Irving, Rossotti and Williams (174) for the case where there is negligible mutual solubility do not apply.

Other metals and halides show similar behavior. Of the recent publications, those on the following systems should be noted: iron(III)–bromide (125), indium–chloride (76), thallium(III)–chloride (160), gallium, indium and gold–chloride and bromide (318), gold(III)–chloride (317), indium–chloride and bromide (78), gallium–chloride and bromide (266). In all cases the species HMX_4 is extracted and the proton is solvated (and possibly hydrated) in the organic phase. The species forms ion pairs which dissociate in high dielectric constant solvents (with decreasing distribution coefficients with increasing metal [or perchloric acid] concentrations because of common ion effects) and cluster to higher aggregates in low dielectric constant solvents (distribution coefficients increasing with metal concentrations). The low extractability of indium may be due to its tendency to remain octahedral (256), *i.e.*, because of the possibility of reactions

$$InCl_3(H_2O)_3 + nCl^- \rightleftarrows InCl_{3+n}(H_2O)_{3-n}{}^{n-} + nH_2O \quad (10)$$

competing with the reaction

$$InCl_3(H_2O)_3 + Cl^- \rightleftarrows InCl_4^- + 3H_2O \quad (11)$$

The second reaction is the important one for the other metals, in particular for gallium, which has little tendency to add the first three chloride ions.

It is not clear whether neutral species such as $MA_3(H_2O)_3$ are extracted to an important extent. With strong donor solvents, the metal may be solvated directly and form octahedral MA_3S_3 in the organic phase. The importance of such species depends on the ability of the metal to retain octahedral coördination and of the solvent to compete with the halide ions. Such reactions have been invoked to explain discrepancies occurring when only the species HMA_4 is supposed to be extracted (125, 160). In the absence of extra halide ions, as in the dissolution of anhydrous iron(III) chloride in ether, the tetrahedral monosolvate $FeCl_3 . Et_2O$ is formed, as found by cryoscopy (111).

A somewhat similar case is that of cadmium iodide extraction by hexone, where H(solvated)CdI_3 and Cd(solvated)I_2 are the predominant species, depending on the concentration of iodide ions and on the pH (442). Another case is that of molybdenum(VI) (291), where solvated MoO_2Cl_2 was shown to be the important organic species at relatively low hydrochloric acid concentrations, but solvated $HMoO_2Cl_3$ becomes important at higher acidities, the ion $MoO_2Cl_3^-$ having been shown to exist in the corresponding aqueous solutions by anion exchange (243).

Some other cases, where the nature of the extracted species has not been established beyond doubt, probably belong to the same category of halo-metallic acid extraction. These are the cases of astatine(I) and (III), probably extracted as $HAtCl_2$ and $HAtCl_4$, respectively, from 1–12 *M* hydrochloric acid (293), and of the highly hydrolyzable metals arsenic(III) (16, 45), antimony(III) (332) and -(V) (210, 322, 349), niobium, tantalum and protactinum (56, 122), where species such as $M(H_2O)_h(OH)_y(Cl)_t^{m-(y+t)}$ with $h + y + t = 4$ for $m = 3$, and $h + y + t = 6$ for $m = 5$, predominate in the aqueous phase, while similar species with $h = 0$ predominate in the organic phase, ion-paired to solvated protons. It is difficult to decide on the values of h, y and t, since high concentrations of hydrochloric acid are involved, where the relative activities of hydrogen and chloride ions are not defined. Most workers agree that the extracted species carry a single negative charge, since it is felt that species with higher charge would be too strongly hydrated for the solvation to compensate for loss of hydration energy (77); however, no proof for this has been given.

In fact, there are a few cases where apparently doubly charged species are extracted, such as tellurium(IV) where β,β'-dichlorodiethyl ether was found to extract $TeCl_4$ at low, and H_2TeCl_6 at high, hydrochloric acid concentrations (48), while polonium(IV) probably behaves similarly (71, 274).

The effect of metal halides at relatively low concentrations on the extraction of trace metals by ether from 6 *M* hydrochloric or hydrobromic acid has been studied recently (184, 380). The concentration of the macro halide is too low to show salting-out action in the presence of 6 *M* acid, and only with highly extracted metals such as iron or gallium is the effect noticeable. The observed effect, an enhanced extraction of the tracer, is opposite to what would have been expected from the common ion effect, as shown by perchloric acid, but is in line with aggregation to ion multiplets, observed in low dielectric constant solvents.

Pseudohalides may show extraction behavior similar to the halo-metallic acids. Gold(I) was found to be extracted from cyanide solutions as $HS_q\ Au(CN)_2$ by various alcohols and ketones (465), but little definite additional evidence for pseudohalo acid extraction was found.

C. SOLVATING SOLVENTS (CLASS C)

1. *Solvated Acids and Salts*

Interest in extraction studies has shifted in recent years from halo-metallic acids, chelates and extractants containing oxygenated carbon groups to those involving oxygenated phosphorus and amines. Still, important work has also been done on the former systems.

The once popular extractants such as diethyl ether and hexone contain carbon oxygen groups, the oxygen of which has some basicity, and thus they can directly solvate protons and metal atoms. Extraction of both acids and metal salts is thus possible.

Extraction of the strong mineral acids by inert solvents has been found to be very small; thus concentrated hydrochloric acid shows a distribution coefficient which is 0.0045 for benzene (394), slightly larger (0.01–0.02) for cyclohexane, diisopropyl ether and methyl isobutyl ketone, but appreciably greater for alcohols (60). The distribution coefficients for the latter decrease with increasing aliphatic chain length and are well correlated with the water content of the alcohol; the probable species is $ROH_2(H_2O)_3{}^+Cl^-$. With dibutyl Cellosolve and diisobutyl ketone, dilatometric work has shown that hydrochloric, hydrobromic and perchloric acids are extracted together with 4.2 ± 0.3 moles of water, forming $H(H_2O)_4{}^+A^-$(413), which is indirectly solvated, in contrast to the alcohols (414).

Weaker acids show a different behavior. The difference between the two kinds of behavior lies in the preference of the proton of the weaker acid to associate with the anion rather than with water molecules. Extraction by inert solvents is small; the partition coefficient for molecular (undissociated, monomeric) nitric acid between aqueous solutions and toluene is 0.0012, but the nitric acid dimerizes in the organic phase (141). Extraction by ketones gives a definite solvate, *e.g.*, $HNO_3(MeCO\textit{i}Bu)_2$ with hexone, and a similar species with cyclohexanone. The mixed solvent species is relatively stable to disproportionation, the constant for this reaction being only 0.02 (112). Extraction by diethyl ether, hexone and dibutyl carbitol has been measured over the range 1–10 *M* aqueous acid (112), and the extraction of monohydrated nitric acid into ethers has been shown in the case of ethyl propyl, dipropyl and dibutyl ethers (109a, 253, 422), dibutyl carbitol (408) and Cellosolve (414). This hydrate is further solvated by the solvent, but at organic nitric acid concentrations above 1.5 *M*, more water, up to 1.75 moles per mole nitric acid is found (109a, 417), while with benzene-diluted ethers anhydrous HNO_3R_2O is the main species (253).

The extraction of salts by solvation of the cation does not necessitate the complexing of the metal by the anion as in the extraction of (halo) metallic acids. Hence salts of anions which have little tendency to associate with metals can also be extracted. Thus uranyl perchlorate is extractable by ether (44, 183), just as is the nitrate. Alcohols can solvate the metals efficiently, and cobalt and nickel (229, 278), zinc and cadmium (279) and other (229) perchlorates are extracted with moderately high distribution coefficients (about 8 for butanol). The perchlorates are even better extracted than the chlorides (120, 278), probably because chloride ions may displace the solvating molecules from the first coördination sphere around the metal. This is shown by the thousand-fold higher extraction of zinc chloride by 2-octanol compared with that of cadmium chloride (279), the latter showing much higher association between cation and anion. Papers on the extraction of some bromides by methyl isobutyl ketone (74) and of iodides by ether (213) supplement earlier publications, but do not add much to our understanding of the processes, since they do not provide evidence whether extraction proceeds *via* direct solvation of the cation or solvation of the proton of a halo-acid.

It is sometimes difficult to decide this question. Cobalt thiocyanate is extracted easily by alcohols, ethers, esters (*e.g.*, butyl acetate (227)) and ketones (*e.g.*, hexone (351)), and it is found that the organic phase contains a tetrahedrally coördinated cobalt species, which differs by its blue color and other spectral features from the octahedrally coördinated pink species in the aqueous phase. Brubaker and Johnson (47) explain the extraction in terms of species $(HSq)_2{}^+Co(CNS)_4{}^{2-}$, but do not find complete agreement between the electron donor properties of the ketones they studied and the extraction power. Another possibility which they did not consider is the formation of $Co(S)_2(CNS)_2$, which is also tetrahedral, and does not involve acid. The extraction of zinc by hexone (405) and of iron(III) by ether (231) from thiocyanate solutions is said to occur *via* similar solvates, $Zn(S)_2(CNS)_2$ and $Fe(S)_3(CNS)_3$, but no proof has been put forward. The mechanism of the extraction of zirconium and hafnium thiocyanates by hexone (248) may be similar. Interesting in this respect is the extraction of thiocyanates and iodides (but not chlorides) of transition metals by polyglycols (460). Whereas ethylene glycol or diethylene glycol does not extract these complexes, nor do the polyglycols in diluents such as chloroform, they show good extractive properties in methylene halide diluents. The mechanism is said to involve formation of oxonium cations, which extract complex anions (460). This mechanism, however, does not explain all the features, particularly the specificities shown.

The extraction of nitrates was once a very popular subject, but relatively few significant papers have been added recently to the literature. In 1954, McKay has reviewed the work done by his group at Harwell on the extraction of uranyl nitrate (262). Studies of its salting out by various nitrates (187, 260, 419), also as function of temperature (127) have recently been reported. Assuming that the water extracted by the solvent in presence of uranyl nitrate is the same as in its absence, except for hydrate water, Vdovenko (431, 432, 433) determined the hydration number as the ratio of the excess water to the uranium concentration. However, this does not take into account changes in water activity in the aqueous phase because of the presence of salt, so that the assumption seems to be invalid. In fact, it seems that only two water molecules are strongly bound to uranium, and their deformation is observable in the infrared spectrum, while any other water is present as secondary solvation (327).

The extraction of cerium(IV) by butyl acetate (223), diethyl ether (38), diisopropyl ether (37) and nitromethane (443) has been noted. It is usually assumed that the species extracted by ether is $(H(solvated))_2{}^+Ce(NO_3)_6$, following Wylie's suggestion (451) (but he also suggested $HCe(NO_3)_5$). However, Blaustein and Bryder (37) showed that no ionizable protons accompany the cerium into the ether, so that a directly solvated species such as $Ce(ether)_2(NO_3)_4$ is the main form of cerium in the organic phase. Some extraction of trivalent lanthanide nitrates by ether has been found, and this has been suggested a considerable time ago as a basis for their separation (95, 96). The extraction of neptunium (317) and of uranium, plutonium and various fission products by hexone from nitric acid and calcium nitrate solutions (336) follows the same pattern of behavior. In the extraction of plutonium by dibutyl carbitol, the formation of a nitrato acid, the proton of which is solvated, becomes more important than direct solvation, as the nitric acid concentration increases, as the spectrum, which is typical for $PuO_2(NO_3)_3{}^-$, shows (148). The extraction of astatine (453), bismuth (18, 157), iron (18) and polonium (354, 255) nitrates has been studied recently, but the species formed, whether direct solvates or nitrato acids, have not been specified.

Very little information exists on extraction from sulfate solution, and here it seems that the mechanism involves only direct solvation, as in the case of the extraction of niobium and tantalum by hexone (130).

Extraction by solvation with nitrogen-containing compounds has not been studied extensively. The mode of behavior of amides (375) has been found to be very similar to that of esters as expected, and they do not show any special coördinating and solvating properties. Quinoline has been found to extract silver perchlorate (13) by coördinating to the silver to form $Ag(C_9H_9N)_2{}^+ClO_4{}^-$. In acid solutions, however, basic nitrogen compounds prefer to coördinate protons, and these extractants are described under class F.

2. *Neutral Phosphorus Compounds: TBP*

Neutral phosphorus compounds such as phosphate, phosphonate and phosphinate esters (53), and phosphine oxides (444) have won very widespread use as extracting agents. In fact, the literature on tri-*n*-butyl phosphate (TBP) has exploded to such an extent that a bibliography became obsolete while in preparation (438). However, some of the more important and systematic studies can be reviewed here.

McKay and Healy (263) summarized the properties of TBP. To be noted are the high dipole moment (3.0 Debye units) and relatively high dielectric constant (8.0). TBP has a strong tendency to hydrate, with TBP H_2O the species formed (6, 59, 409), independent of the presence of a diluent, provided the latter does not interact with TBP (181). Hydrated TBP alone, or as a concentrated solution in a diluent, seems to have a higher dielectric constant than pure TBP, and electrolytes in such solutions may dissociate to ions (139, 154), whereas dilute solutions in inert diluents have a very low dielectric constant, and electrolytes are generally weak in such solutions (263).

TBP is completely miscible with many solvents, but has a low solubility in water, 1.65 m*M* at 25° (181), which is further decreased when the TBP is diluted (6, 199), or when the aqueous solution contains salts (158). From solubility measurements and distribution measurements of TBP between its solutions in organic diluents and aqueous solutions, its activity coefficients in the organic phase may be obtained (6, 245). In dilute solution in diluents, TBP behaves approximately ideally, but in more concentrated solutions it may interact with polarizable solvents such as benzene and its activity coefficient increases; with other diluents association between hydrated TBP species occurs and the activity coefficient decreases (6). The observed behavior of different solutes in the organic phase leads one to the assumption that the activity coefficient of all solutes in given TBP diluent systems behave similarly, and their ratios do not vary appreciably with the TBP concentration (6, 104, 245). The presence of not too high amounts of solutes in undiluted TBP does not cause the solutions to deviate from ideality, and in extraction by pure TBP, activity coefficients in the organic phase have often been assumed to remain near unity. In anhydrous systems, activity coefficients for TBP can also be obtained by cryoscopy and similar measurements (181).

The extraction of the strong mineral acids by TBP has received much attention. It is now realized that the behavior conforms to two patterns. For a group of very strong acids (perchloric, hydrohalic and sulfuric) the acids are extracted mainly as $H(H_2O)_4^+A^-$(TBP solvated) ion pairs, partly dissociated (24, 139, 414), with small amounts of other species. On the other hand, weaker acids such as trichloroacetic (414) or nitric are practically unhydrated in the organic phase since the proton associates strongly with the anion and the whole molecule is solvated by TBP (139, 414). It is instructive to see how these concepts developed.

In the case of perchloric acid, Povitskii, Shilin and Solovkin (320) found that it is extracted into benzene diluted TBP as monosolvate $HClO_4$ TBP, with $\log[(HClO_4TBP)/(H^+)(ClO_4^-)(TBP)] = -1.17$. Two years later, three more papers were published on this subject, almost simultaneously. Fomin and Maiorova (109) found that di- and tetrasolvates are formed, and for the latter $\log[(HClO_44TBP)/(H^+)(ClO_{4a}^-)(TBP)^4] = -0.80$ in benzene. In a continuous variation study they found the disolvate in carbon tetrachloride, benzene and kerosene (104). Kertes and Kertes (208), working with undiluted TBP, found mixed solvate hydrates, with molar ratios $HClO_4$:TBP:H_2O of 1:4:8, 1:2:5, 3:4:10 and 1:1:2.5, in order of increasing perchloric acid concentrations. However the physicochemical measurements they employed are not very sensitive to changes in stoichiometry, as may be seen in their graphical data. It may be taken, however, that their other data establish the coextraction of four water molecules with each $HClO_4$ unit (at low acid concentrations), and that the solvation by TBP decreases as the acidity increases. Hesford and McKay (154), on the other hand, found that perchloric acid is largely ionized when extracted into TBP alone. The formation of the hydrated perchloric acid solvates is expressed as

$$H(H_2O)_4^+ + ClO_4^- + TBP\ H_2O \rightleftarrows H(H_2O)_4^+ClO_4^-(TBP) + H_2O \quad (12)$$

by Tuck and Diamond (414), and as

$$H(H_2O)_4^+ + ClO_4^- + TBP(H_2O) \rightleftarrows H(H_2O)_3\,TBP^+ClO_4^- \quad (13)$$

by Hardy (139). Of course, the presence of some TBP-H_2O and non-hydrated TBP $HClO_4$ molecules changes the over-all ratio H_2O: (TBP $HClO_4$), explaining to some extent the results of Kertes (208) given above. Hesford and Hardy agree with the Russian workers that when using diluted TBP at low acid concentrations a tetrasolvate may form, dissociating into disolvate and finally monosolvate as the acid concentration increases (154).

Similar results are obtained with the hydrohalic acids HA, where A = Cl, Br or I. Here again partly dissociated $H(H_2O)_4^+A^-$(TBP solvated) ion pairs exist in the organic phase (414), or $H(H_2O)_3TBPCl(H_2O)_2^-$ (TBP solvated) pairs and ions according to Hardy (450), side by side with TBP H_2O and un-ionized TBP HA. It should be noted that Hardy considers the chloride ion hydrated, contrary to the larger perchlorate ion (and presumably also the heavy halide ions). Measurements of total water content in the presence of the extracted acids (24) confirm that each mole brings with it h = 3.1 (for chloride) to 3.9 (for iodide) moles of water, in addition to the one mole present in the monohydrate, so that the extraction may be expressed as

$$H^+ + A^- + hH_2O + TBP\ H_2O \rightleftarrows H^+(h+1)H_2O,\ TBP\ A^- \quad (14)$$

Earlier measurements showed the extraction of hydrochloric acid into 100% TBP (167, 302), and into diluted TBP (167), and it was concluded that hydrates form, without their composition being stated. More information was given by Kertes (201), who concluded from physicochemical measurements that $HCl(TBP)_2(H_2O)_6$ is formed at low acidities, and $HCl(TBP)(H_2O)_3$ at high acidities, whereas other results point to hydrated $HCl(TBP)_3$ (102). A further complication is the dehydration of the homogeneous TBP hydrochloric acid-water phase on standing, to give essentially $HCl(TBP)$-$(H_2O)_2$ (200). Quite similar results were obtained by Kertes for hydrobromic acid (207). Hesford and McKay (154) consider extracted hydrochloric acid to be a weak electrolyte (pK_a 4.05), which forms a hydrated monosolvate, and express the concentration in the organic phase C_{or} as function of that in the aqueous phase C_{HCl}

$$C_{or} = 0.063\, C^2_{HCl}y^2_{\pm HCl}10^{-0.8C_{or}}\,(1 - \theta_{or})^{-1} \qquad (15)$$

where $(1 - \theta_{or})$ is the fraction of un-ionized acid, and the exponential term describes the non-ideality of the organic phase. This equation is valid in the range 0.1 m*M* to 2 *M* aqueous acid. Hardy (139) criticized this approach by showing appreciable ionization of the acid in the organic phase.

Summarizing, it appears that at medium hydrochloric acid concentrations the species HCl TBP (hydrated, solvated) is the major one in diluted TBP, while an ion pair or unassociated ions of the same molar ratio are important in pure TBP. At low acidities more TBP is incorporated in the adduct; at very high acidities, more HCl. The amount of water is difficult to assess because of inaccuracies in the determination and the small amounts of hydrochloric acid extracted at low concentrations. At medium concentrations there are three to five water molecules associated with the HCl TBP adduct.

A further phenomenon to be noted in this connection is the formation of three liquid phases in the extraction of hydrochloric acid (but not nitric acid) by TBP diluted with a number of solvents (167, 102). A compound HCl H_2O TBP separates out from a kerosene solution of TBP equilibrated with concentrated hydrochloric acid, and a non-hydrated adduct HCl TBP separates when hydrogen chloride is bubbled through TBP in kerosene. The relative insolubility of the polar adduct in the nonpolar kerosene and its power to dissolve additional HCl or TBP may be explained in terms of Hildebrand's (159) solubility parameters (102).

By far the most extensive information on the extraction of the mineral acids exists on nitric acid. It is now taken as established that over a considerable range of nitric acid and TBP concentrations in the equilibrium aqueous and diluent solutions, respectively, the main extracted species is non-hydrated HNO_3TBP, as Alcock, McKay and co-workers have originally shown (6). The reaction for its formation is generally accepted to be (414)

$$H_{aq}^+ + NO_3{}^-_{aq} + TBP\ H_2O_{or} \rightleftarrows HNO_3\ TBP_{or} + H_2O_{aq} \qquad (16)$$

with equilibrium constant $K = 0.16$ at low concentrations in a kerosene diluent (3, 6), while for benzene $K = 0.22$ (106), and other values in the range 0.1–0.4 apply to other diluents (356). Although the thermodynamic data obtained from distribution measurements point to the presence of the definite species HNO_3TBP, the ratios $HNO_3:TBP:H_2O$ in equilibrium organic phases (without diluent) vary continuously, because of the simultaneous presence of various species. At low concentrations of acid it seems that HNO_3 replaces H_2O bound to the TBP, and indeed the variation in the ratio $[(H_2O) + (HNO_3)]/(TBP)$ is only slight as the nitric acid concentration changes (409). The exact nature of the adduct is, however, still unclear. Infrared spectral evidence points to $(C_4H_9O)_3P \rightarrow O..\ H\text{–?–}NO_3$ (303) where ... is a strong hydrogen bond; whether the nature of the bond marked –?– denotes ion pair formation (6), partial or complete dissociation (139) or undissociated nitric acid (66, 67, 303) has not been decided. Another possibility, the presence of undissociated HNO_3 molecules as an important species (66, 67), seems unlikely in the light of the other evidence (303). The thermodynamics of the extraction may, of course, be described with the hypothetical species (66, 67) HNO_{3or} with the equilibria

$$H^+ + NO_3{}^- \rightleftarrows HNO_{3aq} \quad (\log K\ -1.36) \qquad (17)$$

$$HNO_{3\,aq} \rightleftarrows HNO_{3\,or} \quad (\log K\ -0.72) \qquad (18)$$

$$HNO_{3\,or} + TBP \rightleftarrows HNO_3TBP_{or} \quad (\log K\ 1.30) \qquad (19)$$

so that for the over-all reaction

$$H^+ + NO_3{}^- + TBP_{or} \rightleftarrows HNO_3TBP_{or} \qquad (20)$$

$\log K = -0.78$, of the same magnitude as found by other workers. This agreement could have been expected since the data are similar.

The nature of the excess nitric acid, extracted by TBP from aqueous solutions more concentrated than about 7 *M*, over the composition HNO_3 TBP is uncertain. The views range from that of Collopy (66, 67), that undissociated HNO_3 is simply distributed between the aqueous and the organic phase (composed of TBP HNO_3), through that of Tuck (409, 412) that hydrated nitric acid adds to the ester C–O–P bond, or that of Hardy (450), that it adds to nitrate oxygens, to those of authors who do not deal with the nature of the bonding but rather with the stoichiometry and the equilibrium constants. The latter find the equilibrium

$$H^+ + NO_3{}^- + HNO_3\ TBP_{or} \rightleftarrows (HNO_3)_2TBP_{or} \qquad (21)$$

with log *K* values −2.7 (108), −3.36 (92), at room temperature or varying from −3.39 at 23° to −3.24 at 70° (3). Formation of $(HNO_3)_3TBP$ side by side with undissociated HNO_3 (192), formation of three different complexes in diluted TBP (219) and the equilibria

$$HNO_3\ TBP + H^+ + NO_3{}^- + H_2O \rightleftarrows (HNO_3)_2\ H_2O\ TBP \quad (\log K\ -3.2) \qquad (22)$$

between 4.5 and 11 *M* aqueous nitric acid, and formation of $(HNO_3)_3H_2O$ TBP and $(HNO_3)_4TBP$ at higher concentrations (371) have also been reported. All these reviews try to explain the observed facts, *i.e.*, the apparent linear relationship between the concentration of the excess nitric acid and of undissociated acid in the concentrated aqueous phase, as well as the increase of water concentration, after the minimum it reaches when displaced completely from TBP H_2O by nitric acid.

In conclusion, it is seen as established that nitric acid displaces water from TBP H_2O to form TBP HNO_3 (except at the lowest concentrations where some TBP H_2O HNO_3 may form (371)) with a strong hydrogen bond, but there is no agreement on the degree of ionization or nature of the nitric acid. Also, it seems established that excess nitric acid dissolves, together with water, in TBP HNO_3, but again, because of the possibility of there being many species side by side, there is no agreement on whether this is a simple dissolution, or whether definite species are formed, and, if so, how they are bonded. Present theorp on the behavior of highly polar compounds in concentrated solutions is not sufficiently advanced to allow a reliable interpretation of the available data.

Perchlorate is often considered to be an "inert" anion, not forming complexes with metal cations, and hence not allowing extraction. However TBP, as has been shown above, extracts perchloric acid by solvating the proton, and may extract perchlorates by solvating the cations. Thus, above 5 M aqueous acid, zirconium is extracted better from perchloric than from nitric acid by 30% TBP in carbon tetrachloride (284). Tetravalent plutonium is extracted as $Pu(ClO_4)_4$ 2TBP (387) and zirconium, thorium and trivalent cerium, promethium and yttrium are extractable from perchloric acid, fairly well above about 6 M (376). Spectrophotometric work shows neptunium(VI) (191) and uranium(VI) (324) to be extracted as $MO_2(i\ ClO_4, j\ NO_3)$ 2TBP with $i + j = 2$, $i,j = 0$, 1 and 2 from mixed nitric and perchloric acids. This means that perchlorate cannot serve in this and similar cases as an inert anion, *i.e.*, it cannot be taken as a reference point from which to measure complexing by nitrate and the extraction of the nitrate complex TBP solvate, contrary to what would have been conventionally assumed (191). Hesford and McKay (155) find that uranyl perchlorate is extracted as $UO_2(ClO_4)_2$ 2TBP, which is considerably ionized in hydrated TBP. In TBP diluted with benzene, the distribution coefficients of uranium vary with the second to sixth power of the TBP concentration (357), although the ratio TBP:U nears two as saturation is approached, as also found by Hesford and McKay. Because of competition, distribution coefficients are low in perchloric acid, but increase when the salting agent is lithium perchlorate, or even more with sodium perchlorate.

Many more elements were found to extract from chloride solutions. From not too concentrated hydrochloric acid, uranium(VI) is extracted as UO_2Cl_2 2TBP both by pure TBP (206) and by TBP diluted with carbon tetrachloride (365) or benzene (429). At high concentrations of uranium and chloride, and with kerosene as diluent, a third liquid phase is formed (365, 429). At high hydrochloric acid concentrations, acid also extracts, either independently of the uranium (365) or as HUO_2Cl_3 2TBP (429). This latter view is confirmed by spectrophotometric evidence of a new uranium species, which is also produced by dissolving gaseous hydrogen chloride or solid hydroxylamine hydrochloride in UO_2Cl_2 TBP solutions.

Other elements are extractable from hydrochloric acid solutions: not only transition metals (58, 167) that are complexed by chloride and zirconium (310, 381), but also those which are only slightly complexed like scandium and thorium (310) and heavy actinides (175). Electronegative metal chlorides or complexes like those of tellurium(IV) (165), polonium (12), gold(III), which forms $HAuCl_4$ 3TBP (411), and platinum metals (27) are also extracted, and differences in the distribution coefficients may be utilized for separations. When cobalt is extracted from concentrated cobalt chloride solutions, it is said to form a dimer in the organic phase (58), but when extracted as a trace it forms $CoCl_2$ 2TBP, as suggested by the second power dependence of the distribution coefficient on chloride concentration (or hydrochloric acid activity) and TBP concentration (167, 280). A general important point to be noted, and to which little attention has been given, is the possibility of extraction by two different mechanisms. One involves direct coördination of the TBP to the metal, as in the above-mentioned cobalt and uranium solvates. The other is the extraction of transition metal halo-acids where the TBP solvates the proton. This possibility was suggested by Morris and Bell as occurring in the extraction of cobalt from concentrated hydrochloric acid, where the species $(TBP\ H)_2CoCl_4$ is formed (280). Similarly, iron(III) is extracted as $FeCl_3$ 3TBP at low, and as $H(TBP)_2FeCl_4$ at high concentrations of hydrochloric acid (238). Extraction of iron by TBP in kerosene may lead at high concentration to an insoluble adduct, which forms a third liquid phase, and may be utilized to recover TBP from kerosene since the adduct is decomposed easily by water (356).

General compilations of the extraction of many elements by TBP from nitric acid have been published (99, 176). Much more information is available on these systems than on the others. Rare earth cations are probably extracted as direct metal cation solvate salts $M(TBP)_3(NO_3)_3$ (152). Earlier publications reported slopes of 1.5 (346) and 2.0 (346, 307) for the logarithmic distribution coefficient *vs.* TBP concentration plots, but in these cases the organic solutions were not ideal; hence the slopes did not correspond to the solvation numbers (153). The variation of the distribution coefficient of cerium(III) (105) and plutonium(III) (368) with nitrate concentration was analyzed in terms of complex formation in the aqueous phase, taking into account the competition of nitric acid for available TBP, and a similar description probably can be derived also for the other trivalent actinides and lanthanides from available data. Distribution coefficients increase with atomic number Z for the light lanthanides up to about

$Z = 64$ for all nitric acid concentrations (152, 301, 346). For all heavy lanthanides they fall again at low nitric acid concentrations, but continue to increase at concentrations above about 4 M (152, 301). An interesting odd–even Z effect was found in that distribution coefficients did not change monotonically (152) with Z, as was demonstrated also in anion exchange from lithium nitrate solutions (246). The lanthanides are extractable from nitric acid solutions, from high nitrate and low acid solutions (346), and also from concentrated lanthanide nitrate solutions. The latter may be used for large scale separations. In this case, interference from mutual salting out and competition for available TBP is possible (214, 295, 403). Other techniques applied to lanthanide separation by TBP extraction are reversed phase partition chromatography (377) (in which, contrary to most ion exchange processes, the lighter lanthanides are eluted first) and gel–liquid extraction (378, 379). Similarly to lanthanides, yttrium (301, 346) and scandium (310) are extracted as are also the trivalent actinides (31, 101, 368), and a break in the distribution coefficient *vs.* Z curve is observed at $Z = 96$, again at the point of a half-filled f-shell (31).

Of the tetravalent elements, zirconium, hafnium and thorium are extractable, and separable in the TBP–HNO_3 system (92, 161, 218). The organic species is most likely to be $M(TBP)_2(NO_3)_4$ (4, 5, 92, 107, 156, 381), although the monosolvate (92, 330) is formed at low TBP concentrations and at high concentrations the trisolvate (284, 310) and tetrasolvate (156) are said to be formed. The difficulties of interpretation of the slopes of logarithmic distribution coefficient *vs.* TBP concentration plots make the last two species rather suspect. More complicated species like $Zr(NO_3)_4\ 4HNO_3\ 2TBP$ are allegedly extracted from concentrated nitric acid (407), but because of the non-ideality of the system, the interpretation is doubtful. For the reaction

$$Th^{4+} + 4NO_3^- + 2TBP_{or} \rightleftarrows Th(TBP)_2(NO_3)_{4or} \qquad (23)$$

$\log K = 1.56$ was found (237), while for plutonium $\log K = 3.33$ (271), and its change with temperature also was studied. The tetravalent actinides also are extracted as $M(TBP)_2(NO_3)_4$, while the hexavalent ones are extracted as $MO_2(TBP)_2(NO_3)_2$ (5, 28, 191, 331). TBP is able to displace nitrate anion and dibutyl carbitol (DBC) solvating molecules from the species $H^+(DBC)_qPuO_2(DBC)_q(NO_3)_3$ to form $PuO_2(TBP)_2(NO_3)_2$ (148), as shown by changes in the absorption spectrum.

Because of its connection with nuclear fuel reprocessing, most information is available about the uranyl nitrate–nitric acid–TBP system. Apart from many technological papers and publications giving distribution coefficient data for various diluents and concentrations of uranium, nitric acid and TBP (5, 12, 79, 188, 340, 342, 343), and effects of competing anions (important in the stripping step) (65, 220, 341), a few also deal with the mechanism of extraction, and thermodynamic problems connected therewith. Shevchenko pointed out the importance of the considerable polarity of the organic species (which is $UO_2(TBP)_2(NO_3)_2$, as all authors agree) in determining the distribution coefficients in the various diluents. Although there is little correlation between the distribution coefficients and the dielectric constants of the diluents (323), the distribution coefficients decrease with increasing molar polarization of the solvents, *e.g.*, in the series benzene, carbon tetrachloride, toluene, xylene, isopropylbenzene, kerosene, butyl bromide and dibutyl ether (130). The diluents with lower polarization show a positive deviation from the square law, those with higher a negative one, while some such as ethyl and butyl ethers, benzene and toluene are nearly ideal (366). Deviations from a square dependence law on TBP concentrations are partly due to choice of concentration units (see below), and only partly to non-ideality of the TBP–diluent solutions (367). With some diluents mixed solvates are formed, like $UO_2(NO_3)_2$ TBP BuOH with butanol (268), so that deviations from second power dependence on TBP concentration occur, but this is not so with the inert diluents. Rozen and Khorkhorina (330) presented a detailed thermodynamic analysis, particularly of the case where considerable amounts of uranium and nitric acid are coextracted. Jury and Whatley utilized this treatment, together with empirical functions connecting the activity coefficients with the TBP concentration and the ionic strength, to correlate experimental extraction data (182). A similar treatment was used by Codding (62) to explain quantitatively the extraction from an acid-deficient aluminum nitrate medium. More recently, Marcus reviewed these treatments (244), and in particular developed the ideas of Hesford and McKay (153), presenting an equation which accurately represented diverse data for the extraction of trace uranium up to 1 *M* (30%) TBP and 7 *M* nitric acid (245) using independent data for evaluating various correction functions

$$D_U = K_U' C_T^2 (NO_3^-)^2_{aq} y{\pm}_U^{t3} / F_N F_T D_T \qquad (24)$$

Here D_U is the distribution coefficient of trace uranyl ion, K_U' a constant depending only on the diluent, C_T the total TBP molarity, $(NO_3^-)_{aq}$ the nitrate ion concentration, $y^t{\pm}_U$ the activity coefficient of uranyl nitrate tracer in nitric acid, F_N a function correcting for nitrate complexing in the aqueous phase, F_T a function correcting for TBP bound to nitric acid, and D_T the distribution coefficient of TBP between the two phases.

Under extreme conditions of high nitric acid and TBP concentrations, direct solvation of uranyl by TBP yields to formation of proton-solvated trinitrato uranyl acid $H(TBP)_2UO_2(NO_3)_3$ identified spectrophotometrically, and which is insoluble in kerosene, forming a third phase (388).

Many other elements were shown to be extractable from nitric acid by TBP, mainly as direct solvates, like niobium (144) and protactinum (352) or mixed solvated-hydrates, as found in the case of copper, from distribution and solubility measurements (358). Various nitrato complexes of nitrosyl ruthenium show slow and complicated interconversion, and have different TBP solvating power, hence extractabilities (133, 332). Both the neutral complex $RuNO(NO_3)_3(TBP)_2$ (178) and nitrato acids such as $[HTBP_n]_2RuNO(NO_3)_5$ (100) are extracted, depending on conditions (133). Rhenium is extracted as acid $H(TBP)_qReO_4$ from nitric acid with $q = 4$ (202) or more probably $q = 3$ (68), as obtained at lower TBP concentrations, where solutions are more nearly ideal. Similarly, chromium is extracted as chromic acid trisolvate H_2CrO_4 3TBP (359), perhaps as $[H(TBP)_3]HCrO_4$.

Workers in this field must beware of the pitfalls entailed in the analysis of the dependence of distribution coefficients on concentration. Thus Shevchenko (367) pointed out that deviations from linearity of logarithmic plots of the distribution coefficient *vs.* TBP concentration do not necessarily result from changes in the solvating number. Since concentrations are expressed as volume per cent or molarities, at high TBP concentrations changes in total volume relative to total number of moles are considerable and must be taken into account in the mass action law expressions based on molarities (although not in those based on mole fractions). In addition there are true deviations from ideality which at relatively low TBP concentrations in inert diluents are expressible in terms of activity coefficients, the logarithms of which are linear with TBP concentrations (153). Considerable differences may occur between the true and the apparent solvation numbers q and q', respectively, and when C_T is expressed in volume per cent $C_T'(1\%\ \text{TBP} = 0.0365\ M)$, then usually q' lies between $q - 0.06C_T'$ and $q + 0.02C_T'$, and may by chance have nearly integral values, without chemical significance.

Comparatively little work has been done on extraction with TBP from solutions other than those dealt with above. The extraction of uranium(VI) from sulfuric acid (369, 434) and the effects of the presence of sulfate and other anions on the extraction from nitrate (65, 220) and the back extraction of uranyl nitrate from TBP into solutions containing sulfate, carbonate, oxalate, acetate and chloride (341) have been studied. With most of these ions, uranyl forms stable anionic complexes, and TBP has little opportunity to solvate it, hence extraction is slight. Similarly, the extraction of thorium nitrate is depressed by sulfate ions (237). Iron(III) is extracted from thiocyanate solutions as $Fe(TBP)_q(CNS)_3$ (265), and other thiocyanate complexes should also be extractable by metals strongly solvated by TBP. The extraction of sulfuric acid by pure TBP has been studied by Hardy (139) relying mainly on data of Hesford and McKay (154). He found the main species to be $(TBP\ H(H_2O)_3)^+\ HSO_4^-$ ion pairs with some dissociation into ions and some formation of unionized TBP H_2SO_4. Hydrogen peroxide is able to replace water in TBP

$$TBP\ H_2O_{or} + H_2O_{2\,aq} \rightleftarrows TBP\ H_2O_{2\,or} + H_2O_{aq} \quad (K = 86) \tag{25}$$

The total concentration of water and hydrogen peroxide is approximately constant (410). The extraction of nitrous acid leads to the formation of HNO_2 TBP, with molecular, undissociated nitrous acid, as shown by the ultraviolet spectrum (101). The distribution coefficient for nitrous acid is quite high, about 100 (for 0.5 M acid, 100% TBP) compared to about 1 for perchloric and hydrofluoric acids, and still lower values for other mineral acids (154).

3. Neutral Phosphorus Compounds: Other Reagents

It was realized early that the solvating power of TBP depends on the basicity of the P=O group. Compounds with a more basic phosphoryl group should therefore show better extractive properties. Exchange of butyl groups for others has a relatively small effect (374), except when electron sinks are present in the substituting groups. Phenyl or chloroalkyl groups in esters decrease the distribution coefficients considerably (54, 149, 150, 296). Another exception is thorium, which is solvated by three ester molecules, and its extraction is depressed by exchange for bulky alkyl groups (374). It is generally observed that the extraction improves in the order phosphate, phosphonate, phosphinate and phosphine oxide, as alkoxy groups are substituted by alkyl groups on the phosphorus atom. A direct correlation exists between the distribution coefficients of uranium and the wave length of the infrared absorption of the phosphoryl group. The latter is also a measure of the shift from P=O configuration to $P^+\!-\!O^-$, and the increase of basicity (53, 54). Also the equilibrium constants for the reaction

$$UO_2^{2+} + 2NO_3^- + 2S_{or} \rightleftarrows UO_2(NO_3)_2S_{2or} \tag{26}$$

vary in the same order: for S = $(BuO)_3PO$ log K = 1.08 (437), for S = $(BuO)_2BuPO$ log K = 2.78 (324) or 2.98 (437), for S = $(BuO)Bu_2PO$ log K = 4.47 and for S = Bu_3PO log K = 6.53 (324) or 6.58 (437). Similar observations were made by many workers, studying extraction of uranium (53, 54, 149, 196, 402), neptunium (441), plutonium (54) and zirconium (415). Compounds of the type $RC(O)CH_2P(O)(OR)_2$ where the R's may be the same or different, show good extraction of scandium and yttrium (439). They probably do not act as neutral solvating reagents because of enolization of the carbonyl group and ionization of the OH group formed. Stable "chelate" solvates are probably not formed, since compounds like $R_2P(O)YP(O)R_2$ where R is alkyl or alkoxy, and Y is –O– or $-CH_2-$ show smaller distribution coefficients than monofunctional esters (149). They also form disolvates with uranium, which indicates that they act as monofunctional solvents with electronegative substituents, except at high uranium loadings, where polymeric chains probably are formed. Tetrabutyl ethylene diphosphonate also extracts zirconium, yttrium and lanthanides (337) and uranium and thorium (338) from nitric acid. In the case of uranium a monosolvate was found to form, which may indicate polymerization.

Phosphonates are promising extracting agents, as they show higher distribution coefficients than the phosphates. Again these depend little on the nature of the alkyl groups (372). The free energies, enthalpies and entropies of the extraction process for uranium were given by Siddall (373). The extraction of thorium nitrate with dibutyl butylphosphonate (233) shows formation of a trisolvate $Th(NO_3)_4$ 3DBBP, in agreement with Siddall's (374) findings on the extraction with phosphate esters.

Diisoamyl methylphosphonate (DAMP) is a popular solvent with Russian workers. In solutions in diluents below 30% the monohydrate DAMP H_2O is formed, and in more concentrated solutions, up to pure solvent, the dihydrate $DAMP(H_2O)_2$ (384). Extraction of hydrochloric acid proceeds as with TBP, but because of the higher hydration, the acid is more dissociated, and solvation numbers could not be obtained (292). Contrary to TBP, DAMP extracts hydrated nitric acid. Pure DAMP extracts this acid according to the reactions

$$HNO_3 + 3H_2O + DAMP_{or} \rightleftarrows HNO_3\ 3H_2O\ DAMP_{or} \quad (\log K\ 1.21) \qquad (27)$$

and at higher concentration the reaction is

$$2HNO_3 + H_2O + DAMP \rightleftarrows 2HNO_3\ H_2O\ DAMP \quad (\log K\ 0.04) \qquad (28)$$

With diluted DAMP, mono- and trihydrates of a 1:1 nitric acid–DAMP adduct are formed (385). Sulfuric acid is extracted as H_2SO_4 H_2O 2DAMP (382). Uranium(IV) is extracted above 4 *M* hydrochloric acid as UCl_4 2DAMP, and uranium(VI) is extracted as UO_2Cl_2 2DAMP (362). From nitric acid, uranyl nitrate is extracted as $UO_2(NO_3)_2$ 2DAMP (364, 383, 386), and the salting out of this complex by various nitrates has been studied by Solovkin (386), as described above.

The use of gel–liquid distribution, with TBP-swelled polystyrene, has been mentioned above (387, 379). Instead of absorbing the phosphorus ester in a polymer, it may be incorporated as a functional group attached to the polymer framework. Kennedy (196) showed that phosphate, phosphonate or aminophosphonate resins show selectivity for uranyl ions. Resins may be made by polymerizing alkyl esters, or attaching the phosphorus to polystyrene (methylene). He later showed that diethyl (polystyrenemethylene) phosphonate can replace the strong chelating and solvating ligand dibutyl phosphate from solvated uranyl ions in benzene solution (195). The reaction was formulated as

$$UO_2(HX_2)_2 + 2S \rightleftarrows UO_2X_2S_2 + (HX)_2 \qquad (29)$$

where S is the neutral resin phosphate and H_2X_2 the acid phosphate dimer. The solvating power of the resin phosphate may also be seen in the formation of SHX with the acid butyl phosphate, where a resin site can displace one HX unit from the dimer.

As already mentioned, even stronger solvating solvents than the phosphonates are the phosphine oxides, because of their higher basicity, *i.e.*, the more pronounced contribution from $P^+–O^-$ to the phosphoryl group. The most widely used compound in this group is tri-*n*-octylphosphine oxide (TOPO), although the butyl, phenyl and 2-ethylhexyl compounds have also been studied. A recent review by White and Ross, who pioneered the use of these solvents, mainly gives details of their analytical use (444). This review also contains material not published elsewhere on the extraction and determination of iron, molybdenum and uranium in addition to previous reported systems such as titanium thiocyanate (452) or thorium sulfate or phosphate (328). More recently, British workers studied the extraction of plutonium (250). The solvation processes with TOPO are quite similar to those with TBP, although not necessarily with the same solvation numbers. Mineral acids are extracted very well, in particular nitric acid which forms an adduct TOPO HNO_3 even when extracted from diluted solutions, and reaches a ratio of 2:1 above 6 *M* aqueous acid. Hydrochloric acid reaches a 1:1 ratio at 3 *M* and a 2:1 ratio at 6 *M* aqueous acid. The perchloric acid adduct is not very soluble, and three phases are formed above 3 *M* aqueous acid concentrations. Sulfuric and phosphoric acids are extracted to an even smaller extent, but more than with TBP. An interesting feature is the negligible hydration of TOPO compared with TBP, only less than 0.02 mole of water being found per mole of TOPO, in 0.1 *M* solution in cyclohexane, when equilibrated with water or dilute acid (444).

In general, TOPO forms more definite solvates than TBP and binds more strongly to acids, and thus is intermediate in properties between the oxygenated, slightly basic solvents and the highly basic amines.

Other interesting phosphorus-containing solvents, which act as solvating solvents, are trialkyl thiophosphates and triphenyl phosphites. The former (137) extracted silver and mercury, and, in general, elements which form stronger covalent bonds to sulfur than to oxygen. Mercury is extracted by triisooctyl thiophosphate (TOTP) as $Hg(TOTP)_2(NO_3)_2$, while silver forms a monosolvate, which interacts with solvated nitric acid to form a disolvate $HAg(TOTP)_2(NO_3)_2$. The phosphite (138) extracts copper(I) halides, forming a 1:1 compound, which was shown by cryoscopy (15) to be trimetric in benzene, *i.e.*, $((C_6H_5O)_3PCuA)_3$, where A is chloride, bromide, iodide or thiocyanate. Distribution coefficients of the order of 100 to 500 were observed with 10% reagent solution in carbon tetrachloride.

D. ACIDIC EXTRACTANTS (CLASS D)

Some twelve years ago it was realized that the hydrolysis products of TBP, *i.e.*, mono- and dibutylphosphoric acids, are good extractants for uranium (69, 392). An early publication in the open literature (391) showed the efficiency of dibutylphosphoric acid for extracting uranium from sea water. The use of acid phosphate esters and related reagents has mushroomed since then. Burger (53) and Blake, Baes and Brown (34) published useful reviews on the properties of these materials and their extractive applicability, respectively. Kimura reviewed the extraction of various elements from hydrochloric acid with di-2-ethylhexylphosphoric acid (211, 212).

It was realized quite early that these reagents are not monomeric in most organic diluents. Peppard, Ferraro and Mason (304) measured the molecular weight of mono- and dialkylphosphoric acids and found the former to be polymeric, the latter dimeric. Cryoscopic measurements (305) later confirmed this for solutions in benzene or naphthalene of dibutyl-, dioctyl-, di-2-ethylhexyl-, diphenyl-, bisdimethylheptyl- and bistetramethylbutylphenylphosphoric acids as the dialkyl phosphates, and butyl-, 2-ethylhexyl- and tetramethylbutylphenylphosphoric acids as the monoalkylphosphates. Dyrssen (82) measured the distribution of dibutyl phosphate between aqueous solutions and various diluents and analyzed the data in terms of dissociation of the dibutylphosphoric acid in the aqueous phase, its distribution between the two phases, and its dimerization. Dyrssen (89) later found that the dimerization reaction competes with association with the diluent. Dimerization is strongest in the inert solvent hexane (and in octane some trimerization was apparently obtained (20)) and decreases with more strongly hydrogen bonding solvents, while association with the diluent is strongest with hexol and diminishes with more inert diluents, in the order TBP, diisopropyl ether, chloroform, carbon tetrachloride and hexane. Similar results were obtained by Peppard (305), who noted the strong association with ethylene glycol, and by Hardy and Scargill (143), who measured solubilities and distribution coefficients for mono- and dibutyl phosphate with chloroform and kerosene as diluents. Their distribution coefficients between aqueous solutions and TBP were measured by Ilozhev, Poddubskaya and Rozen (164) and Hardy and Scargill (143), who noted the strong interaction between dibutyl phosphate and TBP, giving $(BuO)_2POOHOP(OBu)_3$. The dibutyl phosphate–TBP complex is stronger in carbon tetrachloride (log K for its formation is 2.84) than in chloroform (log K is 1.6), because of the association of the latter diluent with the acid (82, 89). The interaction of TBP with a monoalkyl phosphate, mono-2-ethyl hexylphosphoric acid (94), yields a more complex species, $((EtHexO)PO(OH)_2)_6((BuO)_3PO)_2$.

It is thus generally accepted that monoalkyl phosphates are polymeric in organic solutions, while dialkyl phosphates are dimeric, except in diluents which interact with them through hydrogen bonding.

The alkyl phosphates associate not only with basic solvents through their acidic hydrogen, or hydrogen bonding solvents like hexol or chloroform through their phosphoryl oxygen, but also with acids which they extract. The stronger acid suppresses the ionization of the phosphoric acid ester (143), and is hydrogen bonded to the phosphoryl oxygen as found by an infrared study (303). Two recent papers on the extraction of nitric acid by dibutyl phosphate show the differences encountered when working with diluted and undiluted esters. The undiluted ester is strongly hydrated, forming $(DBP\ H_2O)_2$ dimers, which extract nitric acid to form $(DBP\ H_2O)_2\ HNO_3$, partly dissociated to ions (205). With toluene diluted DBP this species cannot account for the results, but the species $DBP\ HNO_3$ with a proportion of $DBP\ H_2O\ HNO_3$ does so (134). This becomes the main species at higher acid concentrations, between 10 and 14 M aqueous acid (205) as it is also with undiluted DBP, and at still higher acid concentrations all authors agree that $DBP\ H_2O(HNO_3)_2$ is an important species, although in toluene this might be made up from DBP and $H_2O(HNO_3)_2$ (134). The physicochemical measurements given by Kertes (205) are rather unconvincing, but the finding of a constant ratio of water to DBP, independent of nitric acid concentration, leaves little doubt that the species reported are essentially correct. The changes in the solubility of DBP in aqueous nitric acid (134, 205) point to interaction also in the aqueous phase. Even phosphoric acid may be extracted by dibutyl phosphate as $((BuO)_2POOH)_2(PO(OH)_3)_2$ (401). Di-2-ethylhexylphosphoric acid shows higher solubility in hydrochloric and nitric than in sulfuric and phosphoric acids (23), probably because of stronger interaction with the former two.

The general mechanism of extraction of metals by a dialkyl phosphate

$$M^{m+} + m(\mathrm{HX})_{2\ \mathrm{or}} \rightleftarrows \mathrm{M(HX_2)}_{m\ \mathrm{or}} + m\mathrm{H}^+ \qquad (30)$$

has been verified many times. The distribution coefficient usually shows an mth power dependence on the reagent concentration and an inverse mth power dependence on the hydrogen ion concentration, and since the reagent is dimeric, the results conform to the above reaction.

Much work has been done on the extraction of trivalent lanthanide and actinide elements with acidic phosphate esters. Solvent extraction with these reagents may show better separation factors between neighboring elements than present ion exchange methods. In particular, Peppard's group at Argonne National Laboratory developed methods of extraction and separation of these elements. They showed the usefulness of di-2-ethylhexylphosphoric acid, particularly if purified (311) in separating the lanthanides (312a) and in separating tetravalent berkelium (314) from all elements except cerium. The monoester is polymeric in the diluent, and the distribution coefficients show first power dependence on the monoester concentration, so that the composition of the extracted species is not clear (307). Nevertheless, this reagent is useful in separations, *e.g.*, for that of neptunium(IV) from other elements, utilizing the large separation factor of neptunium(IV) from uranium(VI) and plutonium(III), and of these elements from neptunium(V) or -(VI) (313). Further separations of the actinides, using these reagents and also diphenylphosphoric acid, and the antisynergistic effect of high concentrations of trialkylphosphates (see above) were subsequently reported (306), while extraction with monobasic phosphonates has been introduced recently (308, 309). Here, too, the distribution coefficients show third power dependence on reagent concentration for the trivalent elements.

Generally similar results were obtained using dibutyl phosphate in separating yttrium from strontium (81, 85) and lanthanides and actinides (83, 86, 90, 221). However, in certain solvents the species involved were not solely $M(HX_2)_3$, since in hexane further solvation to $M(H_2X_3)_3$ occurs, whereas in TBP and hexol these solvents replace HX molecules to give MX_3 TBP_n or MX_3 $hexol_n$ (90). Further results obtained by others with dibutyl phosphate (80), diamyl phosphate (299) and di-2-ethylhexyl phosphate (257) are in agreement. With monoalkyl esters, however, Warren and Suttle (440) find a much higher reagent concentration dependence (third power for scandium, fourth for yttrium and lanthanum) than did Peppard's group (307). This is probably due to monomerization of the polymeric ester in the hydrogen bonding diluent used by the former authors, amyl alcohol. Dialkylphosphoric acids may also be utilized in the separation of lanthanides by the recently developed method of gel–liquid extraction (379).

The extractability of tetra- and hexavalent actinides was found to be much higher than that of the trivalent ones or the lanthanides. Thus cerium and berkelium may be separated from other elements by an oxidation–reduction between their two valence states (257, 314) while an oxidation–reduction process utilizing the tetra-, penta- and hexavalent states of neptunium may be based on the known extractive properties of this element (290, 313, 441). The extraction of thorium (312) seems to be more complicated than that of other elements, since with di-2-ethylhexyl- and bistetramethylbutylphenylphosphoric acids, apart from the regular complex $ThX_2(HX_2)_2$ in the organic phase, species containing nitrate (or chloride, or possibly also perchlorate) like $ThNO_3X(HX_2)_2$ were found.

The extraction of the uranyl ion has received much attention. In dilute solution the extraction follows the pattern described above. Thus, with dialkyl phosphate in non-solvating solvents the organic species is $UO_2(HX_2)_2$ (21, 87, 149), whereas with solvents like hexone (87), TBP (88, 355) or TBPO (88), these may replace the solvating molecules to form UO_2X_2 hexone, UO_2X_2HX TBP, UO_2X_2 TBP or $UO_2X_2(TBPO)_2$, respectively. However, in solution more concentrated in uranium, the organic species polymerizes (21, 149), probably in order to attain a more favorable coördination number. Furthermore, in the presence of an efficient ligand for uranium like nitrate, ligand ions may replace the end groups on the polymer, and at high nitric acid concentrations, depolymerization sets in, together with replacement of the dialkyl phosphate chelating ligands by simple nitrate ligands, and suppression of the ionization of the dialkylphosphoric acid. The final uranium species in this process is $UO_2(NO_3)_2$-$((RO)_2P(OH)O)_2$, where the dialkylphosphoric acid plays a role similar to trialkyl phosphates in the respective solvates (149). A summary of these processes and a review of previous work on the extraction of uranium(VI) by DBP was published recently by Hardy (140).

The chelation of uranium by dialkyl phosphates is very strong, and a reagent like dibutylphosphoric acid in kerosene may extract uranium from its relatively strong complexes in phosphoric acid (400), where few other reagents are effective. Phosphate oxygens show some specificity toward the uranyl ion, and ion exchange resins incorporating acid phosphate groups as exchange sites are effective in removing uranium and separating it from other ions (196).

The acid phosphate esters have been applied also to other elements, with generally similar results. Heptavalent technetium (43) and rhenium (204) show some extraction by a dialkyl phosphate, which, in strongly acid solutions, probably can solvate the protons of the dissociated peracid $[(RO)_2P(OH)_2]^+MO_4^-$. Zirconium (145), niobium (144), protactinium (146), beryllium (142) and molybdenum(VI) (180) were found by British workers to be extractable by dialkyl phosphates. The beryllium and zirconium species extracted were $Be(HX_2)_2$ and $Zr(NO_3)_2(HX_2)_2$, respectively, whereas at high anion concentrations the anions replaced some of the dialkyl phosphate also in the beryllium complex. Similar results for di-2-ethylhexylphosphoric acid were also obtained with copper, cobalt and nickel (232) and with iron(III), where the species is $Fe(HX_2)_3$ at low concentrations (20) but polymeric at high iron concentrations, as with the uranyl ion. Protactinium was reported to be extracted by diisoamyl phosphate as PaX_5 (267), but this formulation conflicts with the accepted dimeric nature of dialkyl phosphates.

In searching for more effective extracting agents for uranium from phosphoric acid, it was found that what were believed to be pyrophosphate esters were very effective (430). Extraction of uranium(IV) from phosphoric acid by "di-*n*-butyloctyl pyrophosphate, $(RO\text{-}POOH)_2O$," to form uranium species containing the organic "pyrophosphate" with or without additional dihydrogen phosphate anions (455) or a tetra(dialkylpyrophosphate)uranium(IV) species (132) has been reported. Extraction of uranium(VI) by OPPA, "dioctylpyrophosphoric acid," to form $UO_2(ROPO_2)_2O)$-(136) and by "caprylpyrophosphate" (68a) has also been described. However, it was later found that all these reports were erroneous (456), since the material used, prepared by the reaction of phosphoric anhydride with the stoichiometrically required amount of alcohol, far from being a pure pyrophosphate, was a complex mixture containing many components (457), up to ten in the case of ethanol, seven with octanol and only three with 3,9-diethyltridecanol-6. This mixture was more effective by two orders of magnitude than the true pyrophosphates, probably because of synergistic effects.

In conclusion, the effectiveness of the acid phosphoric acid esters as extractants is based, on the one hand on their ability to chelate the metal to be extracted, and on the other on their ability to solvate this chelate further. Whereas the basic mechanism (at least with the dialkyl phosphates) is usually the same, the various esters vary in their extractive ability according to their basicity and steric availability. However, the relative effectiveness is best discussed together with that of the neutral phosphorus compounds.

Little work has been done on other, non-chelating, acidic extractants. Dinonylnaphthalenesulfonic acid (446) is a useful "liquid cation exchanger." Its extraction of indium from hydrochloric acid solution has served for the study of chloride complex formation. Logarithmic plots of the distribution coefficient *vs.* reagent concentration show the expected third power dependence for iron(III) and indium, and second power dependence for cobalt, zinc and manganese. Carboxylic acids are also able to extract metal cations. Copper propionate was found to be extracted into chloroform as the dimer (13), and higher molecular weight acids were found to extract cesium (185) and transition metal elements (118, 119, 186). Conflicting reports of the pH dependence of the extraction have been published. Iron(III) was found to be extracted as $HFeR_4$, where R is a carboxylate anion, and the distribution coefficient was found to *increase* with increasing pH: $\log D = -0.74 + 2.10\text{pH}$ (186). On the other hand, extraction of cesium (185) and of divalent transition metals were found to *decrease* with increasing pH, with $\log D = \text{const.} - \text{pH}$ (119). However, the same authors previously showed that the decrease follows the law $\log D = \text{const.} - 2\text{pH}$ for divalent metals, and $\log D = \text{const.} - 3\text{pH}$ for aluminum (118).

E. CHELATING EXTRACTANTS (CLASS E)

A comprehensive review of chelating extractants is outside the scope of this review; in any event little material which is new in principle has appeared since the monograph of Morrison and Freiser (281). However, some recent work on two chelating extractants which are capable of extracting metals from solutions of considerable acidity, contrary to most others, will be mentioned. Thenoyltrifluoroacetone (TTA) is fairly acid because of its strong electronegative groups, and forms strong chelates. Beryllium forms the excepted chelate $Be(TTA)_2$, extractable as such into xylene (51). The ordinary complex formed by uranium(VI) may add another molecule of TTA to form $HUO_2(TTA)_3$, with an equilibrium constant of 2.7 in benzene (439), while at very low concentrations it hydrolyzes to form $OH(UO_2)_2(TTA)_3$ in alcoholic aqueous solutions (1). The further solvation shown by $UO_2(TTA)_2$ toward excess TTA is also shown by thorium toward acetic acid, and species $Th(TTA)_4\ CH_3CO_2H$ and $Th(TTA)_4\ 2CH_3CO_2H$ have been identified in carbon tetrachloride solutions, when thorium is extracted from acetic acid (126). Further solvation by other solvents, principally TBP, also has been observed, and leads to a large enhancement of the distribution coefficients, as discussed below. A general review of TTA extraction was published by Poskanzer and Foreman (319). Using the extraction reaction

$$M^{m+} + mHX_{or} \rightleftarrows MX_{m\ or} + xH^+ \qquad (31)$$

with x equal to m only when no hydrolysis or protonation occurs, the equilibrium constant is obtained as

$$K = D(H)^x(HX)^{-m}y_{HX_{or}}^{1-m} \qquad (32)$$

provided that it is assumed that $y_{MX_{m\ or}} = y_{HX_{or}}$. Further assuming the activity coefficient to be given by $1 - 0.24(HX)_{or}$, they correlated many data by the equation

$$pH_{50} = (1/x)(pK - 0.75m - 0.05) \qquad (33)$$

where pH_{50} is the pH where 50% of the metal is in each phase (*i.e.* $D = 1$).

Another promising reagent which has been introduced recently is β-isopropyltropolone, which can be utilized over a wider pH range than TTA and can also extract alkaline earth metal ions (84, 86).

F. BASIC EXTRACTANTS (CLASS F)

The basic extractants differ from the classes discussed above more in degree than in kind; they comprise the range from weakly basic reagents like quinoline to strongly basic quaternary ammonium salts. Very little work has been reported on basic extractants that do not contain nitrogen as the basic atom.

Surveys on the extractive properties of various amines have been published (64, 69, 316, 375), mainly in connection with the recovery of uranium from ore leach liquors and of plutonium from spent nuclear fuel. A recent review (276) stresses their application to the extraction of various metals from different media, mainly in view of the applicability of separations.

The amines may interact in the organic phase by hydrogen bonding and may form micellar aggregates (63). Thus, Allen (7) tried to explain the insensitivity of the activity of tri-*n*-octylamine and didecylamine sulfates and bisulfates to changes in their concentration by assuming them to form large colloidal aggregates. A similar behavior is ascribed to a mixture of primary heptyl- to nonylamine nitrates (427). Cryoscopic measurements also indicate that tri-*n*-octylamine bisulfate forms di- or trimers (113) while the sulfate is monomeric. At high concentration, tri-*n*-hexylamine nitrate forms di- and trimer hydrates (418). Light scattering experiments (8) showed that tri-*n*-octylamine sulfate is monomeric, while the bisulfate is dimeric. Other amines, such as methyl dioctylamine and didecylamine, form monodisperse aggregates with 9 and 38 members, respectively. It seems that symmetric tertiary amines are monomeric in sulfate form. It is generally assumed by workers in this field that such amines (like tri-*n*-octyl or lauryl) are monomeric also in nitrate, chloride and other salt forms.

An interesting phenomenon connected with the strong surfactant properties of the amine salts has been observed. It was found that anomalous results are obtained on extraction with trioctyl- or didecylamine sulfates in benzene (259) when the agitation is vigorous, and a large surface area is generated. This anomaly persists also after apparent phase separation, but is not observed when the surface area is kept small, and diffusion is aided by gentle agitation within each phase separately. This effect demands that much care be exercised when interpreting amine extraction results, and that the attainment of equilibrium be ensured.

The effects of the diluent and other interactions, particularly with acidic diluents or reagents, will be discussed in the section on synergism.

Work on extraction with amines has been usually confined to extraction from acid solution; under such conditions the amine is converted to its salt form (272), which is practically undissociated in the amine–diluent solution of low dielectric constant. Thus, for a tertiary amine

$$R_3N_{or} + H^+ + A^- \rightleftarrows R_3NH^+ \ldots A^-{}_{or} \qquad (34)$$

The amine salt, however, has the power to dissolve additional acid. Some authors prefer to describe this phenomenon in terms of more complex species: $R_3N(HA)_2$, $R_3N(HA)_3$, etc., and calculate stability constants for their formation (363, 395, 404). There is, however, no real proof that this is the case (350), and the alternative explanation, *i.e.*, that excess acid simply dissolves in the diluent (accounting for a small part of the excess (55, 350)) and in the amine salt–diluent solvent system (29, 350) is equally probable. It is observed, at least for nitric acid, that the concentration of excess acid, over one mole per mole of amine, is proportional to both the (undissociated) acid concentration in the aqueous phase and to the amine salt concentration.

Most workers, studying the extraction of metal ions from a given medium, also study the distribution behavior of the acid of the corresponding anion, and much information is thus scattered throughout many papers. Distribution coefficients for various acids were given by Moore (272) and by Bertocci and Rolandi (30). The extraction of sulfate ions was studied extensively by Allen (7, 8) and by Fomin, Zagorets and Morgunov (113), and equilibrium constants were given by Boirie (41, 42) and Verstegen and Ketelaar (435) (Table II). The latter found that TOA displayed a very complicated behavior in kerosene (436). The distribution of nitric acid (55, 421) and its hydration (418) and dissolution in amine nitrate solutions (209, 350, 363) have been studied. Equilibrium constants for the formation of the amine hydrochloride were given by Bizot and Tremillion (32), Newman and Klotz (294), Peak (300) and by Wilson and Wagman (450), who give also data for fluoride, bromide and iodide ions (Table II). The table gives an approximate order of selectivities, which may be extended by noting the relatively high extractability of nitrous acid (29) and dichromate ions (75). For the secondary amine Amberlite LA-1, the corresponding equilibrium constants for nitric acid are log $K = 5.58$ for carbon tetrachloride and log $K = 5.73$ for benzene (209).

The amine salts have limited solubility in some diluents, and a third phase may appear in the system acid–water–amine–diluent. The solubility in decalin or kerosene is lower than in toluene or xylene (179). Addition of long chain alcohols or raising the temperature increases the solubility.

The extraction of various metals has been reviewed by Moore (276), but new publications on this subject flood the literature. Many elements are extractable from chloride solutions. Although, as with anion exchange resins, the trivalent lanthanide and actinide

TABLE II

EQUILIBRIUM CONSTANTS FOR FORMATION OF TRI-*n*-OCTYLAMINE SALTS

Anion, A	Solvent	Reference	Log K^a
Fluoride	Toluene	450	2.96
Chloride	Benzene	294	4.1
	CCl_4	32	4.0
	Toluene	450	5.94
	Toluene	300	4.9^b
Bromide	Toluene	450	7.96
Iodide	Toluene	450	10.23
Nitrate	Toluene	300	6.6^b
	CCl_4	412	5.0^b
Sulfate	Benzene	435	8.27^c
	Benzene	41	8.5^c
	CCl_4	41	6.7^c
	Benzene	92	8.28^c
Perrhenate	CCl_4	203	5.0^b

[a] $K = (Oc_3NHA)_{or}/(Oc_3N)_{or}(H^+)(A^-)$

[b] For triisoöctylamine

[c] $K = [(Oc_3NH)_2SO_4]/(Oc_3N)^2(H^+)^2(SO_4^{2-})$

elements are not extractable from hydrochloric acid, they are extracted to some extent from low acid, high chloride solutions of lithium or calcium chloride (25, 115, 277), and the two groups may be separated in these media, the actinides showing the higher distribution coefficients. Trivalent titanium is extractable from hydrochloric acid by a quaternary amine (448). Zirconium and hafnium are both extractable from hydrochloric acid, and separation coefficients in favor of the zirconium of up to 73 were observed in extraction by triisooctylamine. Thorium is hardly extracted (by the secondary amine Amberlite LA-1 (163)), in agreement with its behavior toward anion exchange resins. Hexavalent uranium is extracted well both by the last named reagent (163), and by tri-*n*-octylamine (32) and triisooctylamine (273). The equilibrium constant for the formation of the complex $(Oc_3NH)_2UO_2Cl_4$ in carbon tetrachloride solution is $\log K = \log[((Oc_3NH)_2UO_2Cl_4)_{or}/(Oc_3NHCl)_{or}^2\ (UO_2^+)(Cl^-)^2] = 1.5$ (32). Neptunium is also extracted in the tetra- and hexavalent states (44) as is plutonium (272, 273). Niobium and tantalum are separable by extraction with tribenzylamine from hydrochloric acid (93); protactinium is also extractable (272), and separations from thorium and uranium are possible (163). Considerable work has been done on the distribution of tervalent iron between hydrochloric acid and amine solutions. It may be extracted by a quaternary amine (418) or tertiary amines (128, 236, 445). White, Kelly and Li (445) tried to prove that it is extracted as $(Oc_3NH)_2FeCl_5$, although from rather few experimental points which indicate a slope of two in a logarithmic plot of the distribution coefficient *vs.* the amine hydrochloride concentration. On the other hand, Good and Bryan (123) showed in loading experiments, that the limiting complex at high iron concentrations is $R_3NHFeCl_4$, and spectrophotometric measurements confirm this species, by analogy with the known spectrum of $KFeCl_4$ in ether. With tracer concentrations of iron, these authors obtained distribution data as a function of hydrochloric acid concentration for a great variety of primary, secondary and tertiary amines. Nickel is only slightly extractable (236), whereas cobalt is extracted well from concentrated hydrochloric acid solutions (236, 448). The absorption spectrum of the extracted cobalt corresponds to $(R_3NH)_2CoCl_4$ (129). The platinum metal chlorides are extractable as stable species (462). Monovalent copper and silver show good extractability from neutral chloride solutions with tributylammonium chloride (459). The distribution coefficient for silver decreases with increasing chloride concentrations, and it was shown by Schindewolf (347) that $(MeOc_2NH)_2AgCl_3$ is the species extracted from hydrochloric acid, lithium and cesium chlorides. Similarly, $(MeOc_2NH)_2ZnCl_4$ is the zinc species extracted as indicated by analyzing the slope of a logarithmic plot of the distribution coefficients *vs.* amine concentration. Data for zinc have also been given by Mahlman, Leddicote and Moore (236) and Wilson, Churchill, Liluk and Hovsepian (448). The extraction of indium has been studied by White, Kelly and Li, who again describe their results in terms of $(R_3NH)_2InCl_5$ (445). Their data, however, may also be fitted by considering the extraction of $(R_3NH)InCl_4$ at low, and $(R_3NH)_3InCl_6$ at high, amine concentrations, and this interpretation agrees quantitatively with results obtained by Maydan (256) in sodium chloride solutions and in solutions of low hydrochloric acid concentrations. Finally, polonium was found to be extractable (272) and separable from bismuth and other elements in hydrochloric acid.

In most of the above-mentioned investigations, it was found that the qualitative behavior of the distribution with respect to chloride or amine concentrations does not vary much from one amine to another. Thus Nakagawa's comprehensive studies on most elements (286, 287, 288, 289), using solutions of the secondary amine Amberlite LA-1, should serve as a useful guide in selecting the best conditions for a required extraction or separation.

Most of the studies with nitric acid dealt with the extraction of the actinides and of fission products. The tetravalent actinides are extracted as $(R_3NH)_2M(NO_3)_6$ where M is Th, U, Np and Pu (29, 46, 55, 163, 192, 193, 215, 354, 375, 449), whereas hexavalent uranium is extracted as $(R_3NH)UO_2(NO_3)_3$ (29, 163, 192, 193, 215, 361, 421, 428) as probably also are neptunium and plutonium (192, 441). The spectra of the tetra- and hexavalent actinides in the organic phase have been published (192) and found to be similar to the solid compounds obtained with quaternary ammonium salts. The extractability of pentavalent neptunium is negligible (441), but that of protactinium is relatively high (163, 193); nevertheless it may be separated easily from the tetravalent actinides which are extracted extremely well.

Trivalent actinides and lanthanides show only very small distribution coefficients between amine solutions and nitric acid (135, 162), but much higher ones with lithium nitrate solutions (246, 248). The spectra of tervalent plutonium, samarium and erbium in the organic solutions are similar to those in concentrated lithium nitrate solutions (248). The slope of a logarithmic plot of the distribution coefficients *vs.* amine concentration was found to be two, which would indicate species like $(R_3NH)_2M(NO_3)_5$, which have an odd coordination number. A similar slope also was obtained with the chlorides (25, 115). Tetravalent cerium is reduced by tertiary amines (416), but may be extracted with tetrabutylammonium nitrate from nitric acid into nitromethane (443).

Of the fission products, zirconium (215, 375, 427), ruthenium (360) and molybdenum (215, 416) in particular have been studied. The report by Vaughen and Mason (416) summarizes a considerable amount of work on the relative extractability of fission products and uranium and plutonium with various amines.

A paper by Kertes and Beck (203) describes the extraction of perrhenic acid by triisooctylamine, forming $(Oc_3NH)ReO_4$ in the organic phase, which is much more stable than the nitrate salt; perrhenate can displace nitrate ions completely from the amine.

Only few elements are extractable from sulfate solutions, and these may be used for selective separations of those few from all the others. Thorium is extracted by didecylamine as $(Dec_2NH_2)_nTh(SO_4)_{2+n/2}$, where $n = 6 \pm 1$, as found from loading experiments. Since the didecylamine sulfate is highly aggregated to micelles, the reagent concentration dependence of the distribution coefficients is very low. A mixture of primary amines with 7 to 9 carbons was also studied, and two amine sulfate molecules were found to accompany thorium sulfate into the organic phase (420). The separation of thorium from uranium (41, 42) and from protactinium (163) is possible in sulfate solutions, and some data for neptunium in various oxidation states are given by Weaver (441). A considerable amount of work has been done on hexavalent uranium (260, 321). In particular, Allen (9, 10) studied its extraction by tri-*n*-octylamine. The species in the benzene solution is $(Oc_3NH)_4UO_2(SO_4)_3$, perhaps with some additional bound amine sulfate, as found from loading experiments. The distribution results permitted Allen to calculate stability coefficients for the uranyl sulfate complexes in the aqueous solution, which are in agreement with published values. Allen also studied the rate of extraction by the amine, and found that the mechanism probably involves the transfer of the cations UO_2^{2+} as the major path (11). Tetravalent plutonium is extracted by a mixture of heptyl- to nonylamines in chloroform as $(R_3NH)_4Pu(SO_4)_4$ (430). Tervalent iron is also extractable from sulfate solutions, in particular with primary amines (19, 64).

Little work has been done on extraction from other solutions, but the following is indicative of the possibilities. Beryllium may be extracted by triisooctylamine from oxalate, malonate or other dibasic aliphatic acid solutions as $(Oc_3NH)_2$ $Be(C_2O_4)_2$, *etc.* (49, 50). Iron(III) and cobalt(III) are extracted by various amines such as $(R_3NH)_3M(C_2O_4)_3$, and cobalt(II) and nickel(II) as $(R_3NH)_2M(C_2O_4)_2$ from oxalate solutions (52). Uranium is extractable from acetic acid solutions by aniline as $(C_6H_5NH_3)UO_2(CH_3CO_2)_3$, and an equilibrium constant $K = 0.13$ was found for the formation of this species from uranyl, acetate and anilinium ions (426). Extraction of uranium and plutonium(VI) acetates by TIOA also has been noted (275). Heptavalent technetium and rhenium can be extracted from acid solutions by various amines (43), the distribution coefficients increasing in the order primary, secondary and tertiary, and also from neutral and basic solutions by a quaternary amine such as didodecyldimethylammonium (43). However, from strongly basic solutions like two molar sodium hydroxide, perrhenate and pertechnetate may also be extracted by pyridine, which is not ordinarily considered as an extraction reagent, since it is miscible with water (326).

By forming a complex with a chelating agent, 8-quinolinol, uranium may be extracted by a quaternary amine from carbonate solutions (61). This is an extension of the well known method of (neutral) chelate extraction, in that anionic chelates can also be extracted as ion pairs with suitable amines.

Many metals are extractable from thiocyanate solutions by amines. In fact, an analytical method for amines in aqueous solutions is based on the extractability of the cobalt thiocyanate complex (17). Ziegler and Glemser (461, 462, 463) have shown that tributylammonium salts of many heavy metals with the pseudohalogen anions thiocyanate, cyanide and azide are soluble in organic diluents, and thus extractable from aqueous solutions.

Most of the recent work on extraction by amines used primary, secondary or tertiary amines, particularly the latter, the most popular being tri-*n*- or triisooctylamine, because of its low cost, low solubility in aqueous solutions, and high solubility in various organic solvents, including kerosene or other aliphatic hydrocarbons. However, other types of amines also have been used occasionally, especially quaternary amines. These have the drawback of incompatibility with many diluents, high aqueous solubility and emulsion-forming properties. They, sometimes, do show useful extraction properties, and quaternary propyl- or butylamines were used to extract uranium and plutonium from nitrate solutions (where they serve also as salting-out agents (234, 396)). As mentioned previously, they were also used to extract tetravalent cerium (443) and the uranyl ion chelate with 8-quinolinol (299). Considerable information was given recently (448) on the extraction of anions such as chloride, bromide, nitrate or thiocyanate, and chlorocomplexes of cobalt, iron(III), zinc, hafnium, tantalum, molybdenum(VI) and titanium(III) by quaternary amines. A general survey on the extractability of many elements from hydrofluoric, hydrochloric, nitric and sulfuric acids and sodium hydroxide solutions was published recently (235). In spite of the considerable amount of data given, the report is tantalizingly short of information from which the composition of the extracted species can be deduced, or from which the distribution coefficients for various concentrations can be calculated. The main usefulness of this survey is for pointing out the cases where more work is desirable.

The use of pyridine (326) and aniline (426) as basic extractants already has been mentioned above. Another unusual reagent is triphenyltin (39), which as the hydroxide may exchange in organic solvents this anion for others in aqueous solution, like halides, phosphate, arsenate, chromate and selenite, but, curiously enough, not nitrate or sulfate.

Apart from liquid–liquid distribution, amines such as trioctylamine also have found applications in partition chromatography, in particular paper chromatography (57, 399), the principles of the applications being the same as those discussed above for solvent extraction.

Although much has been published about the mechanism of the extraction of metals by amines, there is still no complete agreement on it. The most generally accepted view is that the amines act as anion exchange (*e.g.*, 286, 287, 288, 289, 347, 428, 448), according to

$$\mathrm{MA}_n{}^{(m-n)} + (n-m)\mathrm{R_3NHA}_{\mathrm{or}} \rightleftarrows (\mathrm{R_3NH})_{n-m}\mathrm{MA}_n)_{\mathrm{or}} + (n-m)\mathrm{A}^- \quad (35)$$

for a tertiary amine and an univalent ligand. The number of ligands involved, n, would usually correspond to the coördination number of the metal, and the number of amine salt molecules to the difference between that and the charge of the metal cation. The slope of a logarithmic plot of the distribution coefficient *vs.* (free) amine salt concentration at a given constant aqueous ligand concentration is then supposed to be equal to $n - m$.

This interpretation may, however, sometimes lead to erroneous results. In the case that the amine is polymeric, it would behave as if it had constant activity, and the slope of the above-mentioned plot would not be significant. If the interaction of the amine with the aqueous ligand goes beyond neutralization, then with constant aqueous ligand concentration and varying total organic amine concentration, the fraction of free amine will vary, and again the slope will not give the true number of amine cations participating in the organic complex. Equilibrium conditions must in all cases be ensured in view of the surfactant behavior of the amines (259).

The role of the amine is not completely clear. It modifies the solvent, lending polar properties to the diluent amine–salt mixture (thus making possible the dissolution of excess acid). Little is known concerning the water in the organic phase. It is said (418) that the nitrate salt (of tri-*n*-hexylamine) is hydrated with one molecule of water, but nothing is known on the behavior of the water when metals are extracted. From Allen's work it seems that the major path involves the transfer of the cation across the interface (11), and this would then involve the reaction

$$\mathrm{M}^{m+} + n(\mathrm{R_3NHA})_{\mathrm{or}} \rightleftarrows (\mathrm{R_3NH})_{n-m}\mathrm{MA}_{n\ \mathrm{or}} + m(\mathrm{R_3N})_{\mathrm{or}} + m\mathrm{H}^+ \quad (36)$$

An additional formulation would involve only neutral species, as the likely reactants in the low dielectric constant organic phase (256)

$$\mathrm{MA}_m + (n-m)\mathrm{R_3NHA}_{\mathrm{or}} \rightleftarrows (\mathrm{R_3NH})_{n-m}\mathrm{MA}_{n\ \mathrm{or}} \quad (37)$$

where the amine salt may be considered to solvate the metal and replace the hydration water.

In any case, it is likely that the ligands are bound to the metal directly, while the substituted ammonium cations are bound by electrostatic forces (ion pair formation to the complex anion). When the number n is smaller than the maximum coördination number, additional amine salt ion pairs may add to the complex to form that one which has maximum coördination at higher amine concentrations

$$(\mathrm{R_3NH})_{n-m}\mathrm{MA}_{n\ \mathrm{or}} + p(\mathrm{R_3NHA})_{\mathrm{or}} \rightleftarrows (\mathrm{R_3NH})_{n+p-m}\mathrm{MA}_{n+p\ \mathrm{or}} \quad (38)$$

This is what presumably happens with indium chloride, where $n = 4$ and $p = 2$ (256). This kind of interaction, between neutral molecules (or ion pairs), is dissimilar to that which is likely to occur in an anion exchange resin, where because of the strong swelling and hydration, the effective dielectric constant is higher than in amine solutions, but not as high as in aqueous solutions. This would enhance the importance of ionic reactions but limit the species to those with low negative charges. It is therefore dangerous to infer from amine extraction results, as is commonly done, the behavior of metal complexes in anion exchangers.

G. NON-SOLVATED ION PAIRS (CLASS G)

The extraction of large unsolvated cations paired with large unsolvated anions has been fully discussed by Diamond and Tuck (77). The extraction of the alkali metal ions is exemplified by that of cesium with tetraphenyl borate into nitrobenzene (98) and of alkali metal ions by polyiodides (40); that of anions, by the extraction of fluoride by tetraphenylstibonium into carbon tetrachloride, with distribution coefficients of up to 16 (270), in spite of the relatively small size of the fluoride anion. Some recent work with tetraphenylphosphonium ions includes the extraction of chloroaurate (285), and of perchlorate, perrhenate, *etc.*, which are able to displace colored ions such as eosinate (406) and permanganate (249), and can thus be determined colorimetrically.

A large group of unsolvated ion-pair extraction systems is that of the quaternary and other amines in acid solutions, which extract anionic complexes of metals; this already has been dealt with.

IV. EXTRACTION BY MIXED SOLVENTS

In cases of extraction by a mixture of two organic solvents, the system may behave in one of three ways: (a) neither solvent participates in the extracted metal complex; (b) one of the solvents participates, whereas the other is an inert diluent; or (c) both solvents participate in the complex. In the first case, the equation given by Irving and Rossotti (173) applies

$$\log D_{S_M} = \log D_{S_A} - N_{S_B} (\log D_{S_A} - \log D_{S_B}) \qquad (39)$$

where S_M, S_A and S_B apply to the mixture and the pure solvents S_A and S_B, and N is the mole fraction. This equation was verified by extraction of indium from hydrogen bromide solution with mixture of methyl isobutyl ketone and methyl isopropyl ketone, and cyclohexane and benzene (however, the two ketones probably solvate the proton in the extracted species $HInBr_4$ so that this case belongs to category c, not a).

In the second case, the equation that applies is

$$\log D_{S_M} = \log D_{S_A} + \log [1 + K'(S_B)^{q_B}] \qquad (40)$$

where q_B is the solvation number by solvent S_B.

At very low values of (S_B) unity may not be neglected in the second term on the right, as shown by Tuck (411) in the case of extraction of chloroauric acid by TBP in xylene. However, in most cases (S_B) and K' are sufficiently large for unity to be neglected, and putting $K = D_{S_A}K'$ the equation

$$\log D_{S_M} = \log K + q \log (S_B) \qquad (41)$$

is obtained; $\log D_{S_M}$ is linear with $\log (S_B)$, the slope q being the solvation number. This case has been discussed extensively above.

The most interesting case occurs when both solvents participate in the extracted complex. The distribution coefficient may be larger (often much larger) than predicted by equation 39 or smaller than this prediction.

Several explanations have been proposed for this phenomenon, most of them applying only to the particular system dealt with. Katzin (189, 190), who investigated the solubility and heat of solution of cobalt nitrate in mixtures of ketones and alcohols, suggested that the formation of $CoS_4(NO_3)_2$ with coördinated nitrate groups is more exothermic than the formation of $CoS_6^{2+}(NO_3)_2^{2-}$. However, the latter ion pair will form more easily with stronger solvating agents. Dilution with a weaker solvent will therefore favor the formation of the former complex, increasing the heat of solution and the distribution coefficient.

Goble and Maddock (123, 124) found maxima in plots of the distribution coefficient of protactinium between hydrochloric acid and mixtures of diisopropylcarbinol with ketones, nitro compounds and nitriles *vs.* the composition of the solvent. Similarly, Mottola and Sandell (283) found that mixtures of isoamyl alcohol and acetate extract bismuth iodide better than either solvent alone. The distribution coefficient increases with stronger solvation of the proton and with more complete dissociation into ions of the extracted ion pair. Hence, if one solvent in a mixture contributes high basicity, the other a high dielectric constant, the distribution coefficients would be higher than in each solvent alone.

There is another explanation of this, however, which also applies to other cases where one of the solvents is highly self-associated. The second solvent, acting as a diluent, reduces the association of the active solvent, thus making it more available for solvation. Hence when the diluent shows a low intrinsic distribution coefficient, a maximum in the extraction curve will occur.

In general, positive deviation from Raoult's law for the solvents will cause maxima in extraction curves (124, 334). Thus, with the mixture methyl isobutyl ketone and diisobutyl ketone, a maximum occurs for the extraction of niobium from hydrochloric acid, as expected (441). In other cases, mixed solvates (374) may form, and these may be more stable than the pure solvates (247); hence higher distribution coefficients are obtained. This was observed by Vdovenko (423, 424, 425) in the extraction of nitric acid, uranyl nitrate and other nitrates with mixtures of diethyl ether and acetophenone or of dibutyl ether and β,β'-dichlorodiethyl ether. Each solvent forms a disolvate, as found when it was diluted with an inert solvent like benzene. In the mixtures a mixed solvate probably is formed, which showed the higher distribution coefficient expected.

The important role that seemingly inert diluents can play was noted by many authors (147). Taube (396, 397, 398) discussed this problem extensively. He found that with some solvents such as hexone, dibutyl phosphate, TBP and TTA the diluent is inert in the extraction of tetravalent plutonium from nitric acid (179), with non-polar diluents (such as cyclohexane and heptane), polar ones (like chloroform) giving lower distribution coefficients. Similar results were obtained for TBP extraction of uranium(VI) and neptunium(IV) and -(VI) (263). Tetrabutylammonium nitrate as extractant of plutonium(VI) from nitric acid, however, behaved differently (397). Diluents could be classified as P = polar (chloroform), H = non-polar but highly polarizable (benzene) and L = non-polar, slightly polarizable (carbon tetrachloride). The following types of behavior were found with the various mixtures, as a function of composition.

L + L:	very poor extraction
L + H:	distribution coefficients increase regularly as mole fraction of H increases
L + P:	distribution coefficients increase from low level at pure L to a maximum at 1:1 composition, then decrease as pure P is approached
H + P:	maximum distribution coefficient for 1:1 mixture, except for nitric acid concentrations above 5 *M*, where pure H shows the highest distribution coefficient
P + P:	little changes with composition, or shallow maximum for 1:1 mixture at low acidity

Less extensive results with plutonium(IV) (396), uranium(VI), and neptunium(IV) and -(VI) (398) in the same system confirm the presence of a maximum in the extraction curve when one of the diluents is polar (chloroform). In general, the extractability decreases in the order $H > P > L$ as a function of diluent.

The explanation put forward by Taube involves both the dipole interaction and the space-occupying properties of the extracted complex. The extractability depends principally on the solvation of the $(Bu_4N)_2M(NO_3)_6$ or $(Bu_4M)MO_2(NO_3)_3$ species with polar solvent. In the solvate the dipole in a P-type solvent is antiparallel to that of nitric acid. The combination has a small moment and little solvating power. The induced dipole in an H-type solvent makes the moment of the nitric acid solvate large, and the combination has high solvating power. The work necessary to make a hole in the hydrogen-bonded or dipole-oriented structures favors the extraction into non-polar solvents of smaller species, and those species which are non-polar, like the TBP complex of plutonium(IV). With polar complexes, the solvation energy gained offsets this loss in self-interaction energy. The effective disruption of the structure by another solvent also increases the net energy gained by the extraction (the L + P case), as also seen above with alcohols.

In the phenomena discussed above, the maxima in the extraction curves may have been a few times larger than the distribution coefficients shown by the better solvent of the pair. However, another class of interactions, usually referred to as synergism, may show distribution coefficients higher by a few orders of magnitude than those exhibited by either of the solvents alone. These recently have been studied intensively.

An important case occurs where one of the solvents is a chelating agent like TTA, the other a solvating solvent like TBP. Some years ago Cunninghame, Scargill and Willis (70) found that this mixture extracts neodymium and praseodymium from nitrate solutions much better than either solvent alone, and advanced an explanation based on mixed complex formation. Irving and Edgington (168) later found that with uranium(VI) synergism of the order of 10^3–10^4 occurs. They stipulated that this behavior would occur generally with coördinatively unsaturated neutral chelates where a second solvent may displace water of hydration. Since two molecules of bidentate TTA are involved in the uranyl complex, synergism is here possible, and indeed found, with one TBP or three TBPO molecules occupying the remaining coördination sites. This explanation, however, was invalidated when it was found that trivalent lanthanides and actinides can also be synergistically extracted by these solvents, although they apparently were coördinatively saturated. These species were identified (275, 454): $AmNO_3(TTA)_2\ 2TBPO$, $EuNO_3(TTA)_2\ 2TBPO$; $PuNO_3(TTA)_3\ TBP$, $Pu(NO_3)_2(TTA)_2\ 2TBPO$ and similar species with neptunium(IV) and thorium, $Th(NO_3)_3\ TTA\ TBPO$, $PuO_2(TTA)_2\ TBP$; $Am(TTA)_3\ 2TBP$, $Am(TTA)_3\ TBPO$ and similar species with europium; $Zn(TTA)_2\ TBP$, $Zn(TTA)_2\ 2TBP$ and similar species with manganese. Comparable results, with very high synergistic effects, also were obtained by Healy (147) for calcium, promethium, thulium, americium, curium and thorium. Healy also replaced the solvating solvent TBP by esters varying in basicity from TOPO to triphenyl phosphate. The synergistic effect was found to increase in the same way as extractability by the solvent itself, *i.e.*, with increasing basicity. A remarkable phenomenon is the large effect that so-called inert diluents have on the synergistic extraction in this system. The synergism is weakest with chloroform, improves through the series benzene, carbon tetrachloride, hexane, and is highest with cyclohexane. The diluent effect varies with the metal and the solvating solvent. Irving and Edgington in recent publications (170) showed that the TTA in the uranyl complex is probably monodentate, and that the complex with TBPO contains a molecule of water: $UO_2(TTA)_2\ 3TBPO\ H_2O$, the uranium then being octa-coördinated. They predict synergism with tri-, penta- and hexavalent ions of the octa-coördinated lanthanides and actinides, since here water displacement can occur, but not with tetravalent ions, where the bidentate chelating ligands will occupy all coördination positions. Indeed plutonium(VI) extracts as $PuO_2(TTA)_2\ TBP$ and neptunium(V) as $HNPO_2(TTA)_2\ TBP$. However, if part of the chelating ligand may be displaced by a simple anion like nitrate, synergism becomes possible (by displacement of coördinated water) and was observed for tetravalent thorium, neptunium and plutonium. There is, however, disagreement over the thorium species involved. Whereas Healy (147) found only $Th(TTA)_4\ TBP$ or $Th(TTA)_4\ TOPO$, Irving and Edgington find $Th(TTA)_2(NO_3)_2\ TBP$, $Th(TTA)_3(NO_3)_2\ TBPO$ and $Th(TTA)_2(NO_3)_2\ 2TBPO$. The difference probably lies in the complexing of thorium by nitrate, which is stronger than that by chloride, the medium used by Healy.

In spite of the abundance of data, the mechanism of synergism in this system is still unclear, and the role of the water, the inert diluent, the possible change in coördination and the solvation must be further elucidated. It must also be established whether the solvating solvent is attached directly to the metal, as claimed by Irving and Edgington, or through the chelating agent, a possibility suggested, among others, by Healy.

Another much-investigated system is that involving a dialkylphosphoric acid and a neutral phosphorus ester such as di-2-ethylhexylphosphoric acid–tributyl phosphate (36), dibutyl phosphate–tributyl phosphate (88), dibutyl phosphate–trioctylphosphine oxide (197), *etc.* The word synergism was first applied to extraction studies for these systems (35). The results are qualitatively independent of the nature of the acid phosphate (HX) and the neutral ester (S). The following facts must be noted in order to understand the synergism involved.

When S is added at constant concentration of HX, the position of maximum synergism depends on the nature of S and the required concentration of S decreases as the effectiveness of S, as solvent and synergistic agent, increases in the series phosphate, phosphonate, phosphinate and phosphine oxide (36, 194). The dependence of the distribution coefficient on the concentration of S is pH-independent, *i.e.*, no hydrogen ions are involved in the reactions. Synergism was found for plutonium(IV) and -(VI) and uranium(VI), but not for uranium(IV), vanadium(IV), aluminum, molybdenum, iron, titanium and thorium (36). With high concentrations of S added to HX, distribution coefficients decrease again (36, 194).

Early explanation of the effect involved the addition of one S molecule (35, 36) to the species $UO_2(HX_2)_2$, which is generally accepted as the uranium species extracted by the acid phosphate. This involves the increase of the coördination number of the uranyl ion, which would explain the limitation of the synergism to this and the plutonyl ion. However, the effect with plutonium(IV) remains unexplained. A different mechanism was offered by Kennedy (194), who pointed out the gain in energy when the monomerization of $(HX)_2$ is avoided, in that the octa-coördinated $((RO)_3PO-)_2UO_2(=O_2P(OR)_2)_2$ (*i.e.*, $S_2UO_2X_2$) is formed with two molecules of S, instead of $(RO_2P(OH)O-)_2UO_2(=O_2P(OR)_2)_2$ (*i.e.*, $(HX)_2UO_2X_2$) with two monomerized HX molecules. He also maintained that a more basic acid ester, like that of phosphinic acid, R_2POOH, could not be replaced by TBP. Kennedy's explanation requires second power dependence of the distribution coefficient on the concentration of S.

More detailed investigation, however, showed the possibility of replacing either one or two of the solvating HX molecules by S (88, 197), depending on the concentration. Therefore the argument involving avoidance of monomerization of $(HX)_2$ is inadmissible. The solvate composition depends on the strength and concentration of S, thus with S = TBP and HX = dibutyl phosphate, UO_2X_2HXS was found in carbon tetrachloride (88), but with HX = diamyl phosphate, UO_2X_2S and PuX_4S were found in xylene (355). With S = hexone without diluent (about 8 *M*) which solvates the uranyl chelate as a neutral phosphorus ester does, the species is $UO_2X_2hexone_2$ (239). With S a phosphine oxide, Dyrssen and Kuca (88) found only $UO_2X_2S_2$ in carbon tetrachloride solutions, but Kennedy and Deane (197), in an infrared investigation, also found the intermediate species, which they formulate as $(R_3POH)UO_2((RO)_2PO_2)_3$ (*i.e.*, $(SH)UO_2X_3$) with three equivalent X groups similar to the species obtained with tetrabutylammonium cations $(Bu_4N)UO_2((BuO)_2PO_2)_3$ (198).

The antagonistic effect noted above for high concentrations of S is understandable in terms of the interaction of $(HX)_2$ with S to form SHX (36, 89) and $S(HX)_2$ (36). With a monoalkylphosphoric acid the species formed is $S_2(H_2X)_6$ (94). The concentration of free chelating agent is reduced, and therefore also the distribution coefficients. Such effects were noted by Peppard, Mason and Sironen (313) in the extraction of neptunium(IV) and thorium by mono-2-ethylhexylphosphoric acid on the addition of TBP, and utilized by Dyrssen and Ekeberg (85) in facilitating back extraction of yttrium from dibutyl phosphate, when hexol is added. A different antagonistic effect may occur when one solvent competes for a ligand necessary for efficient extraction by another solvent. Thus TBP competes for nitric acid, which is a component of the plutonium(VI) complex extracted by dibutylcarbitol, $HPuO_2(NO_3)_3$ (148), as found by changes in the absorption spectrum.

Synergism involving amines and chelating extractants as the two solvents also has been reported recently. At very low acidities, acid phosphate esters can convert the free amine to the ammonium cation effective for the extraction of dichromate or sulfatouranyl anions (35). At higher concentrations, the association of amine with phosphate reduces the effective concentrations of the extracting agents. Thus maxima in the extraction curve could be observed (75). However, the association product may also be effective as an extractant, and synergism may occur. This was observed by Newman and Klotz (294) who found that the interaction product between TTA(HX) and trioctylamine in benzehe, Oc_3NHX, extracts thorium from 2 *M* hydrochloric acid, whereas each of the reagents alone does not.

There appears to be no general explanation to the multitude of phenomena covered by the word synergism. Some effects may be due to changes in the self-association in one of the solvents, or to more favorable dielectric constants on the introduction of a second solvent. Other effects depend on the specific solvation of the species extracted by one solvent (as chelate) by the other. However, it is still unclear how this solvation operates, and enormous variations in the distribution coefficients are found.

V. CONCLUDING REMARKS

The last decade has seen considerable advances in our understanding of the solvent extraction of inorganic species. General methods have been devised to analyze distribution data in terms of the participating species for most extraction systems. In fact, although many new extractants are added yearly to the large list of efficient solvents, essentially all of them can be fitted into existing extraction schemes and mechanisms.

The following information can often be obtained from careful measurements of distribution as function of the concentration of the reagents: the nature of the extracted species (solvation and ligand numbers, degree of polymerization), their activity coefficients in the organic phase, the equilibrium coefficient for the main extraction reaction (sometimes the partition constant for a neutral species), the nature of the predominating species in the aqueous phase, and the equilibrium constants for their interconversion. The latter information is applicable also to inextractable species in equilibrium with the main distributing species.

Since distribution measurements can be made on tracer quantities of metals (often with advantage, using radioactive tracers), solvent extraction is an important tool in the study of the new, radioactive, elements where macro quantities are not, or sometimes can never be, available for investigation.

There are, however, many unsolved problems that should be tackled in the near future. The general question of the behavior of (mixed) electrolytes at high concentration in aqueous solutions is far from being solved, and solvent extraction studies can contribute toward its solution. Even at low concentrations, the phenomena of salting-out and salting-in lack a comprehensive theory. More information on the hydration of ions, and in particular of anions, including anionic complexes, both with respect to hydration numbers and to the enthalpy and entropy of hydration is needed. As regards the organic phase, both experimental and theoretical methods to handle the activities of the various species in the mixture sometimes containing diluent, solvent, water, acid and metallic salt, are necessary. The role of the so-called "inert" diluent is not at all clearly understood, although in some cases it can exert an enormous influence on the distribution. Some of these problems can be better understood if more (and more accurate) thermodynamic data regarding the enthalpies and entropies of extraction reactions are known.

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