4
Solvent Extraction Equilibria

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4.1 INTRODUCTION

The ability of a solute (inorganic or organic) to distribute itself between an aqueous solution and an immiscible organic solvent has long been applied to separation and purification of solutes either by extraction into the organic phase, leaving undesirable substances in the aqueous phase; or by extraction of the undesirable substances into the organic phase, leaving the desirable solute in the aqueous phase. The properties of the organic solvent, described in Chapter 2, require that the dissolved species be electrically neutral. Species that prefer the organic phase (e.g., most organic compounds) are said to be lipophilic ("liking fat") or hydrophobic ("disliking water"), while the species that prefer water (e.g., electrolytes) are said to be hydrophilic ("liking water"), or lipophobic ("disliking fat"). Because of this, a hydrophilic inorganic solute must be rendered hydrophobic and lipophilic in order to enter the organic phase.

Optimization of separation processes to produce the purest possible product at the highest yield and lowest possible cost, and under the most favorable environmental conditions, requires detailed knowledge about the solute reactions in the aqueous and the organic phases. In Chapter 2 we described physical factors that govern the solubility of a solute in a solvent phase; and in Chapter 3, we presented the interactions in water between metal cations and anions by

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which neutral metal complexes are formed. This chapter discusses the equations that explain the extraction data for inorganic as well as organic complexes in a quantitative manner; i.e., the measured solute distribution ratio, \( D_{\text{solute}} \), to the concentration of the reactants in the two phases. It presents chemical modeling of solvent extraction processes, particularly for metal complexes, as well as a description of how such models can be tested and used to obtain equilibrium constants.

The subject of this chapter is broad and it is possible to discuss only the simpler—though fundamental—aspects, using examples that are representative. The goal is to provide the reader with the necessary insight to engage in solvent extraction research and process development with good hope of success.

4.1.1 The Distribution Law

The distribution law, derived in 1898 by W. Nernst, relates to the distribution of a solute in the organic and in the aqueous phases. For the equilibrium reaction

\[ \text{A (aq)} \rightleftharpoons \text{A (org)} \]

the Nernst distribution law is written

\[ K_{D,A} = \frac{\text{Concentration of Species A in organic phase}}{\text{Concentration of Species A in aqueous phase}} = \frac{[\text{A}]_{\text{org}}}{[\text{A}]_{\text{aq}}} \]  

where brackets refer to concentrations; Eq. (4.1) is the same as Eqs. (1.2) and (2.23). \( K_{D,A} \) is the distribution constant (sometimes designated by \( P \), e.g., in Chapter 2; see also Appendix C) of the solute A (sometimes referred to as the distribuend). Strictly, this equation is valid only with pure solvents. In practice, the solvents are always saturated with molecules of the other phase; e.g., water in the organic phase. Further, the solute A may be differently solvated in the two solvents. Nevertheless, Eq. (4.1) may be considered valid, if the mutual solubilities of the solvents (see Table 2.2) are small, say <1%, and the activity factors of the system are constant. If the solute is strongly solvated, or at high concentration (mole fraction >0.1), or if the ionic strength of the aqueous phase is large (>0.1 M) or changes, Eq. (4.1) must be corrected for deviations from ideality according to

\[ K_{D,A}^0 = \frac{y_{\text{A,org}}[\text{A}]_{\text{aq}}}{y_{\text{A,aq}}[\text{A}]_{\text{aq}}} = \frac{y_{\text{A,org}}}{y_{\text{A,aq}}} K_{D,A} \]  

where \( y \)’s are activity coefficients [see Eq. (2.25)]. For aqueous electrolytes, the activity factors vary with the ionic strength of the solution (see sections 2.5, and 3.1.3, and Chapter 6). This has led to the use of the constant ionic medium method (see Chapter 3); i.e., the ionic strength of the aqueous phase is kept constant during an experiment by use of a more or less inert “bulk” medium.
like NaClO₄. Under such conditions the activity factor ratio of Eq. (4.2) is assumed to be constant, and $K_D$ is used as in Eq. (4.1) as conditions are varied at a constant ionic strength value. In the following derivations, we assume that the activity factors for the solute in the aqueous and organic solvents are constant. Effects due to variations of activity factors in the aqueous phase are treated in Chapter 6, but no such simple treatment is available for species in the organic phase (see Chapter 2).

The assumption that the activity factor ratio is constant has been found to be valid over large solute concentration ranges for some solutes even at high total ionic strengths. For example, the distribution of radioactively labeled GaCl₃ between diethyl ether and 6M HCl was found to be constant ($K_{D,Ga} = 18$) at all Ga concentrations between $10^{-3}$ and $10^{-12}$ M [1].

In the following relations, tables, and figures, the temperature of the systems is always assumed to be 25°C, if not specified (temperature effects are discussed in Chapters 3 and 6, and section 4.13.6). We use org to define species in the organic phase, and no symbol for species in the aqueous phase (see Appendix C).

### 4.1.2 The Distribution Ratio

The IUPAC definition of the distribution ratio, $D$, is given in the introduction to Chapter 1 and in Appendix C. For a metal species M it can be written

$$D_M = \frac{\text{Concentration of all species containing } M \text{ in organic phase}}{\text{Concentration of all species containing } M \text{ in aqueous phase}} = \frac{[M]_{org}}{[M]_{aq}}$$

When M is present in various differently complexed forms in the aqueous phase and in the organic phase, $[M]$ refers to the sum of the concentrations of all M species in a given phase (the subscript t indicates total M). It is important to distinguish between the distribution constant, $K_D$, which is valid only for a single specified species (e.g., $MA_2$), and the distribution ratio, $D_M$, which may involve sums of species of the kind indicated by the index, and thus is not constant.

### 4.1.3 Extraction Diagrams

Solvent extraction results are presented typically in the form of diagrams. This is schematically illustrated in Fig. 4.1a for three hypothetical substances, A, B, and C. The distribution ratio is investigated as a function of the concentration of some reactant Z, which may be pH, concentration of extractant in the organic phase (e.g., an organic acid $HA$, $[HA]_{org}$), the extractant anion concentration in the aqueous phase (e.g., $[Cl^-]$), salt concentration in the aqueous phase, etc. The
Fig. 4.1  Liquid-liquid distribution plots. (a) The distribution ratios $D$ for three different substances A, B, and C, plotted against the variable $Z$ of the aqueous phase. $Z$ may represent pH, concentration of extractant in organic phase ([HA]$_{org}$), free ligand ion concentration in the aqueous phase ([A$^-$]), aqueous salt concentration, etc. (b) Same systems showing percentage extraction $\%E$ as a function of $Z$. $D$ and $Z$ are usually plotted on logarithmic scale.

range of $D$ is best measured from about 0.1–10, though ranges from about $10^{-3}$–$10^4$ can be measured with special techniques (see section 4.15).

In many practical situations, a plot like Fig. 4.1a is less informative than one of percentage extraction, $\%E$, where:

$$\%E = 100D/(1 + D)$$  \hspace{1cm} (4.4)

Such a plot is shown in Fig. 4.1b for the same system as in Fig. 4.1a. Percentage extraction curves are particularly useful for designing separation schemes. A series of such curves has already been presented in Fig. 1.3.

A convenient way to characterize the S-shaped curves in Figs. 1.3 or 4.1b, where the extraction depends on the variable $Z$, is to use the log $Z$ value of 50% extraction, e.g., log[Cl$^-$]$_{50}$. The pH$_{50}$-value indicates $-\log[H^+]$ for 50% extraction. This is shown in Fig. 4.1 for distribuends A and B.
Very efficient separations are often needed in industry, and a single extraction stage may be insufficient. The desired purity, yield, etc. can be achieved by multiple extractions, as discussed in Chapter 7 (see also section 1.2). In the design of separation processes using multistage extractions, other extraction diagrams are preferred. Only single stage extraction is discussed in this chapter, while multistage extraction is discussed in the second part (Chapters 7–14) of this book.

4.2 THERMODYNAMICS OF EXTRACTION SYSTEMS

Extraction from aqueous solutions into organic solvents can be achieved through different chemical reactions. Some may seem very complicated, but usually occur through a number of rather simple steps; we assume this in making a model of the system. The subdivision of an extraction reaction into its simpler steps is useful for understanding how the distribution ratio varies as a function of the type and concentration of the reagents. Often these models allow equilibrium constants to be measured.

As solute, we consider both nonelectrolytes (abbreviated as A or B, organic or inorganic), and electrolytes (e.g., as metal-organic complexes, metal ions rendered soluble in organic solvents through reactions with organic anions A$^-$ and with adduct formers B). The system of equations shown later is only valid as long as no species are formed other than those given by the equations, all concentrations refer to the free concentrations (i.e., uncomplexed), and activity factors and temperatures are constant. Further, we assume that equilibrium has been established. It may be noted that the use of equilibrium reactions mean that the reactions take place in the aqueous phase, the organic phase or at the interface, as is illustrated in the next examples, but do not show any intermediates formed; this information can be obtained by kinetic studies, as described in Chapter 5, or by “fingerprinting” techniques such as molecular spectroscopy.

Before a detailed analysis of the chemical reactions that govern the distribution of different solutes in solvent extraction systems, some representative practical examples are presented to illustrate important subprocesses assumed to be essential steps in the overall extraction processes.

4.2.1 Case I: Extraction of Uranyl Nitrate by Adduct Formation

This is a purification process used in the production of uranium. The overall reaction is given by

$$\text{UO}_2^{2+} + 2 \text{HNO}_3 + 2 \text{TBP(org)} \rightarrow \text{UO}_2(\text{NO}_3)_2(\text{TBP})_2(\text{org})$$

(4.5)

where TBP stands for tributylphosphate. The organic solvent is commonly kerosene. In Table 4.1 this extraction process is described in four steps. In Table
Table 4.1 Schematic Representation of the Hypothetical Steps in U(VI) Extraction
by TBP and Their Associate \( \Delta G^i \) of Reaction

<table>
<thead>
<tr>
<th>First step</th>
<th>Second step</th>
<th>Third step</th>
<th>Fourth step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic phase (TBP + diluent)</td>
<td>TBP</td>
<td>UO(_2)(TBP(_2))(NO(_3)_2)</td>
<td></td>
</tr>
<tr>
<td>Aqueous solution (HNO(_3) + UO(_2)(^{2+}) + H(_2)O)</td>
<td>( 2 \text{ HNO}_3 + \text{UO}_2^{2+} \rightarrow \downarrow )</td>
<td>( \text{UO}_2(\text{NO}_3)_2 \downarrow + 2\text{TBP} \uparrow )</td>
<td>( \text{UO}_2(\text{TBP})_2(\text{NO}_3)_2 )</td>
</tr>
</tbody>
</table>

\[ \Delta G_1^i > 0 \quad \Delta G_2^i > 0 \quad \Delta G_3^i \neq 0 \quad \Delta G_4^i \ll 0 \]

4.1, the sign of the free energy change, \( \Delta G^i \), in each step is given by qualitatively known chemical affinities (see Chapter 2). The reaction path is chosen beginning with the complexation of U(VI) by NO\(_3^-\) in the aqueous phase to form the uncharged UO\(_2(\text{NO}_3)_2\) complex (Step 1). Although it is known that the free uranyl ion is surrounded by water of hydration, forming UO\(_2\)(H\(_2\)O\(_6\))\(^{2+}\), and the nitrate complex formed has the stoichiometry UO\(_2\)(H\(_2\)O\(_6\))(NO\(_3\)_2), water of hydration is not listed in Eq. (4.5) or Table 4.1, which is common practice, in order to simplify formula writing. However, in aqueous reactions, water of hydration can play a significant role. As the reactive oxygen (bold) of tributylphosphate, OP(OC\(_4\)H\(_9\))\(_3\), is more basic than the reactive oxygen of water, TBP, which slightly dissolves in water (Step 2), replaces water in the UO\(_2\)(H\(_2\)O\(_6\))(NO\(_3\)_2) complex to form the adduct complex UO\(_2\)(TBP\(_2\))(NO\(_3\)_2). This reaction is assumed to take place in the aqueous phase (Step 3). Adduct formation is one of the most commonly used reactions in solvent extraction of inorganic as well as organic compounds. (Note: the term adduct is often used both for the donor molecule and for its product with the solute.) The next process is the extraction of the complex (Step 4). Even if the solubility of the adduct former TBP in the aqueous phase is quite small (i.e., \( D_{\text{TBP}} \) very large), it is common to assume that the replacement of hydrate water by the adduct former takes place in the aqueous phase, as shown in the third step of Table 4.1; further, the solubility of the adduct UO\(_2\)(TBP\(_2\))(NO\(_3\)_2) must be much larger in the organic than in the aqueous phase (i.e., \( D_{\text{UO}_2(\text{TBP})_2(\text{NO}_3)_2} \gg 1 \)), to make the process useful. Other intermediate reaction paths may be contemplated, but this is of little significance as \( \Delta G_{\text{ex}}^i \) depends only on the starting and final states of the system. The use of such a thermodynamic representation depends on the knowledge of the \( \Delta G^i \) values as they are necessary for valid calculations of the process.

The relation between \( \Delta G_{\text{ex}}^\circ \) and \( K_{\text{ex}} \) is given by

\[
\Delta G_{\text{ex}}^\circ = \sum \Delta G^i = -RT \ln K_{\text{ex}}
\]  

(4.6)
Omitting water of hydration, the equilibrium constant for the net extraction process in Eq. (4.5) is $K_{ex}$, where

$$K_{ex} = \frac{[\text{UO}_2\text{(NO}_3\text{)}_2\text{(TBP)}_2]_{\text{org}}}{[\text{UO}_2^{2+}]\text{[HNO}_3\text{]}\text{[TBP]}^2_{\text{org}}}$$

(4.7)

The extraction constant, $K_{ex}$, can be expressed as the product of several equilibrium constants for other assumed equilibria in the net reaction:

$$K_{ex} = \prod K_i = \beta_{2,\text{NO}_3}^2 K_{\text{DR}} \beta_{2,\text{TBP}} K_{\text{DC}}$$

(4.8)

where $\beta_{2,\text{NO}_3}$ is the complex formation constant of $\text{UO}_2\text{(NO}_3\text{)}_2$, and $\beta_{2,\text{TBP}}$ the formation constant of the extractable $\text{UO}_2\text{(NO}_3\text{)}_2\text{(TBP)}_2$ complex from from $\text{UO}_2\text{(NO}_3\text{)}_2$ and TBP. $K_{\text{DR}}$ and $K_{\text{DC}}$ are the distribution constants of the uncharged species, the reagent and the extractable complex, respectively.

$K_{ex}$ determines the efficiency of an extraction process. It depends on the “internal chemical parameters” of the system, i.e., the chemical reactions and the concentration of reactants of both phases. The latter determine the numerical value of the distribution factor for the solute, which for our example is

$$D_U = \frac{[\text{U}]_{\text{tot,org}}}{[\text{U}]_{\text{tot,aq}}} = \frac{\left[\text{UO}_2\text{(NO}_3\text{)}_2\text{(TBP)}_2\right]_{\text{org}}}{\left[\text{UO}_2^{2+}\right] + \left[\text{UO}_2\text{(NO}_3\text{)}_2\right]^{2-n}}$$

(4.9a)

In the aqueous phase we have included the $\text{UO}_2\text{(NO}_3\text{)}_2^{2-n}$ complexes but excluded the $\text{UO}_2\text{(NO}_3\text{)}_2\text{(TBP)}_2$ complex, because the concentration of the last complex in the aqueous phase is negligible compared to the other two. In dilute solutions, the nitrate complex can be neglected compared to the free $\text{UO}_2^{2+}$ concentration. In the latter case the U distribution equals

$$D_U = K_{ex}\frac{[\text{HNO}_3]}{[\text{TBP}]}$$

(4.9b)

Of the reaction steps, only the first three have values of $\Delta G^0 > 0$; however, the large negative value of the fourth step makes the overall reaction $\Delta G^0$ negative, thus favoring the extraction of the complex. The first step can be measured by the determination of the dinitrato complex in the aqueous phase. The second is related to the distribution constant $K_{\text{D,TBP}}$ in the solvent system. Also, the formation constant of the aqueous $\text{UO}_2\text{(NO}_3\text{)}_2\text{(TBP)}_2$ can be measured (for example by NMR on $^{31}\text{P}$ of TBP in the aqueous phase). Thus, $\Delta G^0$ can be derived.

### 4.2.2 Case II: Synergistic Extraction of Uranyl Ions by Chelation and Adduct Formation

Solvent extraction is a powerful technique in research on metal complexes. Consider a metal complexed by a chelate compound (see Chapter 3), where the chelate is a weak organic acid. For example, the uranyl ion can be neutralized...
by two TTA\(^-\) (Appendix D:5e) anions to form the neutral \(\text{UO}_2(\text{TTA})_2(\text{H}_2\text{O})_2\) complex. This complex is extractable into organic solvents, but only at high concentrations of the TTA anion.

A large adduct formation constant increases the hydrophobicity of the metal complex and thus the distribution ratio of the metal. This is commonly referred to as a *synergistic effect*. Figure 4.2 illustrates the extraction of the \(\text{UO}_2(\text{TTA})_2\) complex from 0.01 M HNO\(_3\) into cyclohexane. Because the linear \(\text{O}--\text{U}--\text{O}\) group is believed to have five to seven coordination sites, where only

![Graph](image_url)

**Fig. 4.2**  Synergistic extraction: Distribution of U(VI) between 0.01 M HNO\(_3\) and mixtures of thenoyltrifluoroacetone (TTA) and tributylphosphosphate (TBP), or tributylphosphineoxide (TBPO), at constant total molarity ([TTA]\(_{org}\) plus [TBP]\(_{org}\) or [TBPO]\(_{org}\) = 0.02 M) in cyclohexane. (From Ref. 2.)
four are occupied in this complex, the uranyl group is coordinatively unsaturated. At the left vertical axes of Fig. 4.2, the free coordination sites are occupied by water and/or NO$_3^-$ only; and the U(VI) complex is poorly extracted, log $D_U$ about $-1$. When TBP or TBPO (tributylphosphine oxide*) [both indicated by B] are added while [HTTA] + [B] is kept constant, the $D_U$ value increases to about 60 for TBP and to about 1000 for TBPO. At the peak value, the complex is assumed to be UO$_2$(TTA)$_2$B$_{1-2}$. The decrease of $D_U$ at even higher [B] is due to the corresponding decrease in [TTA$^-$], so that at the right vertical axes of Fig. 4.2 no U(VI)—TTA complex is formed. For this particular case, at much higher nitrate concentrations, the U(VI) is complexed by NO$_3^-$ and is extracted as an adduct complex of the composition UO$_2$(NO$_3$)$_2$B$_{1-2}$, as discussed earlier for Case I.

The primary cause for synergism in solvent extraction is an increase in hydrophobic character of the extracted metal complex upon addition of the adduct former. Three mechanisms have been proposed to explain the synergism for metal + chelant† + adduct former. In the first suggested mechanism, the chelate rings do not coordinately saturate the metal ion, which retains residual waters in the remaining coordination sites and these waters are replaced by other adduct-forming molecules. The second involves an opening of one or more of the chelate rings and occupation by the adduct formers of the vacated metal coordination sites. The third mechanism involves an expansion of the coordination sphere of the metal ion upon addition of adduct formers so no replacement of waters is necessary to accommodate the adduct former. As pointed out before, it is not possible from the extraction constants to choose between these alternative mechanisms, but enthalpy and entropy data of the reactions can be used to provide more definitive arguments.

The HTTA + TBP system can serve to illustrate the main points of thermodynamics of synergism. The overall extraction reaction is written as:

$$M^{n+} + n \text{HTTA(org)} + p \text{TBP(org)} \rightleftharpoons M(\text{TTA})_n(\text{TBP})_p(\text{org}) + p \text{H}^+ \quad (4.10a)$$

We assume that the first step in the extraction equation is complexation in the aqueous phase

$$M^{n+} + n \text{TTA}^- \rightleftharpoons M(\text{TTA})_{n-a}^a(\text{aq}) + n \text{H}^+ \quad (4.10b)$$

leading to the formation of the uncharged complex $M(\text{TTA})_n$, which immediately dissolves in the organic phase due to its high hydrophobicity/lipophilicity

$$M(\text{TTA})_n(\text{aq}) \rightarrow M(\text{TTA})_n(\text{org}) \quad (4.10c)$$

---

*TBPO = (C$_4$H$_9$)$_3$PO, see Appendix D, example 16, at the end of this book.
†Chelant or chelator is the chelating ligand.
The adduct formation reaction in the organic phase (the “synergistic reaction”) is obtained by subtracting Eqs. (4.10b) and (4.10c) from Eq. (4.10a):

\[
\text{M(TTA)}_{\text{org}} + p\text{TBP(org)} \rightleftharpoons \text{M(TTA)}_n(\text{TBP})_p(\text{org}) \quad (4.10d)
\]
Thermodynamic data for the extraction reactions of Eqs. (4.10a) and (4.10c) allow calculation of the corresponding values for the synergistic reaction of Eq. (4.10d). Measurements of the reaction

\[
\text{UO}_2(\text{TTA})_{2\text{org}} + \text{TBP(org)} \rightleftharpoons \text{UO}_2(\text{TTA})_{2\cdot\text{TBP}}(\text{org}) \quad (4.11)
\]

at different temperatures gives \( \log K = 5.10, \Delta H^0 = -9.3 \text{ kJ} \cdot \text{mol}^{-1}, \Delta S^0 = 20.0 \text{ kJ} \cdot \text{mol}^{-1} \).

In another experiment, it was found for \( \text{Th(TTA)}_4 \)

\[
\text{Th(TTA)}_{4\text{org}} + \text{TBP(org)} \rightleftharpoons \text{Th(TTA)}_{4\cdot\text{TBP}}(\text{org}) \quad (4.12)
\]
the corresponding values: \( \log K = 4.94, \Delta H^0 = -14.4 \text{ kJ} \cdot \text{mol}^{-1}, \Delta S^0 = 13.7 \text{ kJ} \cdot \text{mol}^{-1} \).

Both \( \text{UO}_2(\text{TTA})_{2\text{org}} \) and \( \text{Th(TTA)}_4 \) have two molecules of hydrate water when extracted in benzene, and these are released when TBP is added in reactions Eqs. (4.11) and (4.12). The release of water means that two reactant molecules (e.g., \( \text{UO}_2(\text{TTA})_{2\cdot2\text{H}_2\text{O}} \text{ and TBP} \) formed three product molecules (e.g., \( \text{UO}_2(\text{TTA})_{2\cdot\text{TBP}} \text{ and } 2\text{H}_2\text{O} \)). Therefore, \( \Delta S \) is positive. Since TBP is more basic than \( \text{H}_2\text{O} \), it forms stronger adduct bonds, and, as a consequence, the enthalpy is exothermic. Hence, both the enthalpy and entropy changes favor the reaction, resulting in large values of \( \log K \).

### 4.2.3 Case III: Maintaining Metal Coordination Number

A guiding principle for the solvent extraction chemist is to produce an uncharged species that has its maximum coordination number satisfied by lipophilic substances (reactants). For trivalent lanthanides and actinides (Ln and An, respectively), the thermodynamic data suggest a model in which addition of one molecule of TBP displaces more than one hydrate molecule:

\[
\text{An(TTA)}_3(\text{H}_2\text{O})_n \xrightarrow{\text{TBP}} \text{An(TTA)}_3(\text{TBP})(\text{H}_2\text{O})_{n-2}
\]

\[
\xrightarrow{\text{TBP}} \text{An(TTA)}_3(\text{TBP})_{n-3} \quad (4.13)
\]
This scheme of steps reflects the ability of some metals, like the trivalent actinides and lanthanides, to vary their coordination number; since the trivalent Ln and An may go from 9 to 8 and, finally, back to 9. The last step reflects the operation of the third mechanism proposed for synergism.

\( \text{Th(TTA)}_4 \) can be dissolved in dry benzene without hydrate water. The values of the reaction of Eq. (4.12) in the system are: \( \log K = 5.46, \Delta H^0 = -39.2 \).
The negative entropy is understandable as the net degrees of freedom are decreased (two reactant molecules combine to form one product molecule). However, the $\Delta H^\circ$ value is much more negative.

These equations do not provide complete definition of the reactions that may be of significance in particular solvent extraction systems. For example, HTTA can exist as a keto, an enol, and a keto-hydrate species. The metal combines with the enol form, which usually is the dominant one in organic solvents (e.g., $K = [\text{HTTA}]_{\text{enol}}/[\text{HTTA}]_{\text{keto}} = \sim 6$ in wet benzene). The kinetics of the keto $\rightarrow$ enol reaction are not fast although it seems to be catalyzed by the presence of a reagent such as TBP or TOPO. Such reagents react with the enol form in drier solvents but cannot compete with water in wetter ones. HTTA $\cdot$ TBP and TBP $\cdot$ H$_2$O species also are present in these synergistic systems. However, if extraction into only one solvent (e.g., benzene) is considered, these effects are constant and need not be considered in a simple analysis.

In section 4.13.3 we return briefly to the thermodynamics of solvent extraction.

### 4.3 OVERVIEW OF EXTRACTION PROCESSES

Many organic substances as well as metal complexes are less extracted from aqueous solutions into organic solvents than expected from simple considerations such as the amount of organic matter in the solute or their solubility in organic solvents. Such substances are hydrated (see Chapter 3). More basic donor molecules can replace such water, forming adducts. For the most common oxygen-containing adduct molecules, the efficiency of the replacement depends on the charge density, also referred to as basicity, of the oxygen atoms. The sequence in which these donor groups are able to replace each other is

$$RCHO < R_2CO < R_2O < ROH < H_2O = (RO)PO$$
$$< R^RNCOR = (RO)RPPO < R,PO$$

where $R$ stands for organic substituent. In Chapter 3 the basicity was presented in form of donor number. The larger the difference between the donor number of water and the adduct former, the larger the adduct formation constant. Often the donor property has to be rather strong, which is the case for many phosphoryl compounds (like TBP, TBPO, TOPO, etc.), because the concentration of H$_2$O in the aqueous phase is very large (often $>50$ M), even though H$_2$O is only a moderately strong donor.

Table 4.2 gives a survey of the most common extraction processes. In general, Type I extraction refers to the distribution of nonelectrolytes, without (A) or with adduct former (B). Type II refers to extraction of (mainly organic) acids, Type III to the extraction of metal complexes, and Type IV to the special (but common) use of solvent extraction for evaluation of formation constants.
<table>
<thead>
<tr>
<th>Type</th>
<th>Process Description</th>
<th>Equilibrium Reaction</th>
</tr>
</thead>
</table>
| Type I-A     | Nonelectrolyte extraction\(^b\)  
Solute A extracted into organic phase (solvent)  
(Equilibrium governed by the Nernst distribution law)  
Solute is the nonelectrolyte A in water | $A \downarrow \uparrow A$ |
| Type I-B     | Nonelectrolyte adduct formation and extraction\(^c\)  
Adduct AB in organic phase (plus eventually B)  
Solute A and adduct former (or extractant) B | $B \downarrow \uparrow AB$ $A + B \Leftrightarrow AB$ |
| Type II-A    | Extraction of nonadduct organic acids  
Acid and dimer (and possible polymers) in organic phase  
Acid dissociation in aqueous phase | $HA \Leftrightarrow H^{1/2}H_{A2} + \ldots$ $\downarrow \uparrow HA \Leftrightarrow H^+ + A^-$ |
| Type II-B    | Extraction of acid as adduct  
Acid adduct (and acid and adduct former) in organic phase  
Acid dissociation in aqueous phase | $HAB \Leftrightarrow B (+) HA$ $\downarrow \uparrow (\downarrow \uparrow)$ $HAB \Leftrightarrow B + HA \Leftrightarrow H^+ + A^-$ |
| Type III-B\(^d\) | Extraction of saturated metal complex  
Neutral, coordinatively saturated metal complex in organic phase  
Metal ion $M^{z+}$ is complexed by $z A^-$ ligands | $MA_z \downarrow \uparrow$ $M^{z+} + zA^- \Leftrightarrow MA_z$ |
Type III-C  Adduct extraction of unsaturated metal complex
Coordinatively saturated metal complex in organic phase (and B)
Formation of saturated metal complex through adduct former B

\[
\begin{align*}
M^{z+} + zA^- + bB & \rightleftharpoons MA_bB^n \\
\end{align*}
\]

Type III-D  Liquid anion exchange extractions
Organic phase with anion exchanger and metal complex
Metal with complexing anions L\(^-\) and organic amine

\[
\begin{align*}
M^{z+} + nL^- + pRNH^+L^- & \rightleftharpoons (RNH^+)^nML_p^n \\
\end{align*}
\]

Type III-E  Extraction of ion pairs, and other unusual complexes
Ion pair C\(_1\)A\(_2\) (and counter species) in organic phase
Aqueous cation C\(_1\) and anion A\(_2\) associated into ion pair C\(_1\)A\(_2\)

\[
\begin{align*}
C_1A_2^- & \rightleftharpoons C_1A_1^- + C_2A_1^- \\
\end{align*}
\]

Type IV  Hydrophilic complex formation and solvent extraction
Coordinatively saturated metal complex in organic phase
Formation of extractable and nonextractable complexes

\[
\begin{align*}
M^{z+} + zA^- + nX^- & \rightleftharpoons MA_z + MX_{z+n} \\
\end{align*}
\]

The organic phase (solvent, diluent) is assumed to be “inert” (shaded area). The aqueous phase (nonshaded area) is unspecified, but may contain various salting agents, not considered here.

A nonelectrolyte solute is denoted A, an electrolyte solute is assumed to be the cation M\(^+\) and anion A\(^-\), L\(^-\), or X\(^-\).

The extractant (or reactant) is denoted A\(^-\) (from acid HA), or ligand L\(^-\), and by B (for adduct).

Type III-A (denoted Class A in first edition of this book) is closely related to and covered by Type I-A.

If B is undissociated HA, the self-adduct MA\(_z\)(HA) may be formed.
for hydrophilic complexes. An arrow within parentheses suggests a reaction of secondary importance. Our three examples are all of Type III-C, but contain also elements of Type I-A (the distribution of TBP) and II-A (the distribution of the weak acid HTTA), though the presence of undissociated acid (HTTA) or the acid adduct (TBP-HTTA) is not discussed. In evaluations of experiments, all molecular species present and all equilibria must be taken into account, as demonstrated subsequently for a number of cases.

Solutes containing metals can further be classified according to the type of ligand; \( N \) refers to the maximum coordination number of the metal relative to the ligand:

**Class A:** Type \( MX_n \). (Note: We generally assume that the ligand is monovalent.) A small number of almost purely covalent inorganic compounds that are extracted by nonsolvating organic solvents. As these complexes are nonelectrolytes and almost as inert as the solutes of Type I-A, they are treated jointly in section 4.4.

**Class B:** Type \( MA_z \). Neutral coordinatively saturated complexes formed between the metal ion and a lipophilic organic acid. This class contains the large group of metal-organic chelate compounds. For monobasic acids forming bifunctional chelates, \( z = N/2 \). They belong to the extraction Type III-B, treated in section 4.8.

**Class C:** Type \( MA_z B_b \) or \( ML_z B_b \). These Type III-C complexes are discussed in section 4.2. They are neutral complexes formed between the metal ion and ligands \( A^- \) or \( L^- \), where the neutral complex \( MA_z \) or \( ML_z \) is coordinatively unsaturated \( (N > z \) or \( 2z) \) and acts as an acceptor for uncharged organic compounds (adducts \( B \)) containing lipophilic donor groups. If the system does not contain any donor molecules \( B \), the water of hydration may be replaced by undissociated HA (assuming the ligand \( A^- \) to be a dissociation product of HA), at least at high HA concentrations; the \( MA_z (HA)_b \) complexes are referred to as self-adducts. Both types of complexes are discussed in section 4.9.

**Class D:** Ion pairs, consisting of the metal bound in an anionic complex (e.g., \( ML_{z-n} \), where \( n > z \)) and one or more large organic (usually monovalent) cations (symbolized by RNH\(^+\)); the extracted complex is written \( (RNH)_{n-c} ML_{z-n} \). These complexes are treated in section 4.10.

**Class E:** Metal complexes that do not fit into these categories; e.g., other types of ion pairs and chlatrate compounds (see section 4.11).

All metal ions in water are hydrated, and at higher pH most of them also hydrolyze. It can be difficult to distinguish between the hydrolyzed and the complexed species, as well as their self-adducts. For such systems, plots of \( D_M \) against \( [A^-] \) at various pH and total concentrations of [HA] show three types of curves: (a) for the simple chelate \( MA_n \), (b) for the self-adduct \( MA_a(HA)_b \), and
(c) for the (mixed) hydroxide MAₙ(OH)ₚ, see Fig. 4.3. It should be noted that the mixed MAₙ(OH)ₚ complexes include the MAₙ + M(OH) complexes. As mixed complexes are more difficult to determine, they are less often described. However, it is important to realize that if metal hydroxy complexes are formed and not corrected for, the result of the investigation can be misleading. A test of the system according to Fig. 4.3 rapidly establishes the type of metal complexation.

Because metals differ in size, charge, and electronic structure, no two metals behave exactly the same in the same solvent extraction system, not even for the same class of solutes. Nevertheless, there are systematic trends in the formation and extraction of these complexes, as described in Chapter 3. Here, the emphasis is on models that give a quantitative description of the extraction within each type or class.

In the subsequent discussion, the following simplifications are made:

1. The systems behave “ideally,” i.e., the activity factors are assumed to be unity, unless specifically discussed;
2. The metal extracted is in trace concentration: [M]ᵣ ≪ [Extractant]ᵣ, as this simplifies the equations;
3. The reactants are at very low concentrations in both phases.

These are great simplifications in comparison with the industrial solvent extraction systems described in later chapters. Nevertheless, the same basic reactions occur also in the industrial systems, although activity factors must be introduced or other adjustments made to fit the data, and the calculation of free

![Diagram](Fig. 4.3)

**Fig. 4.3** Extraction curves for various types of metal chelate complexes, when log Dₘᵣ is plotted against free ligand ion concentration, pA = −log[A⁻], or against [HA][H⁺]⁻. From such plots, the general type of metal chelate complex may be identified: (a) type MAₙ, (see also Fig. 4.10); (b) type MAₙ(OH)ᵣ(HA)ᵣ, (see also Figs. 4.14 and 4.30); (c) type MAₙ(OH)ₚ, (see also Fig. 4.19). (From Refs. 3a and 3b.)
ligand concentrations are more complex. Some of these simplifications are not used in later chapters.

4.4 EXTRACTION OF INERT MOLECULES (TYPE I-A)

Here, and in later sections, we begin with same kind of rectangular figure to indicate the type of extraction: to the right we indicate the distribution of the solutes in a two-phase system (the organic phase is shaded); the system is also briefly described by the text to the left, and—of course—in detail in the main text.

| Solute A extracted into organic phase (solvent) | A |
| (Nernst distribution law for regular mixtures and solvents:) | ↓↑ |
| The non-electrolyte solute A in water | A |

If the solute A does not undergo any reaction in the two solvents, except for the solubility caused by the “solvation” due to the nonspecific cohesive forces in the liquids, the distribution of the solute follows the Nernst distribution law, and the equilibrium reaction can be described either by a distribution constant $K_{D, A}$, or an (equilibrium) extraction constant $K_{ex}$:

$$\text{A}^{\text{aq}} \Leftrightarrow \text{A}^{\text{org}}; \quad K_{D, A} = K_{ex} = \frac{[A]_{\text{org}}}{[A]_{\text{aq}}}$$

(4.14)

$k_{ex}$ always refers to a two-phase system. The measured distribution ratio for the solute A, $D_A$, equals $K_{D, A}$, and is a constant independent of the concentration of A in the system. Only “external” conditions influence the $K_{D, A}$ value. In “external” conditions we include the organic solvent, in addition to physical conditions like temperature and pressure.

The noble gases and the halogens belong to the same type of stable molecular compounds: RuO$_4$, OsO$_4$, GeCl$_4$, AsCl$_3$, SbCl$_3$, and HgCl$_2$. The simplest example is the distribution of the inert gases, as given in Table 4.3. The larger

<table>
<thead>
<tr>
<th>Solute</th>
<th>Permittivity $\epsilon$</th>
<th>Xenon</th>
<th>Radon</th>
<th>Bromine</th>
<th>Iodine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>1.91</td>
<td>41</td>
<td>80</td>
<td>14.5</td>
<td>36</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.24</td>
<td>35</td>
<td>59</td>
<td>28</td>
<td>86</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.90</td>
<td>35</td>
<td>56</td>
<td>37</td>
<td>122</td>
</tr>
<tr>
<td>Benzene ($\pi$-bonds)</td>
<td>2.57</td>
<td>27</td>
<td>55</td>
<td>87</td>
<td>350</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>34.8</td>
<td>14</td>
<td>21</td>
<td>41</td>
<td>178</td>
</tr>
</tbody>
</table>

*Source:* Ref. 4.
Rn is extracted more easily than the smaller Xe, because the work to produce a cavity in the water structure is larger for the larger molecule. The energy to produce a cavity in nonpolar solvents is much less, because of the weaker interactions between neighboring solvent molecules. Energy is released when the solute leaves the aqueous phase, allowing the cavity to be filled by the hydrogen-bonded water structure. Thus the distribution constant increases with increasing inertness of the solvent, which is measured by the dielectric constant (or relative permittivity). The halogens Br₂ and I₂ show an opposite order due to some low reactivity of halogens with organic solvents. Very inert solvents with low permittivity, such as the pure hydrocarbons, extract inert compounds better than solvents of higher permittivity; conversely, liquids of higher permittivity are better solvents for less inert compounds. Molar volumes should be used for accurate comparisons; such data are found in Table 2.1 and in Ref. [6].

In benzene, the distribution constant depends on specific interactions between the solute and the benzene pi-electrons. Table 4.4 shows the importance of the volume effect for the mercury halide benzene system (Cl<Br<I).

Undissociated fatty acids (HA) behave like inert molecules. Figure 4.4 shows the distribution \( D_{HA} = K_{D,HA} \) between benzene and 0.1 M NaClO₄ of fatty acids of different alkyl chain lengths (Cₙ, \( n = 1 \) to 5); the distribution constant for an acid with chain length \( n \) is given by the expression \( \log K_{D,HA} = -2.6 + 0.6n \). Similar correlations between \( K_{D,HA} \) and molecular size or chain length are observed also for other reagents (e.g., normal alcohols).

For organic solutes, not only the size but also the structure is of importance. Table 4.5 gives distribution constants for substituted oxines. When the substitution increases the size of the molecule, the distribution constant increases. The variations within Table 4.5 and position of the substitution in the oxine molecule reflect structural effects. Table 4.6 shows distribution constants for \( \beta \)-diketones. The increasing \( K_D \) with molecular size for the series acetylacetone, benzoylacetone, and dibenzoylmethane, reflects the decreasing solubility in the water phase, mainly governed by the increased energy necessary to overcome the solute-solvent interactions for the larger extractant molecules in water. Thenoyltrifluoroacetone has a greater hydrophilic character than the other \( \beta \)-diketones due to its O− and F− atoms, which interact with the water molecules,

<table>
<thead>
<tr>
<th>Solute</th>
<th>Log ( K_D )</th>
<th>Solute</th>
<th>Log ( K_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgCl₂</td>
<td>-0.96</td>
<td>HgClBr</td>
<td>-0.42</td>
</tr>
<tr>
<td>HgBr₂</td>
<td>0.15</td>
<td>HgICl</td>
<td>0.28</td>
</tr>
<tr>
<td>HgI₂</td>
<td>1.79</td>
<td>HgIBr</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Source: Ref. 5.
Fig. 4.4 Distribution constants $K_{D,HA}$ of fatty acids as a function of the number $n$ of carbon atoms in the alkyl chain ($C_1$ is acetic acid) in the system 0.1 M NaClO$_4$/benzene. (From Ref. 7.)

Table 4.5 Dissociation, $K_a$, and Distribution, $K_{D,HA}$, Constants for Substituted Oxines$^a$

<table>
<thead>
<tr>
<th>Reagent</th>
<th>$pK_a$</th>
<th>log $K_{D,HA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxine</td>
<td>9.7</td>
<td>2.7</td>
</tr>
<tr>
<td>2-Methyloxine</td>
<td>10.0</td>
<td>3.4</td>
</tr>
<tr>
<td>5-Methyloxine</td>
<td>9.9</td>
<td>3.3</td>
</tr>
<tr>
<td>5-Acetyloxine</td>
<td>7.8</td>
<td>2.8</td>
</tr>
<tr>
<td>4,7-Dichloroxine</td>
<td>7.4</td>
<td>3.9</td>
</tr>
<tr>
<td>7,7-Diiodooxine</td>
<td>8.0</td>
<td>4.2</td>
</tr>
<tr>
<td>5-Chloro-7-iodooxine</td>
<td>7.9</td>
<td>3.9</td>
</tr>
</tbody>
</table>

$^a$Aqueous phase 0.1 M NaClO$_4$, organic phase chloroform at 25°C.
Source: Refs. 8a, b.
Table 4.6  Dissociation $K_a$ and Distribution Constants $K_{D,HA}$ for $\beta$-Diketones; Aqueous Phase 0.1 M NaClO$_4$*  

<table>
<thead>
<tr>
<th>Reagent (solute)</th>
<th>$pK_a$</th>
<th>$K_{D,H}$</th>
<th>CHCl$_3$</th>
<th>CCl$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylacetone, AA; CH$_3$ R CH$_3$</td>
<td>8.76</td>
<td>0.76</td>
<td>1.36</td>
<td>0.51</td>
</tr>
<tr>
<td>Benzoilacetone, BZA; CH$_3$ R C$_6$H$_5$</td>
<td>8.74</td>
<td>3.15</td>
<td>3.60</td>
<td>2.81</td>
</tr>
<tr>
<td>Dibenzoilmethane, DBM; C$_6$H$_5$ R C$_6$H$_5$</td>
<td>9.35</td>
<td>5.34</td>
<td>5.40</td>
<td>4.51</td>
</tr>
<tr>
<td>Thenoyltrifluoroacetone, TTA; R'R CF$_3$</td>
<td>6.3</td>
<td>1.61</td>
<td>1.84</td>
<td>1.54</td>
</tr>
</tbody>
</table>

$R$ is $-C\text{CH}_2\text{C}--$  
$R'$ is thenoyl, H$_3$C$\text{SC}$--

*Organic phases 0.1 M in solute; 25°C.  
Source: Ref. 4.

leading to a reduction in the distribution constant. Thus, either the size effect related to the water structure or the presence of hydrophilic groups in the solute determines the general level of its distribution constant.

4.5 EXTRACTION OF ADDUCT-FORMING NONELECTROLYTES (TYPE I-B)

The extraction of a solute A may be improved by its reaction with another solute ("extraction reagent", or extractant), B, forming an adduct compound, AB. This occurs through chemical interaction between A and B.

\[
B \rightleftharpoons B\text{(org)} \quad K_{D,B} = [B]_{\text{org}}/[B] \quad (4.15a)
\]

\[
A + B \rightleftharpoons AB \quad K_{d,AB} = [AB]/[A][B] \quad (4.15b)
\]

where $K_{d,AB}$ is the adduct formation constant (in the aqueous phase)

\[
AB \rightleftharpoons AB\text{(org)} \quad K_{D,AB} = [AB]_{\text{org}}/[AB] \quad (4.15c)
\]

and $K_{D,AB}$ the adduct distribution constant. The extraction constant for the overall reaction is
A(aq) + B(org) ⇄ AB(org)  
\[ K_{ex} = \frac{[AB]_{org}}{[A]_{aq}[B]_{org}} = K_{D,AB}K_{ad}K_{D,B} \]  
(4.15d)

and also

\[ D_A = K_{ex} [B]_{org} \]  
(4.15e)

For the extraction reaction it may suffice to write the reaction of Eq. (4.15d), though it consists of a number of more or less hypothetical steps. As mentioned, equilibrium studies of this system cannot define the individual steps, but supplementary studies by other techniques may reveal the valid ones. Equation (4.15) indicates that the reaction takes place at the boundary (interface) between the aqueous and organic phases. However, it is common to assume that a small amount of B dissolves in the aqueous phase, and the reaction takes place in the steps

\[ A(aq) + B(aq) \rightarrow AB(aq) \rightarrow AB(org) \]

These equations allow definition of a distribution constant for the species AB, \( K_{D,AB} \) [see Eq. (4.15c)]. Distribution constants can also be defined for each of the species A, B and AB (\( K_{D,A} \), etc.) but this is of little interest as the concentration of these species is related through \( K_{ex} \). A large \( K_{ex} \) for the system indicates that large distribution ratios \( D_A \) can be obtained in practice. As shown in Eq. (4.15), the concentration of B influences the distribution ratio \( D_A \).

Consider first the extraction of hexafluoroacetylacetone (HFA) by TOPO by Example 1, and, second, the extraction of nitric acid by TBP (Example 7). The principles of volume and water-structure effects, discussed for the solute A in section 4.4, are also important in the distribution of the adducts.

Example 1: Extraction of hexafluoroacetylacetone (HFA) by trioctylphosphine oxide (TOPO).

Abbreviating HFA (comp. structure 5e, Appendix D) by HA, and TOPO by B, we can write the relevant reactions

\[ HA(aq) \leftrightharpoons HA(org) \]

\[ K_a = \frac{[HA]_{org}}{[HA]_{aq}} = D_o \]  
(4.16a)

\[ HA(org) + B(org) \leftrightharpoons HAB(org) \]

\[ K_{ad} = \frac{[HAB]_{org}}{[HA]_{org}[B]_{org}} \]  
(4.16b)

\[ HA(org) + 2B(org) \leftrightharpoons HAB_2(org) \]

\[ K_{ad} = \frac{[HAB_2]_{org}}{[HA]_{org}[B]_{org}^2} \]  
(4.16c)

assuming that 2 adducts are formed, HAB and HAB2, the latter containing 2 TOPO molecules. Equation (4.16a) denotes the distribution of “uncomplexed HA” by \( D_o \). Combining these equations yields

\[ D \cdot D_o^{-1} = 1 + K_{ad}[B] + K_{ad}^2[B]^2 \]  
(4.16d)

Figure 4.5 shows the relative distribution, \( D \cdot D_o^{-1} \), of hexafluoroacetylacetone as a function of the concentration of the adduct former TOPO. HFA
Relative increase, $D/D_o$ in extraction of hexafluoroacetylacetone (HFA) into hexane from 0.1M NaClO$_4$ at pH = 2, at different concentrations of the adduct trioxyl-phosphine oxide (TOPO) in the organic phase. The fitted curve is $D/D_o = 1 + 10^{4.22} [\text{TOPO}]_{\text{org}} + 10^{7.51} [\text{TOPO}]_{\text{org}}^2$. (From Ref. 9.)

is a moderately weak acid, while TOPO associates strongly with hydrogen-bond donors in nonpolar solvents like hexane. The constants were determined to $\log K_{\text{ad1}} = 4.22$ and $\log K_{\text{ad2}} = 7.51$. Thus even at moderately low TOPO concentrations, the “dimer adduct” dominates.

### 4.6 EXTRACTION OF NONADDUCT ORGANIC ACIDS (TYPE II-A)

| Acid and dimer (and possibly polymers) in organic phase | $HA \rightleftharpoons \frac{1}{2} H_2A_2 + \cdots$ |
| Acid dissociation in aqueous phase (and protonation) | $(H^+A) \rightleftharpoons HA \rightleftharpoons H^+ + A^-$ |

Tables 4.5–4.7 and Fig. 4.6 list organic acids commonly used as metal extractants. When the acids are not protonated, dissociated, polymerized, hydrated, nor form adducts, the distribution ratio of the acid HA is constant in a given solvent extraction system:

$$HA(\text{aq}) \rightleftharpoons HA(\text{org}) \quad K_{D,HA} = [HA]_{\text{org}}/[HA] = D_{HA} \quad (4.17)$$

This is shown by the horizontal trends in Fig. 4.6, for which Eq. (4.17) is valid; i.e., the distribution constant $K_{D,HA}$ equals the measured distribution ratio. When
### Table 4.7  Physical Properties of Some Commonly Used Acidic Extractants

<table>
<thead>
<tr>
<th>Acid</th>
<th>Organic diluent</th>
<th>$S_{org}(M)^c$</th>
<th>$-\log K_a$</th>
<th>$\log K_{DR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylic acid</td>
<td>Chloroform</td>
<td>0.17</td>
<td>2.9</td>
<td>0.5</td>
</tr>
<tr>
<td>Cupferron</td>
<td>Chloroform</td>
<td>0.4</td>
<td>4.2</td>
<td>2.3</td>
</tr>
<tr>
<td>8-Hydroxyquinoline (oxine) (OQ)</td>
<td>Chloroform</td>
<td>2.63</td>
<td>9.66</td>
<td>2.66</td>
</tr>
<tr>
<td>D:o</td>
<td>CCl$_4$</td>
<td>—</td>
<td>9.66</td>
<td>2.18</td>
</tr>
<tr>
<td>Acetylacetone (AA)</td>
<td>Benzene</td>
<td>$\infty$</td>
<td>8.85</td>
<td>0.78</td>
</tr>
<tr>
<td>D:o</td>
<td>Chloroform</td>
<td>—</td>
<td>—</td>
<td>1.36</td>
</tr>
<tr>
<td>D:o</td>
<td>CCl$_4$</td>
<td>—</td>
<td>8.67</td>
<td>0.51</td>
</tr>
<tr>
<td>Benzyolacetone (BA)</td>
<td>CCl$_4$</td>
<td>—</td>
<td>8.39</td>
<td>2.81</td>
</tr>
<tr>
<td>Benzoyltrifluoroacetone (BTFA)</td>
<td>CCl$_4$</td>
<td>—</td>
<td>6.03</td>
<td>2.39</td>
</tr>
<tr>
<td>Thenoyltrifluoroacetone (TTA)</td>
<td>Benzene</td>
<td>5.27</td>
<td>6.3</td>
<td>1.6</td>
</tr>
<tr>
<td>D:o</td>
<td>Chloroform</td>
<td>—</td>
<td>—</td>
<td>1.84</td>
</tr>
<tr>
<td>1-Nitroso-2-naphthol</td>
<td>Chloroform</td>
<td>1.35</td>
<td>7.6</td>
<td>2.97</td>
</tr>
<tr>
<td>Di(2-ethylhexyl)phosphoric acid</td>
<td>$n$-Octane</td>
<td>$\infty$</td>
<td>1.4</td>
<td>3.44</td>
</tr>
<tr>
<td>Mono(2-ethylhexyl)phosphoric acid</td>
<td>$n$-Octane</td>
<td>$\infty$</td>
<td>1.3</td>
<td>—</td>
</tr>
<tr>
<td>Dinonylnaphthalene sulfonic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The aqueous phase is mostly 0.1 M NaClO$_4$ at 25°C.*

*The choice of organic diluent only affects the distribution constant, not the acid dissociation constant.*

*S$_{org}$ is solubility in M in organic solvent.

*$K_{a}$ is $\log K_a = 5.00$.

*$K_{int}$.*

*Dimerization constant: $\log K = 4.47$; see also section 4.6.3.

HA is used for the extraction of a metal, $K_{D,HA}$ is abbreviated $K_{DR}$, for the distribution constant (of the unmodified) reagent (or extractant).

Figure 4.7a shows the effect of aqueous salt concentrations on the $D_{HA}$ value of acetylacetone at constant total HA concentration and pH. The salt has two effects: (1) it ties up H$_2$O molecules in the aqueous phase (forming hydrated ions) so that less free water is available for solvation of HA; and (2) it breaks down the hydrogen bond structure of the water, making it easier for HA to dissolve in the aqueous phase. Figure 4.7 shows that the former effect dominates for NH$_4$Cl while for NaClO$_4$ the latter dominates. We describe the increase of the distribution ratio with increasing aqueous salt concentration as a *salting-out* effect, and the reverse as a *salting-in* effect.

Figure 4.7b shows $D_{HA}$ for the extraction of acetylacetone into CHCl$_3$ and C$_6$H$_6$ for two constant aqueous NaClO$_4$ concentrations at pH 3, but with varying concentrations of HA. Acetylacetone is infinitely soluble in both CHCl$_3$ and C$_6$H$_6$; at [HA]$_{org} = 9$ M, about 90% of the organic phase is acetylacetone (M$_w$ 100), so the figure depicts a case for a changing organic phase. Figure 4.7b also
Fig. 4.6  Distribution ratios calculated by Eq. (4.22) for acetylacetone (HAA); benzoylacetone (HBA); bezoyltrifluoroacetone (HBTA); and oxine (8-hydroxyquinoline, HOQ), in the system 0.1 M NaClO₄/CCl₄, using the following constants. (From Refs. 8a, b.)

<table>
<thead>
<tr>
<th></th>
<th>HAA</th>
<th>HBA</th>
<th>HBTFA</th>
<th>HOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>log $K_D$</td>
<td>0.51</td>
<td>2.81</td>
<td>2.39</td>
<td>2.18</td>
</tr>
<tr>
<td>log $K_a$</td>
<td>8.67</td>
<td>8.39</td>
<td>6.03</td>
<td>9.66</td>
</tr>
<tr>
<td>log $K_{si}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>5.00</td>
</tr>
</tbody>
</table>

indicates different interactions between the acetylacetone and the two solvents. It is assumed that the polar CHCl₃ interacts with HA, making it more soluble in the organic phase; it is also understandable why the distribution of HA decreases with decreasing concentration (mole fraction) of CHCl₃. C₆H₆ and aromatic solvents do not behave as do most aliphatic solvents: in some cases the aromatics seem to be inert or even antagonistic to the extracted organic species, while in other cases their pi-electrons interact in a favorable way with the solute. For acetylacetone, the interaction seems to be very weak. The salting-in effect is shown both in Figs. 4.7a. and 4.7b.

4.6.1 Dissociation

Acids dissociate in the aqueous phase with a dissociation constant $K_a$.
HA ⇌ H⁺ + A⁻  \quad K_a = [H⁺][A⁻]/[HA]  \quad (4.18)

The distribution ratio incorporates the $K_a$ for extraction of acids, HA, as:

\[ D_A = [HA]_{aq} / ([HA] + [A⁻]) = K_{D,HA} (1 + K_a [H⁺]^+) \quad (4.19) \]

Index $A$ indicates that the distribution ratio refers to the concentration of all species of A in the organic and in the aqueous phase. In Fig. 4.6 the distribution of the β-diketones is constant in the higher hydrogen ion concentration range (lower pH) where they are undissociated. In the higher pH region, $D_A$ becomes inversely proportional to the hydrogen ion concentration due to increase in the concentration of the dissociated form of the acid $A^-$, in agreement with Eq. (4.19).

The free ligand concentration, [A⁻], is an important parameter in the formation of metal complexes (see Chapter 3 and section 4.8). In a solvent extraction system with the volumes $V$ and $V_{org}$ of the aqueous and organic phases, respectively, [A⁻] is calculated from the material balance:

\[ \log [A⁻] = \log K_a - \log[H⁺] + \log (m_{HA, org} V_{org}) - \log F \quad (4.20a) \]

where

\[ F = K_{D,HA} + V^{-1} V_{aq}^{-1} + K_a [H⁺]^{-1} V_{aq}^{-1} \quad (4.20b) \]

$m_{HA, org}$ is the total amount (in moles) of HA (reagent) added to the system. Often $m_{HA, org}$ is abbreviated $[HA]_{org}$, indicating the original concentration of HA in the organic phase at the beginning of the experiment (when $[HA]_{aq} = 0$). When $V_{aq} = V$ and $pH \ll pK_a$, $F = 1 + K_{D,HA}$. From Eq. (4.20) it can be deduced that [A⁻] increases with increasing pH, but tends to become constant as the pH value approaches that of the $pK_a$ value. In the equations relating to the extraction of metal complexes, HA is often identical with reagent R; the indexes may be changed accordingly, thus e.g., $K_{D,HA} \equiv K_{DR}$. (Note: Various authors use slightly different nomenclature; here we follow reference Appendix C.)

### 4.6.2 Protonation

At low pH, some organic acids accept an extra proton to form the $H_2A^+$ complex. This leads to a decrease in the $D_A$ value at pH < 6, as shown in Fig. 4.6:

---

**Fig. 4.7** Distribution ratio $D_{HA}$ of undissociated acetylacetone. (a) Distribution between benzene and aqueous phase containing different inorganic salts; 25°C. (b) Distribution between CHCl₃ (upper curves) or C₆H₆ (lower curves) and aqueous phase 0.1 and 1.0 M in NaClO₄ as a function of [HA]ₐq. The uncertainty at the lowest $D$ values is ±1 for CHCl₃ and ±0.2 for C₆H₆. (From Ref. 10.)

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Because \( \text{H}_2\text{A}^+ \) is ionic, it is not extracted into the organic phase, and thus the distribution ratio becomes

\[
D_A = \frac{[\text{HA}]_{\text{org}}([\text{H}_2\text{A}^+])+[\text{HA}]+[\text{A}^-])^{-1}
= K_{D,\text{HA}}(K_{\text{dil}}[\text{H}^+] + 1 + K_a[\text{H}^-])^{-1}
\]

as illustrated in Fig. 4.6 for oxine.

### 4.6.3 Dimerization

Figure 2.1 illustrates a number of orientations by which two linear acids may form a dimer. The partial neutralization of the hydrophilic groups leads to increased solubility of the acid in the organic solvent, but is not observed in the aqueous phase. The dimerization can be written as:

\[
2\text{HA(org)} \rightleftharpoons \text{H}_2\text{A}_2\text{(org)} \quad K_{\text{di}} = \frac{[\text{H}_2\text{A}_2]_{\text{org}}}{[\text{HA}]_{\text{org}}^2}
\]

The distribution ratio for the extraction of the acid becomes:

\[
D_A = ([\text{HA}]_{\text{org}} + 2[H_2A_2]_{\text{org}})(HA) + [A^-])^{-1}
= K_{D,\text{HA}}(1 + 2K_{\text{di}} K_{D,\text{HA}}[HA]_{\text{eq}} (1 + K_a[H^-])^{-1}
\]

The last term can be expressed in several different ways. Because the distribution ratio \( D_A \) reflects the analytical concentration of \( A \) in the organic phase, the dimer concentration is given as \( 2[H_2A_2] \), although it is a single species (one molecule). Figure 4.8 illustrates how the dimerization leads to an increase of acid distribution ratio with increasing aqueous acid concentration. For propionic acid \( \log K_a = -4.87 \), \( \log K_{D,HA} = -1.90 \) and \( \log K_{\text{di}} = 3.14 \) in the system. The extraction increases as the size of the acid increases. A dimeric acid may form monobasic complexes with metal ions, as is illustrated by the formulas in Appendix D:14 b–d, for the M(\( \text{H(DEHP)}_2 \)) and UO\( \text{H}_2(\text{DEHP)}_2 \) complexes. The situation may be rather complex. For example, at very low concentrations in inert solvents, dialkylphosphates (RO\( \text{H}_2\text{POOH} \) act as a monobasic acid, but at concentrations \( >0.05 \text{ M} \) they polymerize, while still acting as monobasic acids (i.e., like a cation exchanger). The degree of dimerization/polymerization depends on the polarity of the solvent [11b].

### 4.6.4 Hydration

In solvent extraction, the organic phase is always saturated with water, and the organic extractant may become hydrated. In the extraction of benzoic acid, HBz (Appendix D:2), it was found that the organic phase contained four different
species: the monomer HBz, the monomer hydrate HBz·H₂O, the dimer H₂Bz₂, and the dimer hydrate H₂Bz₂(H₂O)₂. Only by considering all these species is it possible to explain the extraction of some metal complexes with this extractant.

4.7 EXTRACTION OF ACIDS AS ADDUCTS
(TYPE II-B)

| Acid adduct (and acid and adduct former) in organic phase | HAB (⇌ B + HA) ↓↑ (↓↑) (↓↑) |
| Acid HA dissociating and forming adduct in aqueous phase | HAB (⇌ B + HA ⇌ H⁺ + A⁻) |

The solubility of organic acids in water is due to the hydrophilic oxo- and hydroxo-groups of the acid that form hydrogen bonds with water molecules. If the hydrogen ion of the acid is solvated by a donor organic base, B, in the

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organic phase, the adduct B–HA is likely to have much greater solubility in the organic phase.

4.7.1 Weak (Organic) Acids, HA

In extraction of weak organic acids (abbreviated HA) from acidic aqueous solutions, the concentration of undissociated acid, HA, exceeds the concentration of its dissociated anions, $A^-$, as long as $pK_a > pH$. The acid may then act as adduct-forming nonelectrolyte; see section 4.5 and Example 1.

4.7.2 Strong (Inorganic) Acids, HL

To avoid confusion with weak organic acids, strong inorganic acids are denoted by HL. Most strong acids are completely dissociated and both cations and anions are hydrated in aqueous solutions even at pHs as low as 0. The hydration makes them lipophobic and almost insoluble in inert organic solvents. The hydrogen ion is a Lewis acid (Chapter 3) and is solvated by strong organic (donor or base) molecules, such as those in Table 4.8 (e.g., alcohols, ethers, ketones, esters, amines, phosphoryls, etc.). This results in greater lipophilicity, and the acid becomes more soluble in inert organic solvents. The structure of these “solvated hydrogen salts” is not well known, but may be represented symbolically by $HB_L^+$, where B refers to the adduct former or the solvating solvent; $b$ may have a value of 1–4.

The order of extractability changes with aqueous acidity, but in general follows the order $HClO_4 \approx HNO_3 > HI > HBr > HCl > H_2SO_4$ (see Table 4.8). Since the hydration energies of the acids follow the opposite order, dehydration is an essential step in the solvent extraction process. This order of acids has a practical significance: acids higher can be replaced by the acids lower in the sequence; e.g., HF and HNO_3 are extracted from acidic stainless steel pickling waste solutions into kerosene by addition of $H_2SO_4$ (see Chapter 14 of this book).

The extraction of most acids is accompanied by extraction of water. In the extraction of HNO_3 by TBP into kerosene, many different species have been identified, several of which involve hydration. The ratio of acid:adduct is not very predictable. For example, $HClO_4$ apparently is extracted into kerosene with 1–2 molecules of TBP, $HCl$ into ethylether with one molecule of ethylether, etc. Also, the extracted acid may dimerize in the organic solvent, etc. Example 2 illustrates the complexity of the extraction of HNO_3 by TBP into kerosene.

Assuming that B is almost insoluble in the aqueous phase, the equilibrium reaction can be written in two ways:

1. The interface extraction model assumes that HA reacts with B at the interface. Thus

$$ HA(aq) + bB(org) \rightleftharpoons HAB_b \text{ (org)} $$

(4.25a)
Table 4.8  Basicity (Electron Pair-Donating Tendency) of Some Ions and Molecules (R is an alkyl or aryl group)

<table>
<thead>
<tr>
<th>Basicity of some common anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>relative to the (hard type) actinide cations</td>
</tr>
<tr>
<td>ClO₄⁻ &lt; I⁻ &lt; Br⁻ &lt; Cl⁻ &lt; NO₃⁻ &lt; SCN⁻ &lt; acetate⁻ &lt; F⁻</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Basicity of some organic molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine compounds R₃N⁺ &lt; R₂NH⁺ &lt; RNH⁺ &lt; NH₃</td>
</tr>
<tr>
<td>Arsine compounds R₃As</td>
</tr>
<tr>
<td>Phosphine compounds R₃P</td>
</tr>
<tr>
<td>Phosphoryls (RO)₃PO⁺ &lt; R’(RO)₂PO⁺ &lt; R’(RO)PO⁺ &lt; R’PO⁺</td>
</tr>
<tr>
<td>Arsenyls R₃AsO⁺</td>
</tr>
<tr>
<td>Carbonyls RCHO &lt; R₃CO (≤ R₃O &lt; ROH &lt; H₂O)</td>
</tr>
<tr>
<td>Sulfuryls (RO)₂SO₂ &lt; R₂SO₂ &lt; (RO)₂SO⁺ &lt; R₂SO⁺</td>
</tr>
<tr>
<td>Nitrosyls RNO₂⁻ &lt; RNO⁺</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substitutions causing basicity decrease of oxo compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₃CH— &lt; CH₃(CH₂)ₙ— &lt; CH₃— &lt; CH₃O— &lt; ClCH₂—</td>
</tr>
</tbody>
</table>

* Tertiary, secondary, and primary amines.
* 'tri-R' phosphate.
* 'di-R'-R' phosphonate.
* 'R-di-R' phosphinate.
* 'tri-R' phosphine oxide.
* 'arsine oxide.
* ether and hydroxo compounds.
* sulfates.
* sulfones.
* sulfites.
* sulfides.
* nitro compounds.
* nitroso compounds.

Source: Ref. 12.

Since [HA]_eq and [B]_eq are easily measurable quantities, it is common to define the extraction constant K_ex for this model:

\[
K_{\text{ex}} = [HAB_b]_{\text{org}} [HA]^{-1} [B]^{-b}_{\text{org}} \tag{4.25b}
\]

2. The organic phase reaction model assumes all reactions take place in the organic phase. Thus one assumes

\[
\text{HA(org)} + b\text{B(org)} \leftrightarrow HAB_b(\text{org}) \tag{4.26a}
\]

The equilibrium constant for this reaction is

\[
K_{\text{ad,bb}} = [HAB_b]_{\text{org}} [HA]^{-1} [B]^{-b}_{\text{org}} \tag{4.26b}
\]
where $K_{ad,EB}$ is the (organic phase) adduct formation constant. The distribution ratio of the acid in this system becomes

$$D_A = ([HA]_{org} + [HAB]_{org})/[HA] + [A^-]^{-1} = K_{DHA} (1 + \Sigma K_{ad,EB}[B]_{org})/(1 + K_a[H^+])$$

Equation (4.25b) becomes identical to Eq. (4.26b) if $K_a$ is replaced by $K_{DHA}$ $K_{ad,EB}$. Equilibrium measurements do not allow a decision between the two reaction paths.

Example 2: Extraction of nitric acid by pure TBP.

Many metals can be extracted from nitrate solutions by TBP. In those systems it is important to account for the HNO$_3$-TBP interactions. The next set of equations were derived by [13] and are believed to be valid for the extraction of HNO$_3$ at various nitrate concentrations into 30% TBP in kerosene. Abbreviating HNO$_3$ as HL, and TBP as B, and including hydration for all species without specification, one derives

1. The formation of an acid monoadduct:

$$H^+ + L^- + B(\text{org}) \rightleftharpoons HLB(\text{org})$$

For simplicity, we write the adduct HLB, instead of HB$^+$-$L^-$. The extraction constant is

$$K_{ex1} = [HLB]_{eq}[H]^+ [L^-][B]_{org}^{-1}$$

2. The formation of a diacid monoadduct:

$$2H^+ + 2L^- + B(\text{org}) \rightleftharpoons (HL)_2B(\text{org})$$

$$K_{ex2} = [(HL)_2B]_{eq}[H]^2[L]^2[B]_{org}^{-1}$$

3. Ion pair association:

$$H^+ + L^- \rightleftharpoons H'L^-$$

$$K_{ex} = [H'L^-][H^+L^-]$$

This reaction only occurs under strong acid conditions, and the equilibrium constant may be < 1.

4. The distribution of nitric acid is then given by

$$D_{NO3} = ([HLB]_{eq} + 2[(HL)_2B]_{eq} + \ldots )([L^-] + [H^+L^-])^{-1}$$

5. Furthermore, the dimerization of TBP in the organic phase must be taken into account:

$$2B \rightleftharpoons B_2$$

$$K_a = [B_2]_{eq}/[B]_{eq}^2$$

yielding the total concentration of TBP in the organic phase

$$[\text{TBP}]_{eq} = [B]_{eq} + 2K_a[B]_{eq}^2$$
6. The distribution ratio in terms of only \([H^+]\) and monomeric \([B]_{\text{org}}\) can then be expressed by

\[
D_{\text{org}} = K_{\text{org}} \left[ K_{\text{org}} + 2 K_{\text{aq}} [H^+] \right] \tag{4.33}
\]

In this equation it is assumed \([H^+]=\left[L^-\right]\) (electroneutrality in the aqueous phase). Equation (4.33) has been tested, and the results agreed with >2300 experiments under varying conditions, see Fig. 4.9. The example illustrates the rather complicated situation that may occur even in such “simple” systems as the extraction of HNO₃ by TBP.

### 4.8 EXTRACTION OF COORDINATELY SATURATED METAL CHELATE TYPE COMPLEXES (TYPE III-B)

| Neutral, coordinatively saturated metal complex | \(MA_z\) |
| in organic phase | ↓↑ |
| Metal ion \(M^{z+}\) is complexed by \(zA^-\) ligands to form neutral \(MA_z\) |

![Diagram](image)

**Fig. 4.9** Test of the equations in Example 2 for extraction of 0.01–0.5 M nitric acid with 30% TBP in kerosene at temperatures 20–60°C. (From Ref. 13.)

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Section 3.2 describes an important class of organic ligands that are able to complex a metal ion through two or more binding sites of “basic” atoms, like O, N, or S, to form metal chelates. Table 4.9 presents the various types, their number of acidic groups, the chelate ring size, and the coordinating atoms. Neutral chelate compounds are illustrated in Appendix D: 5h, 14b and 14d. In Appendix D:5h the ring size is 6 for the complex between Cu\(^{2+}\) and each of the two acetylacetonate anions, Aa, while for the dimeric HDEHP ligand in the figures in Appendix D:14b and 14c the ring size becomes 7 for the M\(^{10}\) and UO\(_2\)^{2+} complexes (see the structures in Appendix D). As discussed in Chapter 3,

### Table 4.9 Some Organic Compounds Functioning as Polydentate Anions in Metal Extraction

<table>
<thead>
<tr>
<th>Chelate ring size</th>
<th>Acidic groups</th>
<th>Coordinating atoms</th>
<th>Compound group and examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1 O, O</td>
<td>Carboxylic acid, RCOOH; e.g., perfluorobutyric (C(_3)F(_7)COOH), salicylic C(_6)H(_5)(OH)COOH, cinnamic (C6H5(CH)2COOH) acids</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1 O, O'</td>
<td>Di(alkyl or aryl)phosphoric and phosphinic acids, RR′PO(OH); e.g., HDEHP(^b), corresponding thioacids(^a)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1 S, S</td>
<td>Dithiocarbamate, RR′NC(S)SH, xanthate, ROC(S)SH; e.g., NaDDC(^c)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2 O, O'</td>
<td>Mono(alkyl or aryl)phosphoric and phosphinic acid, RPO(OH)(_2); e.g., H(_3)MEHP(^d)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1 O, O</td>
<td>Nitrosohydroxylamine, RN(NO)OH; e.g., cupferron (R = C(_6)H(_5)); hydroxamic acid, RC(O)NHOH</td>
<td></td>
</tr>
<tr>
<td>5 or 6</td>
<td>1 O, N</td>
<td>8-Hydroxyquinoline (oxine), C(_9)NH(_2)OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S, N, or N, N</td>
<td>Diphenylthiocarbazone (dithizone), C(_9)NHNC(SH)NNC(_6)H(_5)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1 O, O</td>
<td>β-Diketone, RC(O)CHC(OH)R'; e.g., acetylacetone (R = R' = CH(_3)); HTTA' (R = C(_3)H(_7); R' = CF(_3))</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1 O, O</td>
<td>1-Nitroso-2-naphthol, C(_9)NOH</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2 O, O</td>
<td>Di(alkyl or aryl)pyrophosphate, RP(O)(OH) (_2), e.g., dioctylpyrophosphate (R = R' = C(_8)H(_17))</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)O, S, or S, S for the corresponding thioacids.
\(^b\)Di(2-ethylhexyl)phosphoric acid.
\(^c\)Sodium diethylthiocarbamate.
\(^d\)Mono(2-ethylhexyl)phosphoric acid.
\(^e\)Thenoyltrifluoroacetone.

*Source:* Ref. 12.
chelation provides extra stability to the metal complex. The formation and extraction of metal chelates are discussed extensively also in references [14–16].

In Chapter 3 we described how an uncharged metal complex $MA_z$ is formed from a metal ion $M^{z+}$ (*central atom*) through a stepwise reaction with the anion $A^-$ (*ligand*) of a monobasic organic acid, HA, defining a *stepwise formation constant* $k_n$, and an *overall formation constant* $\beta_n$, where

$$\beta_n = [M^{z+}A^n] / [M^{z+}] [A^-]^n$$

(4.34)

The $MA_z$ complex is lipophilic and dissolves in organic solvents and the *distribution constant* $K_{DC}$ is defined (index C for complex):

$$K_{DC} = [MA_z]_{org} / [MA_z]_{aq}$$

(4.35)

Taking all metal species in the aqueous phase into account, the distribution of the metal can be written (omitting the index aq for water)

$$D_M = \frac{[MA_z]_{org}}{\sum [MA_n^{z+}]} = \frac{K_{DC} \beta_n [A^-]^n}{\sum \beta_n [A^-]^n}$$

(4.36)

The distribution ratio depends only on the free ligand concentration, which may be calculated by Eq. (4.20). Most coordinatively saturated neutral metal complexes behave just like stable organic solutes, because their outer molecular structure is almost entirely of the hydrocarbon type, and can therefore be extracted by all solvent classes 2–5 of Chapter 2. The rules for the size of the distribution constants of these coordinatively saturated neutral metal complexes are then in principle the same as for the inert organic solutes of section 4.4. However, such complexes may still be amphiphilic due to the presence of electronegative donor oxygen atoms (of the chelating ligand) in the chelate molecule. In aqueous solution such complexes then behave like polyethers rather than hydrocarbons. Narbutt [17] has studied such outer-sphere hydrated complexes and shown that the dehydration in the transfer of the complex from water to the organic solvent determines the distribution constant of the complex. This is further elaborated in Chapter 16.

Example 3: Extraction of Cu(II) by acetylacetone.

Simple $\beta$-diketones, like acetylacetone (*Appendix D: 5d*) can coordinate in two ways to a metal atom, either in the uncharged keto form (through two keto oxygens), or in dissociated anionic enol form (through the same oxygens) as shown in Appendix D: 5c, 5h. It acts as an acid only in the enolic form. Figure 4.10 shows the extraction of Cu(II) from 1 M NaClO$_4$ into benzene at various concentrations of the extractant acetylacetone (HA) [18]. Acetylacetone reacts with Cu(II) in aqueous solutions to form the complexes CuA$^+$ and CuA$_2$. Because acetylacetone binds through two oxygens, the neutral complex CuA$_2$ contains two six-membered chelate rings; thus four coordination positions are taken up, forming a planar complex (*Appendix D: 5f*). This complex is usually considered to be coordinatively saturated, but two additional very
weak bonds can be formed perpendicular to the plane; we can neglect them here.

The distribution of copper, $D_{Cu}$, between the organic phase and water is then described by

$$D_{Cu} = \frac{[CuA_{aq}]}{[Cu^{2+}] + [CuA^{2-}] + [CuA_{organ}]}. \quad (4.37)$$

One then derives

$$D_{Cu} = \frac{K_{DC} \beta_i [A^-]^{i}}{1 + \beta_i [A^-] + \beta_j [A^{-}]^{j}} = \frac{K_{DC} \beta_i [A^-]^{i}}{\Sigma \beta_i [A^{-}]^{j}}. \quad (4.38)$$

where $K_{DC}$ refers to the distribution constant of the uncharged complex $CuA_i$.

In Eq. (4.37), log $D$ is a function of [$A^{-}$], the free ligand concentration, only, and some constants. In Fig. 4.10, log $D_{Cu}$ is plotted vs. log [$H^{+}$] ($= -pH$). Through Eqs. (4.17) and (4.18) it can be shown that log $D_{Cu}$ is a function of pH only at constant [$HA_{aq}$] (or [$HA_{organ}$]), while at constant pH the log $D_{Cu}$ depends only on [$HA_{aq}$] (or [$HA_{organ}$]).
In the insert of Fig. 4.10, log \( D \) is plotted as a function of log \( [A^-] \), where \([A^-]\) has been calculated from pH, \([HA]_{org}\), phase volumes, and \( K_a \) and \( K_{DR} \) (same as \( K_{DHA} \)) for HA by means of Eq. (4.20); it is found that all curves coincide into one at high pH (high \([A^-]\)), as expected from Eq. (4.38). The distribution curve approaches two asymptotes, one with a slope of 2 and one horizontal (zero slope). From Eq. (4.38) it follows that, at the lowest \([A^-]\) concentration (lowest pH), the concentration of CuA\(^+\) and CuA\(_2\) in the aqueous phase becomes very small; Eq. (4.38) is then reduced to

\[
\lim_{[A^-] \to \infty} D_{eq} = \frac{[CuA_2]_{org}}{[Cu^+]_a} = K_{ex} \beta_2 [A^-]^2
\]

At the highest \( A^- \) concentrations a horizontal asymptote is approached:

\[
\lim_{[A^-] \to 0} D_{eq} = \frac{[CuA_2]_{org}}{[CuA_2]_a} = K_{DC}
\]

The horizontal asymptote equals the distribution constant of CuA\(_2\), i.e., \( K_{DC} \).

From the curvature between the two asymptotes, the stability constants \( \beta_i \) and \( \beta_2 \) can be calculated.

This example indicates that in solvent extraction of metal complexes with acidic ligands, it can be more advantageous to plot log \( D \) vs. log\([A^-]\), rather than against pH, which is the more common (and easy) technique.

In order to calculate \( D_{eq} \) from Eq. (4.36), several equilibrium constants as well as the concentration of free \( A^- \) are needed. Though many reference works report stability constants \([19,20]\) and distribution constants \([4,21]\), for practical purposes it is simpler to use the extraction constant \( K_{ex} \) for the reaction

\[\text{M}^{z+} (aq) + z\text{HA} (org) \rightleftharpoons \text{MA}_z (org) + z\text{H}^- (aq) \]

in which case the \( \text{MA}_z^{+n} \) complexes in the aqueous phase are neglected. The relevant extraction equations are

\[ K_{ex} = [\text{MA}_z]_{org} / [\text{H}^+]^z [\text{M}^{z+}]^z [\text{HA}]_{org} \]

and

\[ D_{eq} = K_{ex} [\text{HA}]_{org} / [\text{H}^+ ]^{-z} \]

Thus only one constant, \( K_{ex} \), is needed to predict the metal extraction for given concentrations \([\text{H}^+]\) and \([\text{HA}]_{org} \). Tables of \( K_{ex} \) values are found in the literature (see references given).

Equation (4.41) is valid only when the complexes \( \text{MA}_z^{+n} \) can be neglected in the aqueous phase. Comparing Eqs. (4.37) and (4.41), it is seen that no horizontal asymptote is obtained even at high concentrations of \( A^- \), or HA and H. Thus, for very large distribution constant of the uncharged complex (i.e., \( > 1000 \)) a straight line with slope \(-z\) is experimentally observed, as in the case for the Cu(II)-thenoyltrifluoroacetone (HTTA) system (Appendix D: 5g).
Example 4: Extraction of Cu(II) by Thenoyltrifluoroacetone.

Figure 4.11a shows the distribution of Cu(II) between three organic solvents and water in the presence of isopropyltropolone (HITP) or thenoyltrifluoroacetone (HTTA) as a function of pH [22]. The straight line of slope −2 in the pH-plot fits Eq. (4.41c); thus $z = 2$. It indicates that the aqueous phase does not contain any significant concentrations of the complexes CuA$^+$ or CuA$_2$, yet CuA$_2$ must be formed in considerable concentrations, otherwise there would be no extraction of Cu(II). The line also corresponds to the asymptote Eq. (4.39), or (i.e., $[A^-] \sim [H^+]^{-1}$). Thus the conclusion is that the aqueous phase is completely dominated by Cu$^{2+}$, while the organic phase contains only CuA$_2$. This leads to the copper distribution ratio

$$D_{Cu} = \frac{[CuA_2]_{org}}{[Cu^{2+}]}$$

(4.42)

which is valid for the reaction.

Fig. 4.11 Distribution of Cu(II) between hexone (Δ), carbon tetrachloride (●), or chloroform (○) and 0.1 M NaClO$_4$ in the presence of isopropyltropolone (IPT) or thenoyltrifluoroacetone (TTA); (a) as a function of −log[H$^+$] at constant [TTA]$_{org} = 0.1$ M; (b) as a function of [TTA]$_{org}$ at constant [H$^+$] = 0.1M. (From Ref. 22.)
$$\text{Cu}^{2+} + 2\text{HA(org)} \rightleftharpoons \text{CuA}_\text{org} + 2 \text{H}^+ \quad (4.43\text{a})$$

The extraction constant is

$$K_\text{ex} = \frac{[\text{CuA}_\text{org}][\text{H}^+]^2}{[\text{Cu}^{2+}][\text{HA}]_{\text{org}}} \quad (4.43\text{b})$$

and combining with Eq. (4.42)

$$D_{\text{ex}} = K_\text{ex} [\text{HA}]_{\text{org}} [\text{H}^+]^2 \quad (4.44)$$

From Eq. (4.44) a plot of log $D$ against $-\log[\text{H}^+]$ should yield a straight line with slope +2, as in Fig. 4.11a, and a plot against log [HA]$_\text{org}$ as in Fig. 4.11b should also yield a straight line with slope +2. Continued in Example 14.

This example illustrates a case of considerable analytical importance, especially for the determination of complex formation constants for hydrophilic complexes, as discussed in section 4.12, when the equilibrium constants for the stepwise metal-organic complexes are of secondary interest. $K_\text{ex}$ values are tabulated in several reference works. $K_\text{ex}$ is a conditional constant and only valid provided no other species are formed besides the extracted one.

The distribution constant of the neutral complex $\text{MA}_z$, $K_{\text{DC}}$, has been referred to several times. In favorable cases, when both the organic and the aqueous phases are dominated by the same uncharged complex over a larger concentration region, $K_{\text{DC}}$ can be directly measured, as is the case for most of the data in Table 4.10 [22–23b]. Otherwise $K_{\text{DC}}$ can be estimated or calculated from $K_{\text{ex}}$ data combined with $\beta_{\text{ex}}$, $K_\text{a}$ and $K_{\text{DR}}$ [see Eqs. (4.8) and (4.46)].

### 4.9 EXTRACTION OF METAL COMPLEXES AS ADDUCTS (TYPE III-C)

<table>
<thead>
<tr>
<th>Coordinatively saturated metal adduct</th>
<th>$B$</th>
<th>$\text{MA}_z\text{B}_b$</th>
<th>complex in organic phase (and $B$)</th>
<th>$\text{MA}_z\text{B}_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation neutral complex coordinately</td>
<td>$M^{z+} + zA^+ + bB \rightleftharpoons \text{MA}_z\text{B}_b$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

If the neutral metal complex is coordinatively unsaturated, it forms $\text{MA}_z$ ($\text{H}_2\text{O}$), in the aqueous phase, where $2z + x$ (A being bidentate) equals the maximum coordination number. In the absence of solvating organic solvents, this complex has a very low distribution constant. Obviously, if water of hydration can be replaced by organic molecules $B$, the result is a more lipophilic adduct complex $\text{MA}_z\text{B}_b$; many adduct formers are listed in Appendix D and several tables. Depending on the ligand, several types of such adducts exist: (i) type $\text{MA}_z\text{B}_b$, where A and B are different organic structures; (ii) type $\text{MX}_B$, where $\text{MX}_z$ is a neutral inorganic compound (salt); and (iii) type $\text{MA}_z(\text{HA})_b$, where A and HA are the basic and neutral variant of the same molecule (so-called self-adducts).
Table 4.10  Distribution Constants for Acetylacetone (HA) and Some Metal Acetylacetonates Between Various Organic Solvents and 1 M NaClO\(_4\) at 25°C

<table>
<thead>
<tr>
<th>Organic solvent(^{a})</th>
<th>(\epsilon)</th>
<th>(\log K_{DR})</th>
<th>(\log K_{DC})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>HA</td>
<td>ZnA(_2)</td>
<td>CuA(_2)</td>
</tr>
<tr>
<td>n-Hexane (1)</td>
<td>1.88</td>
<td>−0.022</td>
<td>−1.57</td>
</tr>
<tr>
<td>Cyclohexane (3)</td>
<td>2.02</td>
<td>0.013</td>
<td>−1.16</td>
</tr>
<tr>
<td>Carbon tetrachloride (4)</td>
<td>2.24</td>
<td>0.52</td>
<td>−0.39</td>
</tr>
<tr>
<td>Mesitylene(^{b}) (6)</td>
<td>2.28</td>
<td>0.44</td>
<td>—</td>
</tr>
<tr>
<td>Xylene (7)</td>
<td>2.27</td>
<td>0.57</td>
<td>−0.47</td>
</tr>
<tr>
<td>Toluene (8)</td>
<td>2.38</td>
<td>0.66</td>
<td>−0.37</td>
</tr>
<tr>
<td>Benzene (9)</td>
<td>2.28</td>
<td>0.77</td>
<td>−0.21</td>
</tr>
<tr>
<td>Dibutylether (2)</td>
<td>3.06</td>
<td>—</td>
<td>−1.05</td>
</tr>
<tr>
<td>Methylisobutylketone (5)</td>
<td>13.1</td>
<td>0.77</td>
<td>−0.15</td>
</tr>
<tr>
<td>Chloroform (10)</td>
<td>4.9</td>
<td>1.38</td>
<td>0.82</td>
</tr>
<tr>
<td>Benzonitrile (11)</td>
<td>25.2</td>
<td>0.21</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^{a}\)Numbers in parentheses refer to Figs. 4.23 and 4.26.

\(^{b}\)1,3,5-trimethylbenzene.

\(\text{Source: Refs. 22–23.}\)

### 4.9.1 Metal-Organic Complexes with Organic Adduct Formers, Type MA\(_z\)B\(_b\)

The extraction of the metal complex adduct can be written

\[
\text{M}^{z+} (\text{aq}) + z\text{HA(organ)} + b\text{B(organ)} \rightleftharpoons \text{MA}_{z}\text{B}_b(\text{organ}) + z\text{H}^+ (\text{aq})
\]  

The extraction constant is defined by

\[
K_{ex} = \frac{[\text{MA}_z\text{B}_b]_{\text{org}}[\text{H}^+]^z}{[\text{M}^{z+}][\text{HA}]_{\text{org}}^z[\text{B}]_{\text{org}}^b} \tag{4.45b}
\]

or

\[
K_{ex} = D_M [\text{H}^+]^z [\text{HA}]_{\text{org}}^{-z} [\text{B}]_{\text{org}}^{-b} \tag{4.45c}
\]

Thus the distribution of the metal, \(D\), is shown to depend on the concentrations of \(\text{H}^+\) and \(\text{HA}_{\text{org}}\) to the power of \(z\) of the charge of the metal ion, and on the concentration of \(\text{B}\) to the power of \(b\) (i.e., number of adduct formers in the extracted complex).

It can be shown that

\[
K_{ex} = K_{DR} K_{DC} K_{adMB}
\]

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where (omitting ionic charges) \( K_a = [H][A]/[HA] \) is the acid dissociation constant [see Eq. (4.18)], \( K_{DR} = [HA]_{org}/[HA] \) is the distribution constant for the undissociated acid HA [see Eq. (4.17)], and

\[
K_{ad,B} = \frac{[MA_z B_{org}]}{[MA_z]_{org}} \quad \text{ (4.47)}
\]

is the formation constant for the adduct \( MA_z B \) in the organic phase [see Eqs. (4.15), (4.16), and (4.26)]. The five parameters \( K_a, \beta_n, K_{DR}, K_{DC}, \) and \( K_{ad,B} \) are in principle unrelated, even though it may not always be possible to change one without affecting the others, as each molecular species may take part in several equilibria. Without considering the independent parameters, it is often difficult to understand why \( K_a \) varies in the fashion observed, and it may be impossible to predict improvements of the system. A good example is the extraction of Zn(II) by \( \beta \)-diketones and TBP:

Example 5: The extraction of Zn(II) by \( \beta \)-diketones and phosphoryl adduct formers.

Figure 4.12 illustrates the extraction of Zn(II) from 1 M NaClO\(_4\) into carbon tetrachloride by \( \beta \)-diketones (HA) in the presence of the adduct formers.
TBP and TOPO (B) [12]. The extracted neutral complex is ZnA₂Bₙ The distribution ratio becomes

\[
D_{zn} = \frac{[ZnA]_n + [ZnA,B]_n + [ZnA,B,B]_n + \cdots}{[Zn] + [ZnA] + [ZnA,B] + \cdots} \tag{4.48a}
\]

To analyze these systems, the overall extraction reaction must be broken into its partial reactions, or by introducing Eq. (4.47), to obtain

\[
D_{zn} = \frac{K_{ad}[A]^n (1 + K_{ad1}[B]_n + K_{ad2}[B]^n + \cdots)}{\sum \beta_i [A]^n} \tag{4.48b}
\]

where the adduct formation constant is defined by

\[
K_{ad} = [ZnA,B]_aq \frac{[ZnA]_aq}{[B]_aq} \tag{4.49}
\]

In the absence of any adduct former, \(D_{zn}\) is given as a function of the free ligand concentration by Eq. (4.36), i.e., the parentheses in Eq. (4.48b) equals 1; denoting this \(D_{zn}\)-value as \(D_o\) and introducing it into Eq. (4.48) gives

\[
D_o = D_z (1 + K_{ad1}[B]_aq + K_{ad2}[B]^n + \cdots) \tag{4.50}
\]

\(D_o\) (instead of \(D_{zn}\)) indicates that this expression is valid only at constant \([A]\), or better, constant \([H^+]\) and \([HA]_aq\) [see Eqs. (4.36) and (4.41c)]. In Fig. 4.12, \(\log D_z, D_z\) is plotted as a function of \(\log [B]_aq\). The distribution ratio proceeds from almost zero, when almost no adduct is formed, towards a limiting slope of 2, indicating that the extracted complex has added two molecules of B to form ZnA₂B₂. From the curvature and slope the \(K_{ad}\)-values were determined (see section 4.10). The calculation of the equilibrium constants is further discussed under Example 13.

Tables 4.11–4.13 presents adduct formation constants according to Eq. (4.47). For the alkaline earths TTA complexes in carbon tetrachloride in Table 4.11, the TBP molecules bond perpendicular to the square plane of the two TTA rings, producing an octahedral complex. The higher the charge density of the

### Table 4.11 Adduct Formation Constants

<table>
<thead>
<tr>
<th>M⁺ (r pm)</th>
<th>(\log K_{ad1})</th>
<th>(\log K_{ad2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺ (100)</td>
<td>4.11</td>
<td>8.22</td>
</tr>
<tr>
<td>Sr²⁺ (118)</td>
<td>3.76</td>
<td>7.52</td>
</tr>
<tr>
<td>Ba²⁺ (135)</td>
<td>2.62</td>
<td>5.84</td>
</tr>
</tbody>
</table>

Source: Ref. 4.
Table 4.12  Adduct Formation Constants for the Reaction EuA_{3}(org) + bTBP(org) \rightleftharpoons EuA_{3}(TBP)_{b}(org), Eq. (4.26a), Where org = CHCl_{3}, and HA Substituted Acetylacetone Ligands

<table>
<thead>
<tr>
<th>Ligand (A)</th>
<th>Log $K_a$</th>
<th>Log $K_{all}$</th>
<th>Log $K_{all2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylacetone, AA</td>
<td>8.76</td>
<td>1.90</td>
<td>—</td>
</tr>
<tr>
<td>Benzoyleacetonitrile, BZA</td>
<td>8.74</td>
<td>1.60</td>
<td>—</td>
</tr>
<tr>
<td>Trifluoroacetonitrile, TFA</td>
<td>—</td>
<td>3.32</td>
<td>4.64</td>
</tr>
<tr>
<td>Benzylintrallfluoroacetonitrile, BTA</td>
<td>—</td>
<td>3.64</td>
<td>5.28</td>
</tr>
<tr>
<td>2-Pyruvyltrifluoroacetonitrile, FTA</td>
<td>—</td>
<td>3.50</td>
<td>5.00</td>
</tr>
<tr>
<td>Thenoyltrifluoroacetonitrile, TTA</td>
<td>6.3</td>
<td>3.34</td>
<td>5.28</td>
</tr>
</tbody>
</table>

Source: Ref. 4.

Table 4.13  Constants for Formation of Eu(TTA)_{3}B_{a} Adducts

<table>
<thead>
<tr>
<th>Adduct forming ligand (B)</th>
<th>Chloroform</th>
<th>Carbon tetrachloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log $K_{all1}$</td>
<td>log $K_{all2}$</td>
</tr>
<tr>
<td>TTA (self-adduct)</td>
<td>0.56</td>
<td>—</td>
</tr>
<tr>
<td>Hexone</td>
<td>1.16</td>
<td>1.52</td>
</tr>
<tr>
<td>Quinoline</td>
<td>3.29</td>
<td>—</td>
</tr>
<tr>
<td>TBP</td>
<td>3.63</td>
<td>5.40</td>
</tr>
<tr>
<td>TOPO</td>
<td>5.40</td>
<td>7.60</td>
</tr>
</tbody>
</table>

Source: Ref. 4.

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The difference between the two solvent systems is likely a result of CHCl₃ solvating the Eu complex to some extent, while CCl₄ is inert. This has two effects: the $K_{DC}$ value increases due to the solvation by CHCl₃ (not shown in the table), while the adduct formation constant $K_{ad}$ decreases as the solvation hinders the adduct formation; the more inert solvent CCl₄ causes an opposite effect, a lower $K_{DC}$ and a larger $K_{ad}$.

4.9.2 Metal Inorganic Complexes with Organic Adduct Formers, Type $MX_2B_b$

The extraction of mineral salts is generally less complicated than the extraction of mineral acids. Metal salts with monodentate univalent anions like Cl⁻, ClO₄⁻, SCN⁻, and NO₃⁻ are strongly hydrated in the aqueous phase and have quite small, if any, solubility in inert solvents. In order to extract these acids, they must either form an adduct with a strongly basic extractant like TBP or TOPO, or be in solvating solvents such as ethers, ketones, alcohols, or esters. Examples of extracted metal salt adducts are: Br₃(EtO)₆, PaCl₃(MIBK), UO₂(NO₃)₂(TBP)₂, Co(ClO₄)₂(octanol)₆, etc. ($b$ is uncertain). Tables of the extraction of a large number of metal salts by solvating solvents or commercial adduct formers dissolved in kerosene are given (see Ref. [5]).

It has been shown [25] that monomeric metal hydroxides can be extracted by strong donor molecules; e.g., in the form of the adducts Ln(OH)₃(TOPO)₆ into CHCl₃, where $b$ is 2–3. Under favorable conditions, the $D_{Ln}$ value may exceed 1, though the fraction of hydroxide is quite low.

When the solvent is a good solvater, the determination of the solvation number $b$ is difficult, unless the dependence of the extractant concentration on the solvent can be obtained. Solvation numbers can be obtained in mixtures of a solvating extractant and an inert diluent like hexane. Further, in these systems the extraction of the metal commonly requires high concentrations of salt or acid in the aqueous phase, so the activity coefficients of the solutes must be taken into account.

Example 6: Extraction of Zn(II) thiocyanate complexes by TOPO.

Figure 4.13 shows the extraction of Zn(II) from aqueous thiocyanate (L⁻) solutions into 0.001 M TOPO (B) in hexane; the aqueous phase is 1.0 M Na(SCN⁻, ClO₄⁻) at a pH around 5 [26]. Zn(II) is known to form a number of weak Zn(SCN)₉²⁻ complexes in the aqueous phase. The uncharged one is assumed to accept TOPO to form the adducts Zn(SCN)₉(TOPO)₁₁, where $b$ = 1 or 2.

Assume that the reaction between the neutral complex and the solvating molecule takes place at the interface (to assume the reaction to take place in the organic phase would be unrealistic, as the zinc thiocyanate is insoluble in hexane); thus the extraction reaction is:
Fig. 4.13 Distribution ratio of Zn(II) when extracted from 1 M Na(SCN⁻,ClO₄⁻) into 0.001 M TOPO in hexane, as a function of aqueous SCN⁻ concentration. The following equilibrium constants were obtained with Eq. (4.53): β₁ 3.7, β₂ 21, β₃ 15, $K_{ex}$ 2.5 $10^7$ for $b = 2$. (From Ref. 26.)

\[ \text{ZnL}_b + b \text{B(org)} \leftrightarrow \text{ZnL}_b \text{B (org)}_b \]

(4.51)

for which we may define an equilibrium constant $K_{ex,b}$. Because more than one solvated species may be extracted, the distribution ratio becomes

\[ D_{zn} = \frac{[\text{ZnL}_b \text{B}]_{org} + [\text{ZnL}_b \text{B}]_{aq} + \cdots}{[\text{Zn}] + [\text{ZnL}] + [\text{ZnL}] + \cdots} \]

(4.52)

Inserting the partial equilibrium constants [see Eq. (4.46)],

\[ D_{zn} = \frac{\beta_b [\text{L}] \sum K_{ex,b} [\text{B}]_{aq}}{1 + \sum \beta_b [\text{L}]^{b'}} \]

(4.53)

where both summations are taken from 1. The solvation number $b$ can be determined from the dependence of $D$ on [B]$_{aq}$ while [L] is kept constant. From the slope of the line in Fig. 4.13 at low SCN⁻ concentrations, it follows that $b = 2$; thus only one adduct complex is identified: Zn(SCN)$_b$(TOPO)$_b$. The authors were able to calculate the formation constants $\beta_n$ from the deviation of the curve from the straight line at constant [B]$_{aq}$, assuming $b$ constant. With
these equilibrium constants, the line through the points was calculated with Eq. (4.53).

### 4.9.3 Self-Adducts, Type MAz(HA)b

Hydration only occurs in neutral complexes that are coordinatively unsaturated by the organic ligand. The hydrate water reduces the extractability of the complex. In the absence of strong donor molecules, which can replace this hydrate water, there is still a chance for the undissociated acid to replace the water, leading to a self-adduct according to the reaction

\[
\text{MA}_z(H_2O)_b + b\text{HA} \rightleftharpoons \text{MA}_z(\text{HA})_b + w\text{H}_2\text{O} \quad (4.54a)
\]

This competition between the formation of an adduct with HA or with H2O is observed as an increased extraction with increasing HA concentration. However, stoichiometrically the complexes MAz(HA)b and H2MAzHA, are equivalent. Formally the former is a self-adduct and the latter is an ion pair. Thus Eq. (4.54a) could be written

\[
\text{MA}_z(H_2O)_b + b\text{HA} \rightleftharpoons \text{M}(H_2O)_w\text{A}_{z/2}^b + b\text{H}^+ + w-2b\text{H}_2\text{O} \quad (4.54b)
\]

assuming the HA can replace 2 H2O through its bidentate structure. All of the hydrate water can be displaced by the organic ligand, with formation of negatively charged chelate complexes.

Chemical equilibrium experiments, e.g., distribution ratio measurements, cannot distinguish between these two types of complexes; however, they may be identified by fingerprinting techniques like NMR, IR, or X-ray structure determinations. Existence of similar adducts like MAzBb support the existence of self-adducts. The case of promethium(III) acetylacetone is an interesting illustration of this problem.

Example 7: Extraction of Pm(III) by acetylacetone.

Figure 4.14 shows the distribution ratio log \( D_{\text{org}} \) for promethium in the system acetylacetone (HA), benzene/1 M NaClO4 as a function of \(-\log[A^-] = \text{pA}\) at various starting concentrations, \([\text{HA}]_{\text{org}}\), of HA in the organic phase. The coordination number of Pm(III) with respect to oxygen is reported to be 8 or 9. In the aqueous phase all stepwise complexes up to PmHA, can therefore be expected to be formed. The vacant coordination sites may be filled with water (forming a hydrate) or undissociated acetylacetone (forming a self-adduct). The last assumption is supported by the fact that a large number of adducts of type LnA3Bb are known.

Omitting water of hydration, the distribution ratio becomes

\[
D_{\text{org}} = \frac{[\text{PmA}_n]_{\text{org}} + [\text{PmA}_n\text{HA}]_{\text{org}} + [\text{PmA}_n(\text{HA})_2]_{\text{org}} + \cdots}{[\text{Pm}] + [\text{PmA}] + [\text{PmA}_2] + \cdots + [\text{PmA}_n]} \quad (4.55a)
\]

which is abbreviated, using the earlier relations, to
Extraction of Pm(III) by acetylacetone (HAa) from 1 M NaClO₄ into benzene at three different original concentrations of HAa in the organic phase. pA = −log[AA⁻] is calculated according to Eq. (4.20). The analysis of the system yielded the constants log β₁ = 5.35, log β₂ = 9.20, log β₃ = 13.22, log β₄ = 14.06, $K_{ad1} = 7$, $K_{ad2} = 3$, and $K_{DC} = 0.008$, shown for Pm in Fig. 4.15. (From Refs. 27a,b.)

$D_{Pm} = \frac{K_{∞}\beta_i[A]^i}{(1 + K_{∞}[HA] + K_{∞}[HA]^2 + \cdots)}$ \hspace{1cm} (4.55b)

where $K_{DC}$ refers to the distribution of uncharged Pm₃⁺ between the benzene and the aqueous phase

$K_{∞} = [PmA]_{aq} / [PmA]_i$ \hspace{1cm} (4.56)

$K_{ad}$ is the equilibrium constant for the self-adduct formation in the organic phase, i.e.,

$PmA, B(\text{org}) + b HA(\text{org}) \rightleftharpoons PmA, (HA)_i, (\text{org})$ \hspace{1cm} (4.57a)

$K_{ad} = [PmA, (HA)_i,]_{aq} / [PmA,]_{aq} [HA]_{aq}$ \hspace{1cm} (4.57b)

For pedagogic reasons we rewrite Eq. (4.55b)
\[ D_{\text{pm}} = \frac{K_{\text{ex}}(1 + K_{\text{ad}}[\text{HA}]_{\text{org}} + K_{\text{ad}}'[\text{HA}]_{\text{org}}^2 + \cdots)}{(\beta_1[A^-])^{-1} \sum \beta_n[A^-]^n} \]  

(4.58)

Note that the denominator only refers to species in the aqueous phase. Thus at constant [HA]_aq, the curvature of the extraction curve and its position along the [A^-] axes is only caused by varying [A^-], i.e., the aqueous phase complexation. The numerator refers to the organic phase species only, and is responsible for the position of the extraction curve along the D-axis; thus at three different constants [HA]_aq, three curves are expected to be obtained, with exactly the same curvatures, but higher up along the D-scale with higher [HA]_aq concentration; see Fig. 4.14.

The asymptote with the slope of −3 at high pA (i.e., low [A^-]), fits Eq. (4.58), when Pm^+ dominates the denominator (i.e., the aqueous phase), while the asymptote with slope of +1 fits the same equation when the aqueous phase is dominated by PmA^-4. Between these two limiting slopes, the other three PmA^- complexes are formed in varying concentrations. A detailed analysis of the curves yielded all equilibrium constants \( K_{\text{ex}}, K_n, K_{\text{ad}}, \text{and } K_{\text{DC}} \) (see section 4.14.3), which are plotted in Fig. 4.15. The curves in Fig. 4.14 have been calculated with these constants. \( K_n \) is defined by

\[ \beta_1 = \Pi K_i \]  

(4.59)

according to Eq. (3.5).

The maximum distribution ratio for the Pm-HA system (\( D_{\text{pm}} \), about 0.1) is reached in the pH range 6–7. It is well known that the lanthanides hydrolyze in this pH region, but it can be shown that the concentration of hydrolyzed species is <1% of the concentration of PmA^- species for the conditions of Fig. 4.14, and can thus be neglected.

Self-adducts are rather common, and have been identified for complexes of Ca, Sr, Ba, Ni, Co, Zn, Cd, Sc, Ln, and U(VI) with acetylacetone, thienoyl trifluoroacetone, tropolone, and oxine. Table 4.14 lists some self-adduct constants. The fact that the constants vary with the organic solvent indicates that the self-adduct

---

**Fig. 4.15** The system La(III) acetylacetonate (HA) – 1M NaClO4/benzene at 25°C as a function of lanthanide atomic number Z. (a) The distribution ratio \( D_{\text{pm}} \) (stars, right axis) at [A^-] = 10^-3 and [HA]_aq = 0.1 M, and extraction constants \( K_{\text{ex}} \) (crosses, left axis) for the reaction Ln^3+ + 4HA(org) \( \leftrightarrow \) LnA_3HA(org) + 3H^+. (b) The formation constants, \( K_n \), for formation of LnA_3n- lanthanide acetylacetonate complexes (a break at Gd is indicated); circles \( n = 1 \); crosses \( n = 2 \); triangles \( n = 3 \); squares \( n = 4 \). (c) The self-adduct formation constants, \( K_{\text{ad}} \), for the reaction of LnA_3(org) + HA(org) \( \leftrightarrow \) LnA_3HA(org) for org = benzene. (A second adduct, LnA_3(HA)_2, also seems to form for the lightest Ln ions.) (d) The distribution constant \( K_{\text{DC}} \) for hydrated lanthanum triacetylacetonates, LnA_3(H_2O)_2, between benzene and 1M NaClO4. (From Ref. 28.)

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Table 4.14  Constants for the Formation of Some Metal Self-Adducts
According to $MA_{(org)} + b HA_{(org)} \rightleftharpoons MA_{(HA)}^b$.

<table>
<thead>
<tr>
<th>Metal ion $M^{z+}$</th>
<th>Ligand and adduct former HA Organicsolvent</th>
<th>Log $K_{al}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II)</td>
<td>Isopropyltropolone, IPT</td>
<td>CHCl$_3$</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Isopropyltropolone, IPT</td>
<td>CCl$_4$</td>
</tr>
<tr>
<td>La(III)</td>
<td>Acetylacetone, AA</td>
<td>C$_6$H$_6$</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>Thenoyltrifluoroacetone, TTA</td>
<td>CHCl$_3$</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>Thenoyltrifluoroacetone, TTA</td>
<td>CCl$_4$</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>Isopropyltropolone, IPT</td>
<td>CHCl$_3$</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>Isopropyltropolone, IPT</td>
<td>CCl$_4$</td>
</tr>
<tr>
<td>U(VI)</td>
<td>Acetylacetone, AA</td>
<td>C$_6$H$_6$</td>
</tr>
<tr>
<td>U(VI)</td>
<td>Thenoyltrifluoroacetone, TTA</td>
<td>C$_6$H$_6$</td>
</tr>
</tbody>
</table>

Source: Ref. 4.

reaction probably occurs in the organic phase. Table 4.14 contains both very inert (e.g., CCl$_4$), polar (CHCl$_3$), and pi-bonding solvents (C$_6$H$_6$).

4.10  METAL EXTRACTION BY LIQUID ANION EXCHANGERS (TYPE III-D)

Metals that react with inorganic ligands to form negatively charged complexes as described in Chapter 3 can be extracted into organic solvents with large organic cations in a process referred to as liquid anion exchange.

4.10.1  Two Industrially Important Cases

 Extraction of metals from chloride solutions into kerosene containing trioctyl amine (TOA), as illustrated by Fig. 1.3, has found application in the production of pure Co and Ni metals from their ores, as discussed in Chapter 11. The aqueous phase contains the Co and Ni in addition to other metals in chloride solution, where the chloride concentration goes to 300 g/L (i.e., about 8.5 M). At this high aqueous ionic strength, a rigorous mathematical treatment of the system would require the use of activities in order to explain the extraction.
diagram; however, here it suffices to use concentrations. An interesting feature in Fig. 1.3 is the differences between metals in various oxidation state, notably Fe(II) and Fe(III), the latter being much more easily extracted than the former because Fe(III) forms much stronger complexes with Cl\(^{−}\) ions. The requirement for extraction of metals by an aminelike TOA, or by its amine salt, TOAHCl\(^{−}\), is the formation of negatively charged metal chloride complexes in the aqueous phase. The complex formation from M\(^{z+}\) to MCl\(^{z−}\), where \(z − n ≤ −1\), proceeds in the stepwise manner described in Chapter 3. For example, Fe(III) forms the complex FeCl\(^{3−}\), while cobalt forms CoCl\(^{2−}\). The extraction reaction for Co can be written

\[
\text{CoCl}^{2−} + 2 \text{RHNCl} \overset{\rightleftharpoons}{\text{org}} (\text{RNH})\text{CoCl}_2(\text{org}) + 2 \text{Cl}^{−} \quad (4.60a)
\]

Amine extraction is used also in another important industrial process, the extraction of uranium from sulphuric acid leached ores, which uses trilauryl amine (TLA). In that case, the extraction reaction is

\[
\text{UO}_2(\text{SO}_4)_2^{2−} + 2 (\text{RHN})_2\text{SO}_4^{2−} \overset{\rightleftharpoons}{\text{org}} (\text{RNH})_2\text{UO}_2(\text{SO}_4)_2(\text{org}) + 2 \text{SO}_4^{2−} \quad (4.60b)
\]

These processes are referred to as liquid anion exchange, because the aqueous anionic metal complex replaces the anions Cl\(^{−}\) or SO\(^{2−}\) of the large organic amine complex. The amine complex is an ion pair, or salt, RHN\(^{+}\)L\(^{−}\), where R is a large hydrocarbon group. The amine salt is highly soluble in the organic (e.g., kerosene) phase, and almost insoluble in the aqueous phase. The reaction is presumed to occur either at the interface or in the aqueous phase with a low concentration of dissolved RHN\(^{+}\)L\(^{−}\). Before discussing these reactions in terms of molecular species, it is necessary to consider more specific aspects of liquid anion exchangers.

### 4.10.2 Properties of Liquid Anion Exchangers

As mentioned earlier, hydrogen ions can be solvated by strong donor molecules like TBP, sometimes leading to the extraction of a solvated hydrogen salt, HBL\(^{−}\); in Example 2, TBP extracts nitric acid, HNO\(_3\), in the form of the adduct complex TBP \(\cdot\) HNO\(_3\), which could be considered as the complex HTBP\(^{+}\)NO\(_3^{−}\) ion pair. The amines form stronger adducts with hydrogen ions; in fact, they are so strong that they remain protonated while exchanging the anion. A classical reaction is the formation of the ammonium ion NH\(_3^{+}\) when NH\(_3\) is dissolved in water.

The organic amines (the amine base RN) have a nitrogen atom N attached to a large organic molecule R usually containing >7 aliphatic or aromatic carbon atoms. They are highly soluble in organic solvents (diluents) and almost insoluble in water. In contact with an aqueous phase containing HL, the amine base
RN reacts with the acid HL to form RNH’L−, but extracts with an excess amount of acid HL (over the 1:1 HL:RN ratio) into the organic solvent, and also with additional water. The practical concentration of amine in the organic solvent is usually less than 20%; at higher concentrations the amine solutions become rather viscous. The amine salts dissociate in highly polar solvents, while in more inert diluents they easily polymerize to form micelles, and at higher concentrations a third phase. For example, in xylene (TLA·HBr), aggregates with n = 2, 3, and 30 have been identified, and in other systems aggregation numbers above 100 have been reported. TLA·HNO₃ is mainly trimeric in m-xylene at concentrations 0.002–0.2 M, but larger aggregates are formed at higher amine concentrations. These aggregates seem to behave like monofunctional species, each extracting only one anionic metal complex. The aggregation can be reduced, and the third phase formation avoided, by using aromatic diluents and/or by adding a modifier, usually another strong Lewis base (e.g., octanol or TBP). Such additions often lead to considerable reduction in the $K_{ex}$ value.

Four types of organic amines exist, as shown in Table 4.8: primary amines RNH⁺, secondary R₂NH⁺, tertiary R₃NH⁺, and quaternary R₄N⁺. The hydrocarbon chain R is usually of length C₈−C₁₂, commonly a straight aliphatic chain, but branched chains and aromatic parts also occur. In general the amines extract metal complexes in the order tertiary > secondary > primary. Only long-chain tertiary and—to a smaller extent—quaternary amines are used in industrial extraction, because of their suitable physical properties; trioctylamine (TOA, 8 carbons per chain) and trilauryl amine (TLA, 12 carbons per chain) are the most frequently used. For simplicity we abbreviate all amines by RN, and their salts by RNH’L−.

The tertiary and quaternary amine bases are viscous liquids at room temperature and infinitely soluble in nonpolar solvents, but only slightly soluble in water. The solubility of the ion-pair RNH’L− in organic solvents depends on the chain length and on the counterion, L−: the solubility of TLA·HCl in wet benzene is 0.7 M, in cyclohexane 0.08 M, in CHCl₃ 1.2 M, and in CCl₄ 0.7 M. Nitrate and perchlorate salts are less soluble, as are lower molecular weight amines.

The formation of the ion pair salt can be written

$$RN(\text{org}) + H^+ + L^- \rightleftharpoons RNH^-L^- (\text{org}) \quad K_{ex,am}$$ (4.61)

Table 4.15 gives the equilibrium constants $K_{ex,am}$ (for extraction, amine) for this reaction with trioctylamine in various solvents. Although the ion pairs are only slightly soluble in water, they can exchange the anion L− with other anions, X−, in the aqueous phase. (Note that we use L− to indicate any anion, while X− is used for (an alternative) inorganic anion.)

$$RNH^-L^- (\text{org}) + X^- \rightleftharpoons NH^-X^- (\text{org}) + L^- \quad K_{ex,ch}$$ (4.62)
Table 4.15  Equilibrium Constants $K_{ex,an}$ for Formation of Trioctyl Amine Salts [Eq. (4.61)]

<table>
<thead>
<tr>
<th>Anion</th>
<th>Solvent</th>
<th>Log $K_{ex,an}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$^-$</td>
<td>Toluene</td>
<td>3.0</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>Toluene</td>
<td>5.9</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>Carbontetrachloride</td>
<td>4.0</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>Benzene</td>
<td>4.1</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>Toluene</td>
<td>8.0</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>Toluene</td>
<td>6.6</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>Carbontetrachloride</td>
<td>5.0</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>Carbontetrachloride</td>
<td>6.7</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>Benzene</td>
<td>8.3</td>
</tr>
</tbody>
</table>

*The equilibrium constant refers to the formation of $(R_3NH)_2SO_4$.
Source: Ref. 5.

The equilibrium constant ($K_{ex,exch}$ for extraction, exchange) for this reaction increases in the order ClO$_4^-$ < NO$_3^-$ < Cl$^-$ < HSO$_4^-$ < F$^-$. From Chapter 3 it follows that the formation constants for the metal complex $ML^n_{z^-}$ usually increases in the same order. Therefore, in order to extract a metal perchlorate complex, very high ClO$_4^-$ concentrations are required; the perchlorate complex is easily replaced by anions higher in the sequence.

All negatively charged metal complexes can be extracted by liquid anion exchangers, independent of the nature of the metal and the complexing ligand. Liquid anion exchange has extensive industrial application, and many examples are given in later chapters. Lists of extraction values are found in other works [e.g., 5, 21].

**4.10.3 Equations for Liquid Anion Exchange Extractions**

The discussion on the properties of the amine salts serves to explain why, in metal amine extractions, it is difficult to obtain simple mathematical relations that agree well with the experimental data. While there is no difficulty, in principle, in obtaining reasonably good values for the formation of the negatively charged metal complexes in the aqueous phase, there is a major problem in defining the organic phase species, which may consist of free amine [RN], monomeric [RNHL], and polymeric [RNHL]$_n$ amine salt, and several extracted metal complexes [(RNH$^+$)$_n$](MLm$^a$)$_n$]. A contributing difficulty in practice is the need to use high ligand concentrations, [L$^-$], in the aqueous phase in order to obtain the negatively charged complexes (see Fig. 1.3).
In general the metal $M^{n+}$ reactions with a monobasic anion $L^-$ can be written

$$
M^{n+} + n L^- \rightleftharpoons ML_n^{2-n} \quad \beta_n = [ML_n^{2-n}] / [M^{n+}] [L^-]^n \quad (3.5, 4.34)
$$

When $z - n = p$ is negative, a negatively charged metal complex has been formed, which can be extracted

$$
ML_n^p + p RNH^+ L^- (org) \rightleftharpoons (RNH^+)^p ML_n^p (org) + p L^- \quad (4.63a)
$$

We define the extraction constant by

$$
K_{ex} = \frac{[\{RNH\}_p^p ML_n^p]_{org}}{[ML_n^p] [\{RNHL\}_p^p]_{org}} \quad (4.63b)
$$

A priori, it must be assumed that the aqueous phase contains all the stepwise complexes $ML_n^p$. Thus the distribution ratio is

$$
D_M = \frac{[\{RNH\}_p^p ML_n^p]_{org}}{\Sigma [ML_n^p]} = K_{ex} \frac{\beta_p [L^-]^p [\{RNHL\}_p^p]_{org}}{1 + \Sigma \beta_p [L^-]^p} \quad (4.64)
$$

The distribution of $M$ depends on both the free amine salt in the organic phase and the concentration of free $L^-$ in the aqueous phase until all metal in the aqueous phase is bound in the $ML_n^p$ complex. At constant amine concentration, Eq. (4.64) indicates that a plot of $D_M$ vs. $[L^-]$ would have a linear slope $p$ if the denominator of Eq. (4.64) is $\ll 1$; i.e., the metal species in the aqueous phase are dominated by the uncomplexed metal ion $M^{n+}$. At higher $[L^-]$ concentrations, where the $ML_n^p$ complex begins to dominate in the aqueous phase, the $D_M$ value becomes equal to $K_{ex} [\{RNHL\}_p^p]_{org}$. Equations (4.64) and (4.4) show that S-shaped curves result for metals with large $K_{ex}$ values. In a plot of $D_M$ vs. $[\{RNHL\}_p^p]_{org}$ a straight line of slope $p$ is obtained only at constant $[L^-]$. From such measurements both $p$, $K_{ex}$ and $\beta_p$ can be evaluated. The following example illustrates this.

**Example 8: Extraction of Trivalent Actinides by TLA.**

In an investigation of the extraction of trivalent actinides, An(III) from 0.01 M nitric acid solutions of various LiNO$_3$ concentrations into $o$-xylene containing the tertiary amine salt trilaurylmethylammonium nitrate, TLMA HNO$_3$, Van Ooyen [29] found that the amine was monomeric only at very low concentrations ($\leq$0.1M in the organic phase) but at higher concentration formed both dimers and trimers.

Using trace concentrations of Ce(III) and An(III) a log-log plot of $D_M$ against the nitrate ion activity, $n\gamma_k = [\text{LiNO}_3]^{1/2}$, had a slope of approximately 3, Fig. 4.16b. From Eq. (4.64) this slope corresponds to the $p$-value of 3 when the aqueous phase is dominated by the free metal ion, which is not an unreasonable assumption at low nitrate concentrations.
Fig. 4.16 Distribution ratio of M$^{3+}$ ions between the trilaurylmethyl ammonium nitrate (TLMA) in o-xylene and aqueous phases of varying LiNO$_3$ concentrations. (a) As a function of TLMANO$_3$ concentration at 1–7 M, 2–5 M, 3–3 M LiNO$_3$. (b) Extraction of Eu(III) and three actinide(III) ions at 0.1 M TLMANO$_3$ in o-xylene and varying aqueous salt concentrations. (From Ref. 29.)
In plots of log $D_{\text{Am}}$ against $[\text{TLMA} \cdot \text{NO}_3]_{\text{org}}$ at different nitrate concentrations, the curves in Fig. 4.16a had straight slopes of 1.5–1.8 at low concentrations of TLMA NO$_3$, but bending at higher concentrations, was explained by the formation of polymeric amine species. If Eq. (4.64) is valid, these slopes correspond to the number of TLMA HNO$_3$ groups attached to the extracted Am species. Thus Van Ooyen described his complex as $\{(\text{TLMA NO}_3)\}_n \text{Am(NO}_3)_3$, for which $n = 1$ only at the very low amine concentrations. Thus for $n = 1$ the complex could as well be written $(\text{TLMA})_2\text{Am(NO}_3)_5$. The Ce and other An complexes would have similar configurations.

### 4.11 OTHER EXTRACTABLE METAL COMPLEXES
(TYPE III-E)

<table>
<thead>
<tr>
<th>Ion pair (and possibly “counter species”)</th>
<th>$(C'X^- \text{ and } Y'A^-) \leftrightarrow C'A^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>in organic phase</td>
<td>↓↑</td>
</tr>
<tr>
<td>Aqueous cation $C'$ and anion $A^-$ associated</td>
<td>$C' + A^- \leftrightarrow C'A^-$</td>
</tr>
</tbody>
</table>

There are a few types of complexes that do not fit well into the previous classifications: monovalent metals that form extractable complexes with large organic monobasic anions, and, conversely, monovalent inorganic anions that form extractable complexes with large organic cations. Though the amine-type liquid anion exchangers could fit into the latter group, it is simpler to treat them as a separate homogenous group (class III-D). The large monovalent ion pair, tetraphenylarsonium tetraphenylborate ($\text{Ph}_4\text{As}^+ \text{Ph}_4\text{B}^-$), which has been suggested as a reference in solvent extraction (see Chapter 2), also belongs to this class.

Of some importance is the extraction of alkali ions by tetraphenylborate and by crown ethers (Appendix D: 21), of fluoride by tetraphenylantimonium ions, and of perrhenate by tetraphenylarsonium ions. Because most of the volume of these complexes is taken up by organic groups, the complexes are highly lipophilic and, therefore, extractable into organic solvents without additional solvation. Though these systems have limited applications, the crown ethers offer some interesting extraction systems. The ethers form cage compounds (“clathrates”); i.e., the metal cation fits into a cage formed by the crown structure. Because the cage can be designed to fit almost any ion of a certain size, rather selective extractions are possible with this system, as described in Chapter 15.

Example 9: Extraction of K$^+$ by tetraphenylborate.

Consider the extraction of K$^+$ from aqueous solution into the organic solvent nitrobenzene by addition of NaPh$_3$B. Abbreviating Ph$_3$B$^-$ by A$^-$, the extracted complex is the ion pair K$^+A^-$. In an inert solvent this is a stable ion pair, but in a highly polar solvent like nitrobenzene, the ion pair may dissociate. The organic phase may thus contain both solvated K$^+$ and K$^+A^-$ species, while
the only potassium species in the aqueous phase is free $K^+$.
The extraction equilibria may be written

$$K^+ + A^- \rightleftharpoons K^+ A^- \text{ (org) Equil. const. } K_{eq}$$ (4.65)

while for the reaction in the organic phase

$$K^+ A^- \text{ (org) } \rightleftharpoons K^- (\text{org}) + A^- \text{ (org) Equil. const. } K_{ass}$$ (4.66)

The distribution ratio of $K^+$ becomes

$$D_K = ([K^+ A^-]_{eq} + [K^-]_{eq}) [K^+]^4 = K_{eq} [A^-] (1 + K_{ass} /[A^-]_{eq}) [K]^4 \quad (4.67)$$

When $A^-$ is added into the aqueous phase as a Na$^+$ salt in large excess to $K^+$, the dissociation in the organic phase becomes negligible and Eq. (4.67) is reduced to

$$D_K = K_{eq} [A^-]$$ (4.68)

Figure 4.17 shows the distribution ratio of $K^+$ when a large excess of Na$^+ A^-$ is added to the system. Although the extracted complex should be com-

\[ \text{Fig. 4.17} \quad \text{Distribution ratio of potassium(I) between nitrobenzene and water as a function of initial aqueous tetraphenylborate concentration in 0.1M NaClO}_4. \text{ (From Refs. 30a,b.)} \]
pletely dissociated in the nitrobenzene, the ionic concentration of the organic phase is large enough to suppress dissociation, and the distribution ratio thus becomes proportional to the concentration of the extractant in the aqueous phase.

4.12 STUDIES OF HYDROPHILIC COMPLEXATION BY SOLVENT EXTRACTION (TYPE IV)

Solvextraction has become a common technique for the determination of formation constants, \( \beta_n \), of aqueous hydrophilic metal complexes of type \( MX_n \), particularly in the case when the metal is only available in trace concentrations, as the distribution can easily be measured with radioactive techniques (see also section 4.15). The method requires the formation of an extractable complex of the metal ion, which, in the simplest and most commonly used case, is an uncharged lipophilic complex of type \( MA_z \). The metal-organic complex \( MA_z \) serves as a probe for the concentration of metal \( M^{z+} \) ions in the aqueous phase through its equilibrium with the free \( M^{z+} \), section 4.8.2. This same principle is used in the design of metal selective electrodes (see Chapter 15). Extractants typically used for this purpose are \( \beta \)-diketones like acetylacetone (HAA) or thenoyltrifluoroacteone (TTA), and weak large organic acids like dinonylnaphthalene sulphonlic acid (DNNA).

The pertinent distribution equation is

\[
D_M = \frac{[MA_{z\text{org}}]}{[M] \left( 1 + \Sigma \beta_n [A]^n + \Sigma \beta_p [X]^p \right)}
\]  

(summed from 1 to \( n \) or \( p \)) where the formation constants for \( MA_z \) are \( \beta_z \) and those for the \( MX_p \) complexes \( \beta_p \) and summations are taken from 1. In the absence of \( MX_p \) complexes, the distribution ratio of \( M \) is defined by \( D_M^o \):

\[
D_M^o = \frac{[MA_{z\text{org}}]}{[M] (1 + \Sigma \beta_n [A]^n)}
\]  

If the conditions are chosen so that the aqueous complexes of HA can be neglected [see Eq. (4.41) and Example 4], \( D_M^o \) of Eq. (4.70) equals \( D_M \) of Eq. (4.41c); i.e.,

\[
D_M^o = D_M \text{ [of Eq. (4.41c)]} = K_{oH} [HA_{\text{org}}] [H^+]^{z+}
\]  

for which linear correlations are obtained in plots of \( \log D_M \) against \( \log [HA]_{\text{org}} \) at constant pH, or against pH at constant \( [HA]_{\text{org}} \). Dividing Eq. (4.69) by Eq. (4.70) gives

\[
D_M = \frac{[MA_{z\text{org}}]}{[M] \left( 1 + \Sigma \beta_n [A]^n \right)} \frac{1}{\left( 1 + \Sigma \beta_p [X]^p \right)}
\]  

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Thus a plot of \( D'/D \) against \([X]\) provides a polynomial from which the \( \beta_i \)'s can be calculated (see section 4.14).

Example 10: Determination of formation constants for Be(II) oxalate complexes.

Figure 4.18 shows the extraction of beryllium with HTTA into hexone as a function of the concentration of oxalate ions, \( \text{Ox}^{2-} \), in the aqueous phase. Here the conditions have been chosen so that the aqueous complexes of TTA can be neglected as has been described earlier, and thus Eq. (4.71) is valid, and the relation \( D^* = K_{\text{ex}} [\text{HA}]_2^2 [\text{H}]^2 \) so that

\[
\log D'/D = \log D \frac{K_{\text{ex}}^2 [\text{HA}]_2^2 [\text{H}]}{[\text{H}]^2} = -\log (1+10^{10}[\text{Ox}^{2-}]+10^{10}[\text{Ox}^{2-}])
\]  

(4.73)

The parameter values on the right-hand side of the equation, are the \( \beta_i \) values, and were determined by a curve fitting technique (section 4.14). Introducing these values in Eq. (4.71) gives the solid line through the points in Fig. 4.18.

The advantage of this “strange” ordinate is that the curvature only reflects the oxalate complexation.

Hydrolysis of some metals begins at very low pH (e.g., Zr at pH ~ 0.4, Th(IV) and U(VI) at pH 1–2, the lanthanides at pH 3–5, etc.). However, if complex

\[ D'/D = 1 + \beta_1[X] + \beta_2[X]^2 + \beta_3[X]^3 + \cdots \]  

(4.72)
formation strongly dominates over hydrolysis, the latter can be neglected. In the overview in section 4.3, it was shown in Fig. 4.3 that the general shape of the extraction curves indicates the type of complexes formed. Thus, the extraction of gallium(III) with acetylacetone, Fig. 4.19, indicates a behavior according to Fig. 4.3c. in the plot of log $D$ vs. free ligand concentration, $[A^-]$.

Example 11: Formation of hydrolyzed Ga(III) acetylacetonates.

Figure 4.19 shows the extraction of Ga(III) by acetylacetone into benzene at various concentrations of total acetylacetone, $[HA]_t$, and constant ionic strength, using the AKUFVE technique (see section 4.15.3). By comparing with Fig. 4.3, one may guess that hydroxy complexes are formed (diagram c). If the general complex is designated Ga$_m$A$_4$(OH)$_p$, a first investigation showed

![Graph showing distribution of Ga(III) between benzene and 1 M NaClO$_4$ as a function of $pA = -\log[A^-]$ at 6 different acetylacetone (HA) concentrations (0.06–0.0006 M). The different curves are due to different extent of hydrolysis in the aqueous phase. The concentration of HA decreases from the upper left corner, where $[HA]_{aq}$ is 0.06 M (▲), toward the right lower corner, where it is 0.0006 M (◇). (From Ref. 32.)](image)
that no polynuclear complexes were formed, i.e., $m = 1$, as the extraction curves were independent of the Ga(III) concentration. This was also expected as the total concentration of Ga(III) ranged from $10^{-4}$ to $10^{-6}$ M. Next, using a computer program, the formation constants for the following complexes were determined: GaA$^2$; GaA$^+$, GaA$^+$, Ga(OH)$_3$ and Ga(OH)$_4$; [32]. It was concluded that no mixed complexes with both A$^-$ and OH$^-$ were formed. The organic phase contained only GaA$_3$ (which was hydrated).

In using this technique accurately, it is necessary to consider possible sources of errors. A rather extensive summary of this technique applied to hydrophilic actinide complexation by practically all inorganic ligands, as well as a considerable number of weak organic acids, has recently been presented [33a,33b].

4.13 EFFECTS AND CORRELATIONS

Because of the many parameters involved in solvent extraction, chemical as well as physical, it is a difficult task to draw reliable conclusions about the reactions that are responsible for the observed distribution values. In the introductory part of this chapter, section 4.2, the extraction reaction described by $K_{ex}$ was shown to be a product of a number of parameters related to the different steps involved in the formation of the extracted complex. Sections 4.4–4.11 have described these various subreactions, which are described by Eq. (4.46):

$$K_{ex} = K_a^z \beta_z K_{i\text{tr}}^z K_{a\text{MB}}$$

(4.46, 4.74)

Examples of how $K_{ex}$ data may be interpreted in more fundamental terms follow. In the lack of information on the independent parameters of Eq. (4.74), tenable conclusions can be drawn about their size and effects from known correlations between the parameters. This section explores the effect of such correlations.

4.13.1 Effects of the Dissociation Constant of Acidic Ligands and Formation Constants of the Corresponding Metal Complexes

4.13.1.1 The Ligand (Acid) Dissociation Constant $K_a$

According to Eq. (4.74) $K_{ex}$ increases to the $z$ power of the dissociation constant, $K_a$, for the extractant acid HA. Thus it appears desirable to use stronger acids as extractants, i.e., those with large $K_a$ (or small p$K_a$). Thus factors that affect the dissociation constant of an acid are of importance for extraction behavior.

The acidity of organic acids increases (i.e., p$K_a$ decreases) by electrophilic substitution in the carbon chain. For example, replacing an H atom in the CH$_3$ group of acetic acid (p$K_a$ 4.75) by I, Br, Cl, and F atoms yields monohalide acetic acids with p$K_a$ of 3.0, 2.9, 2.8, and 2.7, respectively. The mono-, di-, and trichloroactic acids have p$K_a$ 2.8, 1.48, and about 1.1, respectively. Other
Electrophilic groups which can increase acidity are HO—, NC—, NO₂—, etc. Conversely, nucleophilic substitution by aliphatic or aromatic groups usually has little effect on the pKₐ, though it may affect the distribution constant KᵢR (see section 4.13.2): e.g., the addition of a CH₂— or C₆H₅— group in acetic acid changes the pKₐ to 4.9 (propionic acid) and 4.3 (phenyl acetic acid). The further the substitution is from the carboxylic group, the less the effect: e.g., while pKₐ for benzoic acid is 4.19, a Cl in orthoposition yields pKₐ 2.92 and in the paraposition, 3.98.

These general rules hold rather well for the acidic organic extractants and can be used to extrapolate from related compounds to new ones as well as to develop new extractants. The effect of various substituents on pKₐ is extensively discussed in textbooks on organic chemistry [e.g., 14, 34].

4.13.1.2 The Complex Formation (or Stability) Constant βₙ

Kₓ also increases with increasing formation constant of the uncharged metal complex, βₓ. Thermodynamic factors and geometrical aspects that influence the size of βₙ are discussed in Chapter 3. Some further observations follow.

To achieve the highest possible D value, the concentration of the extracted uncharged complex (MAₓ, MAₓBₓ or BₓMLₓ+₁) must be maximized. A large value for the formation constant of the neutral complex favors this goal. In Chapter 3 it was pointed out that for hard acids the complex formation constant increases with the charge density of the metal ion, provided there is no steric hindrance. This is seen for the metal fluoride complexes in Fig. 3.4 (no steric hindrance). For the lanthanide acetylacetonates in Fig. 4.15b, the increase in βₙ from 5-La to 6-Gd is due to a reduction in the ionic radius and, accordingly, to the increased charge density. It should be noted that the diminishing lanthanide size leads to a successive diminution of the coordination number (from 9 to 8 for H₂O) for La → Gd; for Gd → Lu the coordination number is probably constant, as is inferred from Fig. 4.15c; see also [35].

4.13.1.3 Correlations Between Kₐ and βₙ

Because the H⁺ ion acts as a hard metal ion, one should expect a close correlation between the formation constants for HA and for MAₓ. Since Kₛ is defined as the dissociation constant of HA, while βₓ is the formation constant of MAₓ, a correlation is therefore expected between pHₒ (=-logKₛ) and logβₓ. The correlations in Figs. 3.5 and 3.6 show that large logβₓ values are usually observed for organic acids with large logKₛ. Since Kₓ is directly proportional to both βₓ and Kₛ [see Eq. (4.74)], and a large βₓ value is likely to be accompanied by a small Kₛ value (large pKₛ); in Eq. (4.74) the two parameters counteract each other. Thus in order to obtain high free ligand concentrations, which favors the formation of the MAₓ complex, [H⁺] must be low, i.e., pH must be high. How-
ever, at high pH the metal may be hydrolyzed. A careful balance must be struck between $\beta_\alpha$, $K_\alpha$, and pH to achieve an optimum maximum concentration of the uncharged complex.

### 4.13.2 Effects of Molecular Volume and Water Structure Upon $K_D$

Chapters 2 and 3 factors are discussed which affect the distribution of uncharged species between the organic and aqueous phases, the most important being (1) the interaction of the species (complex or extractant) with the solvents (solvation); and (2) energy released or required when an uncharged species leaves its original phase (cavity closure) and that required when it enters the new phase (cavity formation). Sections 4.4 and 4.5 discuss the distribution of inert species, including undissociated acid HA, $K_{\text{OR}}$. From Eq. (4.74) it is seen that $K_\alpha$ is negatively influenced by a large distribution constant for the extractant reagent, but favored by a large $K_{\text{DC}}$ for the extraction of the metal complex.

#### 4.13.2.1 Metal Complexes, $K_{\text{DC}}$

There are rather limited data on systematics for the distribution constants $K_{\text{DC}}$ of metal complexes. Table 4.10 gives distribution constants for Zn(II), Cu(II), and Np(IV) acetylacetonates in various solvents. The zinc complex has an octahedral coordination: four oxygen atoms from the ligands and two oxygen atoms from water molecules can occupy six positions in an almost spherical geometry around the zinc atom. The copper complex has a square planar configuration with four oxygen atoms from the acetylacetonates in the plane; a fifth (and possibly sixth) position perpendicular to the plane and at a longer distance from the copper atom can be occupied by an oxygen from a water molecule. The zinc complex has a larger degree of hydration in the aqueous phase and consequently a lower distribution constant. The NpA$_3$ structure is likely a square antiprism with no hydrate water. It has a larger molecular volume than the two other complexes, and its larger distribution constant is in agreement with this, reflecting the release of more water structuring energy when leaving the aqueous phase.

Two further observations can be made from Table 4.10: (1) the distribution constant seems to increase with increasing polarity of the solvent; (2) when the reagent acetylacetone has a large $K_{\text{OR}}$, the metal complexes also show a large $K_{\text{DC}}$ value.

The lanthanide ions, Ln$^{3+}$, are known to contract with increasing atomic number ($Z$), from La$^{3+}$ with a hydrated radius of 103 pm to Lu$^{3+}$ of 86 pm (lanthanide contraction). Thus one expects that the neutral LnA$_3$ complex becomes smaller with increasing atomic number, and consequently that $\beta_\alpha$ should increase and $K_{\text{DC}}$ decrease with increasing $Z$. Figure 4.15d shows that measured
$K_{DC}$ values for the lanthanide acetylacetonates are the reverse from that expected for the size effect. The explanation is likely that the neutral complex with the formula LnA$_3$ is coordinatively unsaturated, which means that a hydrated complex exists in the aqueous phase (possibly also in the organic phase). The more coordinatively unsaturated lanthanide complexes (of the larger ions) can accommodate more water and thus are more hydrophilic. The result is a $K_{DC}$ several orders of magnitude lower for the lightest, La, than for the heaviest, Lu.

The tetravalent metal acetylacetonates [36] have all coordination numbers (CN) 8 or 9 in the neutral complexes. For Th (radius 109 pm at CN 9) there is often one molecule of water in ThA$_4$, whereas for the corresponding complexes of U(IV) and Np(IV) (radius 100 and 98 pm, respectively, CN = 8), there seems to be none. The measured distribution constants (log $K_{DC}$) are for Th 2.55 and for U and Np 3.52 and 3.45, respectively, in 1 M NaClO$_4$/benzene. This agrees with the greater hydrophilic nature of the ThA$_4$ · H$_2$O complex.

4.13.2.2 Correlations Between $K_{DR}$ and $K_{DC}$

Qualitatively, the distribution constants of the complexing reagent and the corresponding neutral metal complex are related due to their similar outer surface toward the solvents. Thus it is reasonable that there should be good correlation between $K_{DR}$ and $K_{DC}$ for homologous series of reagents or complexes. This is indeed the case, as is seen when $K_{DR}$ is plotted vs. $K_{DC}$, in Fig. 4.20 for a complex with a variation of the solvent, and in Fig. 4.21 for complexes of related reagents with the same solvent. This correlation can be related to the solubility parameter concept discussed later.

4.13.3 The Solubility Parameter

In Chapter 2 we learned that the cohesive forces that keep molecules together in a solution can be described by

$$\delta^2 = (\Delta H_v - RT) / V$$

(2.1; 4.75a)

where $\delta^2$ is the cohesive energy density, and $\delta$, the solubility parameter, $V$, the molar volume and $\Delta H_v$, the molar heat of vaporization. This holds for regular solutions [37] that show ideal entropy effects in mixing solute and solvent, and no interactions occur besides the cohesive forces between the solute and solvent molecules. [Note: Regular solutions exhibit heat changes when mixed, while for ideal solutions, the heat of mixing is zero (see section 2.4.1).] There is no change of state in association or in orientation. Thus the work required to produce a cavity, $\Delta G_{cav}$, by the solute in the solvent is given by

$$\Delta G_{cav} = A_{cav} V_B \delta^2$$

(2.10; 4.75b)

where $A_{cav}$ is a proportionality factor and $V_B$ is the molar volume of the solute B.
Pioneering work on the application of this theory for correlating and predicting distribution ratios was done in the 1960s [38a–40c]. Several reviews on the use of this theory for two-phase distribution processes are also available [41,42]. Recently this theory has been refined by the use of Hansen solubility parameters [6,43,44], according to which

\[ \delta_{\text{total}}^i = \delta_{\text{dispersion}}^i + \delta_{\text{polar}}^i + \delta_{\text{hydrogen}}^i \]  

where interactions between the solute and the solvent are described by contributions from the various types of cohesive forces. In general, the dispersion (or London) forces dominate. In Fig. 4.22 the measured distribution ratios of an americium complex between an aqueous nitrate solution and various organic solvent combinations are compared with distribution ratios calculated from tabulated Hansen parameter values [45].

Few solubility parameters are available for the metal-organic complexes discussed in this chapter. Another approach is then necessary. The distribution constant for the reagent (extractant), \( R \), can be expressed as:
Fig. 4.21 Distribution constants, $K_{DC}$, for uncharged metal complexes MA, vs. distribution constants $K_{DR}$ for the corresponding undissociated acid ligand HA; solid circles Zn(II), solid triangles Co(III). Variation with ligand composition: HFA hexafluoroacetylacetone, TFA trifluoroacetylacetone, AA acetylacetone, FTA 2-furoyltrifluoroacetone, TTA 2-thenoyltrifluoroacetone, PTA pivaloyltrifluoroacetone, BFA benzoyltrifluoroacetone, BZA benzoyleacetone. (From Ref. 36.)
Fig. 4.22 Comparison of measured and calculated distribution ratios $D_{am}$ of americium(III)-terpyridine-decanoic acid complexes between 0.05 M HNO$_3$ and various organic solvent combinations. The calculated values are obtained with the Hansen partial solubility parameters. (From Ref. 45.)

\[
RT \ln K_{DR} = V_r[(\delta_{aq} - \delta_r)^2 - (\delta_{org} - \delta_r)^2] + RT V_r (1/V_{org} - 1/V_{aq}) \quad (4.76)
\]

where $K_{DR}$ is given in terms of mole fractions. The solubility parameter of water has to be empirically estimated. The thermodynamic value is 48, but, since the system may be sensitive to the choice of $\delta_{aq}$, it is better to select a “reference $\delta_{aq}^r$” in each set of experiments, assuming constant values for the aqueous systems in the two different two-phase systems. Molar volumes and solubility parameter values are listed in Table 2.1 and Refs. [6,44].

The overall enthalpy and entropy changes for the distribution reaction (i.e., transfer of the metal complex from the aqueous to the organic phase) can be obtained from the temperature dependence of $K_{DR}$ according to

\[
RT \ln K_{DR} = -\Delta H + T \Delta S \quad (4.77)
\]

An enthalpy term corresponding to $-V_r[(\delta_{aq} - \delta_r)^2 - (\delta_{org} - \delta_r)^2]$ and an entropy term corresponding to $RT V_r(1/V_{org} - 1/V_{aq})$ can be obtained formally from Eq. (4.76). If the distribution constant for a standard system is used as a reference, changes in enthalpy and entropy relative to this standard system can be assessed by replacing $\delta_{aq}$ and $V_{aq}$ with the corresponding data for the organic diluent in the reference system, $\delta_{aq}^r$ and $V_{aq}^r$. © 2004 by Taylor & Francis Group, LLC
Thus from solubility parameters, which are specific for the various solutes and solvents, and molar volumes, values for $K_{\text{DR}}$ can be estimated, or deviations from regularity can be assessed. These deviations can be estimated quantitatively and, in individual systems, can be ascribed to specific reactions in either of the phases, e.g., hydration, solvation, adduct formation, etc.

From Eq. (4.76) the relation

$$\log K_{\text{DC}} = (V_C / V_R) \log K_{\text{DR}} + \text{const.}$$

(4.78)
can be derived; the subscript $C$ refers to the neutral metal complex. The molar volume ratio is close to or smaller than $z$, where $z$ is the number of singly charged anionic species attached to the central metal ion $M^{z+}$. From Fig. 4.23 a ratio of ca. 1.5 (for $z = 2$) is obtained. This equation is useful for estimating $K_{\text{DR}}$ values in extraction systems where the corresponding $K_{\text{DC}}$ value is known.

Rearrangement of Eq. (4.75) shows that $\log K_{\text{DR}}/(\delta_{\text{aq}} - \delta_{\text{org}})$ vs. $\delta$, where

$$\delta = \delta_{\text{aq}} - \delta_{\text{org}} - \left( V_{\text{org}} / V_{\text{aq}} \right)$$

(4.79)

should yield a straight line with slope $V_R / RT \ln 10$. A plot of this relation in Fig. 4.23 demonstrates a satisfactory correlation between distribution constants and solvent parameters, indicating the usefulness of the solubility parameter concept in predicting $K_{\text{DR}}$ as well as $K_{\text{DC}}$ values.

Fig. 4.23 Application of the regular solution theory for correlation of distribution constants for ZnA$_2$ and CuA$_2$ with solvent properties (solubility parameters); the numbers refer to the solvents listed in Table 4.10. (From Ref. 22.)
4.13.4 Effects of the Solvent (Diluent) Composition

The composition of the organic phase solvent (diluent) influences the distribution of both the neutral metal organic complex MA, and the complexing reagent HA, through similar interactions ranging from that of cavity formation for very inert diluents like hexane, through dipole-dipole interactions, pi electron interaction, and hydrogen bonding for the more reactive solvents. The expected degree of interaction can be judged from values of permittivity and solubility parameters. Previous tables have illustrated some of these aspects: Table 4.1 on the distribution of inert solutes (hole formation), Table 4.7 on distribution of organic acids (polarity), and especially Table 4.10 on distribution of metal acetylacetonates (solvent permittivity), discussed in section 4.13.2.1. These cases involve the aqueous phase, so some phenomena may be attributed to the interaction with water molecules.

Figure 4.24 shows a decrease in $K_D$ for acetylacetone with increasing number of methyl groups in the substituted benzene solvent. Since acetylacetone is more soluble in aromatics than in aliphatics, as illustrated by the $K_{DR}$ sequence:

![Fig. 4.24](image)

**Fig. 4.24** Distribution constants $K_{DR}$ of acetylacetone between methyl-substituted benzenes at different aqueous ionic strengths: (a) 0.001 M, (b) 0.1 M, and (c) 1.0 M NaClO$_4$ at 25°C. The number of methyl groups, $n$, changes the aromatic character at $n = 0$ to more aliphatic at $n = 3$. (From Ref. 46.)
hexane 0.95, cyclohexane 1.03, ethylbenzene 3.31, and benzene 5.93 (aqueous phase 1M NaClO₄), the decrease observed in Fig. 4.24 may simply be an effect of the increasing aliphatic character of the solvents.

4.13.5 Effects of the Aqueous Medium

The effect of the water activity of the aqueous phase, discussed in Chapters 2, 3, and 6, is determined by the total concentration and nature of the salts. Generally, the distribution constant for a neutral metal complex would increase with increasing ionic strength, as illustrated in Fig. 4.25. This salting-out effect is often ascribed to a reduction in free water available for hydration. On the other hand, the salt also breaks down the water structure, which could reduce the energy to form a hole in the phase.

4.13.6 Effects of the Temperature

The introduction of a neutral complex into a solution phase involves a number of processes that can be associated with large changes in enthalpy (solvation processes) and in entropy (solute orientation and restructuring), leading to considerable temperature effects; see Chapter 2. In general, the distribution of a neutral metal complex increases with increasing temperature for complexes with significant hydrophobic character. The metal acetylacetonate systems in Fig. 4.26 illustrate this effect. In these particular systems, the free energy of distribution between the organic and aqueous phases is dominated by the enthalpy term.

![Fig. 4.25](image)

**Fig. 4.25** The distribution constant $K_{DC}$ for zinc diacetylacetonate, ZnA₂, between benzene and various concentrations of NaClO₄ in the aqueous phase; 25°C. (From Ref. 36.)
Fig. 4.26  Distribution constant $K_{D}$ for metal diacetylacetonates, $\text{MA}_{z}$, between organic solvents and 1 M $\text{NaClO}_{4}$ as a function of temperature: Cu(II) (open circles) and Zn(II) (solid circles) with various solvents (numbers refer to the solvents given in Table 4.10). (From Ref. 36.)

From measurements of the temperature dependency of the equilibrium constant, thermodynamic parameters may be deduced (section 3.4). Very few enthalpy and entropy constants have been derived for the distribution reaction $\text{MA}_{z}(\text{aq}) \rightleftharpoons \text{MA}_{z}(\text{org})$ of neutral complexes; such investigations give information about hydration and organic phase solvation.

4.13.7  Further Structural Considerations

In Chapters 2 and 3 several physicochemical factors of importance to solvent extraction have been described, and many of their effects have been illustrated in this chapter. Here, we summarize some observed regularities. The effect of various structures on the bond strengths in metal organic complexes has been extensively treated in other publications [47–49].

4.13.7.1  Chelate Ring Size

Formation of metal-organic chelate complexes results in stronger complexation (i.e., larger $\beta$ values) compared to interaction with monodentate ligands (Chapter 3). The common types of bidentate ligands are presented in Table 4.9; the chemistry of these complexes has been extensively discussed in the literature [14,47]. Chapter 3 presents the most important factors in the formation of such complexes: (1) the type of binding atom; (2) the chelate ring size (or “bite”);
and (3) the number of chelate rings formed (mono- or polydentate). The following diagram illustrates the general structure of UO$_2$$^{2+}$ and Am$^{3+}$ diamide chelate complexes: two oxygen binding atoms; ring size is $5 + n$, 2–3 chelate rings per complex; the $\text{O}^{-}\text{M}^{-}\text{O}^{-}$ part is commonly referred to as the “claw.”

\[
\begin{array}{c}
\text{N} \\
/ \ \\
\text{CH} \\
O
\end{array} \quad \begin{array}{c}
\text{C}_n\text{H}_{2n} \text{N} \\
/ \\
\text{CH} \\
O
\end{array} \quad \begin{array}{c}
\text{N} \\
/ \ \\
\text{CH} \\
O \\
\text{M}
\end{array}
\]

The extractants TBOA, TBMA, and TBSA are very similar, but their structural differences (see formulas in Table 4.16) allow the formation of only one type of metal chelate complex: 5-, 6-, and 7-membered rings, respectively. Similarly, the reactants DMDOMA and DMDOSA form only 6- and 7-membered chelates. Table 4.16 shows that extraction (i.e., largest $K_{ex}$ value) is favored by 6-membered rings. This is not unexpected as the $K_{ex}$ values in this case reflect the stability constants $\beta_n$ acc. to Eq. (4.74).

The electron shells of the M$^{3+}$ elements with unfilled or partially filled 3d, 4d, and 5f orbitals contract as these shells are being filled with electrons, increasing the charge density ($z/r$) of the cation, leading to increasing stability constants for the MA$_3$ complexes with increasing atomic number. For bidentate ligands the f-electron (lanthanide) MA$_3$ complexes are coordinatively unsaturated, i.e., only six of eight available coordination sites are filled. Therefore, the two remaining sites are occupied by H$_2$O or HA or some other donor molecules B, leading to the self-adduct MA$_3$HA$^{-}$ or adduct MA$_3$B$_{1-2}$. It has been shown that the adduct formation constants for the reaction MA$_3$ + B $\rightarrow$ MA$_3$B decrease.

**Table 4.16** Consultants for Extraction of Actinide Amides from Nitrate Solutions into an Organic Solvent Showing the Effect of Chelate Ring Size

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Extractant$^a$</th>
<th>$K_{ex}$</th>
<th>Ring size</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$$^{2+}$</td>
<td>TBOA</td>
<td>0.005</td>
<td>5</td>
<td>[50]</td>
</tr>
<tr>
<td>UO$_2$$^{2+}$</td>
<td>TBMA</td>
<td>10.6</td>
<td>6</td>
<td>[50]</td>
</tr>
<tr>
<td>UO$_2$$^{2+}$</td>
<td>TBSA</td>
<td>9.3</td>
<td>7</td>
<td>[50,51]</td>
</tr>
<tr>
<td>Am$^{3+}$</td>
<td>DMDOMA</td>
<td>0.47</td>
<td>6</td>
<td>[52]</td>
</tr>
<tr>
<td>Am$^{3+}$</td>
<td>DMDOSA</td>
<td>$&lt;0.0002$</td>
<td>7</td>
<td>[52]</td>
</tr>
</tbody>
</table>

$^a$TBOA (C$_4$H$_9$)NCO$^-$; TBMA [(C$_4$H$_9$)NCO]$^-$CH$_2$; TBSA [(C$_4$H$_9$)NCO]$^-$(CH$_3$)$_2$; DMDOMA (CH$_3$C$_8$H$_{17}$NCO)$^-$CH$_2$; DMDOSA (CH$_3$C$_8$H$_{17}$NCO)$^-$(CH$_3$)$_2$.
in the same order [27a–28], see Fig. 4.15; i.e., the stronger the complex, the weaker the adduct.

The increase, by adduct formation, in the coordination number of the central atom is possible not only for weak but also for strong chelates, provided their ligand bites are relatively short. To make room in the inner sphere of the metal ion for another adduct-forming ligand, three chelating ligands of small bite angle can easily be shifted away without significant energy-consuming distortion of the chelate rings [53a,b]. The electronic structure of the central atom is also of key importance for synergism, as illustrated by the easy adduct formation of metal ions with unfilled or partially filled d or f orbitals, contrary to, e.g., p-block elements. Inner- and outer-sphere complexation is further discussed in the next two paragraphs and in Chapter 16.

4.13.7.2 Donor Ligand Effects

Table 4.17 shows extraction constants for some metal ions with three alkyl phosphates substituted by 0, 1, and 2 sulfur atoms, but with almost identical aliphatic branchings. Section 3.3 discusses hard and soft acids and bases (HSAB theory). According to this theory, hard acids form strong complexes with hard bases, while weak acids form strong complexes with weak bases. In Table 4.17, the metals are ordered in increasing hardness, the sub II.b group being rather soft (Table 3.2). Presumably the $K_{ex}$ values reflect this pattern, as they are proportional to $K_{a}$ and $\beta_{1}$. In Table 4.17, the acidity of the acids increases (i.e., $K_{a}$ increases) in order $R \cdot$ PSSH $< R \cdot$ POSH $< R \cdot$ POOH (consult Tables 4.8 and 4.9), as sulfur is less basic than oxygen. In general, the $K_{ex}$ increases for for the dialkyl phosphoric acid (hard donor ligand) with increasing metal charge density within each group as predicted in Chapter 3. For the soft metals, $K_{ex}$ also increases with increasing softness of the ligand, while the opposite effect is seen for the hard Ln-metal ions. The divalent subgroup II.b metals prefer to bind to sulfur rather than to oxygen because they have a rather soft acceptor character, while the hard metals III.b prefer to bind to the hard O-atom of the ligand.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Hg$^{2+}$</th>
<th>Cd$^{2+}$</th>
<th>Zn$^{2+}$</th>
<th>$\gamma$La$^{3+}$</th>
<th>$\theta$Eu$^{3+}$</th>
<th>$\gamma$Lu$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge density $Z/r$</td>
<td>3.6</td>
<td>4.1</td>
<td>5.4</td>
<td>7.83</td>
<td>8.74</td>
<td>9.68</td>
</tr>
<tr>
<td>log $K_{ex}$ for $R \cdot$ POOH</td>
<td>$-2.20$</td>
<td>$-1.80$</td>
<td>$-1.20$</td>
<td>$-2.52$</td>
<td>$-0.44$</td>
<td>2.9</td>
</tr>
<tr>
<td>log $K_{ex}$ for (C$<em>{4}$H$</em>{9}$O)$_{2}$POSH</td>
<td>5.40</td>
<td>3.70</td>
<td>0.70</td>
<td>$-4.78$</td>
<td>$-4.23$</td>
<td>0.34</td>
</tr>
<tr>
<td>log $K_{ex}$ for (C$<em>{4}$H$</em>{9}$O)$_{2}$PSSH</td>
<td>4.40</td>
<td>3.49</td>
<td>2.40</td>
<td>$-8.28$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Values estimated from Refs. 5, 20, 54, 55, and 56. R is (C$_{4}$H$_{9}$CH(C$_{2}$H$_{5}$)CH$_{2}$O)$_{2}$.

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4.13.7.3 Inner and Outer Sphere Coordination

The extractabilities of metal-organic complexes depend on whether inner or outer sphere complexes are formed. Case I, section 4.2.1, the extraction of uranyl nitrate by TBP, is a good example. The free uranyl ion is surrounded by water of hydration, forming UO$_2$(H$_2$O)$_6^{2+}$, which from nitric acid solutions can be crystallized out as the salt UO$_2$(H$_2$O)$_6^{2+}$(NO$_3$)$_2^{-}$, though it commonly is written UO$_2$(NO$_3$)$_3$(H$_2$O)$_6$. Thus, in solution as well as in the solid salt, the UO$_2^{2+}$ is surrounded by 6 H$_2$O in an inner coordination sphere. In the solid nitrate salt, the distance $d_{U,O}$ (nitrate) between the closest oxygen atoms of the nitrate anions, (O)$_2$NO, and the U-atom is longer than the corresponding distance, $d_{U,O}$ (water), to the water molecules, OH, i.e., $d_{U,O}$ (nitrate) > $d_{U,O}$ (water); thus the nitrate anions are in an outer coordination sphere.

When the adduct former TBP is added, the OP(OC$_4$H$_9$)$_3$ groups are closer to the U-atoms than the OH$_2^-$’s, $d_{U,O}$(TBP) < $d_{U,O}$(water), two waters are expelled, although the OP-bond only occupies one coordination site. The charge distribution around the UO$_2$-group allows the nitrate group to enter the inner coordination sphere of the uranyl complex. The resulting configuration is shown in Fig. 4.27. Thus, the extraction reaction can more correctly be written

$$\text{UO}_2(\text{H}_2\text{O})_6^{2+} + 2 \text{NO}_3^- + 2 \text{TBP} \rightarrow \text{UO}_2(\text{TBP})_2(\text{NO}_3)_2(\text{org}) + 6 \text{H}_2\text{O} \quad (4.5b)$$

In many systems it is difficult to distinguish between inner and outer sphere complexation. In that case, knowledge about the thermodynamic parameters $\Delta H$ and $\Delta S$ may be of help. For inner sphere complexes, the hydration is disrupted more extensively and the net enthalpy and entropy changes are positive. In Eq. (4.5b) it is noted that the number of entities increases from five to seven, an entropy increase. This entropy effect (i.e., $-T\Delta S$) is obviously larger than the enthalpy effect, as the overall energy change $\Delta G$ is negative. In outer sphere complexes, the dehydration is less disrupted, and the net enthalpies and entropies are negative owing to the complexation with its decrease in randomness without a compensatory disruption of the hydration spheres.

Migration experiments have shown that the hydrated cations not only carry with them the water in the inner coordination sphere, but also one or more shells of additional water molecules, for typical total values of 10–15. When the metal ion leaves the aqueous phase in the solvent extraction step, this ordered coordinated water returns to the bulk water structure, contributing an additional factor to consider in evaluating the thermodynamics of extraction.

4.13.7.4 Steric Hindrance

The closer the reactive ligand atoms get to the central metal ion, the stronger the bond, and, consequently, the greater the formation constant. This can be
Fig. 4.27  Structure of the UO$_2$(NO$_3$)$_2$·2(C$_2$H$_5$O)$_3$PO. The uranyl oxygens are situated perpendicular to the plane shown around the central atom. (From Ref. 12.)
studied by making substitutions in the organic ligand, which structurally interferes with the formation of the complex. For example, Dyrsen [8] substituted oxines (8-hydroxyquinolinols), Appendix D.6 in various positions, Table 4.5, and measured their distribution constants, $K_{DC}$. Although the $pK_a$ and $K_{DHA}$ in Table 4.5 did not vary much with the substitution, the $K_{DC}$ for the ThA₄ complex with unsubstituted oxine was 425, and for the 5-methyl substituted complex around 1000, while the 2-methyl substituted complex was not extractable. This can be attributed to the 2-methyl group blocking the complex formation.

Table 4.18 lists $K_{ex}$ values for UO₂⁺ and Pu⁴⁺ with four organophosphorous extractants, TBP and DOBA, and TiBP and DOiBA, the $iso$-forms being more branched. The data in the upper half of the table shows little change in $K_{ex}$ when TBP is replaced by TiBP. Thus the branching has little effect due to the free rotation of the substituents around the phosphorous atom. In the lower group, the amide DOBA, and its branched isomer DOiBA, the nature of $R$, $R'$ and $R''$ in $R''R''NCOR$ is important due to the molecular rigidity of the amide group. The branched substituent strongly depresses the extraction constant, which likely is due to a much lower stability constant for the branched complex. This effect is more pronounced for Pu(IV) than for UO₂⁺. In a search for selective systems for separating trivalent actinides from fission lanthanides, Spjuth et al. [59] investigated the extraction of trivalent ions from aqueous HNO₃ solutions containing 2-bromodecanoic acid (HBDA) by means of terphenyl and triazine derivatives dissolved in the organic diluent tert-butylbenzene (TBB). Figure 4.28 shows the distribution ratio of the system as a function HBDA in TBB with and without the terpyridine (formula in Fig. 4.29). This is an illustration of the

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Extractant</th>
<th>Complex in organic phase</th>
<th>Extraction constant $K_{ex}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂⁺</td>
<td>TBP</td>
<td>UO₂(NO₃)₂(TBP)₂</td>
<td>28.3</td>
<td>[57]</td>
</tr>
<tr>
<td>UO₂⁺</td>
<td>TiBP</td>
<td>UO₂(NO₃)₂(TiBP)₂</td>
<td>26</td>
<td>[57]</td>
</tr>
<tr>
<td>Pu⁴⁺</td>
<td>TBP</td>
<td>Pu(NO₃)₄(TBP)₂</td>
<td>11.7</td>
<td>[57]</td>
</tr>
<tr>
<td>Pu⁴⁺</td>
<td>TiBP</td>
<td>Pu(NO₃)₄(TiBP)₂</td>
<td>8.9</td>
<td>[57]</td>
</tr>
<tr>
<td>UO₂⁺</td>
<td>DOBA</td>
<td>UO₂(NO₃)₂(DOBA)₂</td>
<td>5.75</td>
<td>[58]</td>
</tr>
<tr>
<td>UO₂⁺</td>
<td>DOiBA</td>
<td>UO₂(NO₃)₂(DOiBA)₂</td>
<td>0.55</td>
<td>[58]</td>
</tr>
<tr>
<td>Pu⁴⁺</td>
<td>DOBA</td>
<td>Pu(NO₃)₄(DOBA)₂</td>
<td>0.235</td>
<td>[58]</td>
</tr>
<tr>
<td>Pu⁴⁺</td>
<td>DOiBA</td>
<td>Pu(NO₃)₄(DOiBA)₂</td>
<td>0.003</td>
<td>[58]</td>
</tr>
</tbody>
</table>

*TBP (C₅H₅)₃PO; TiBP [(CH₃)₂CHCH₂O]₃PO; DOBA [C₂H₅CH(CH₃)CH₂]₂NCOCH₂; DOiBA [C₂H₅CH(CH₃)CH₂]₂NCOCH(CH₃).
necessity to achieve synergistic effects by using adduct formers for extraction of metal ions that otherwise are too strongly hydrated to be extractable. The structures of the terphenyls (adduct formers) tested are listed in Fig. 4.29 with the distribution ratios achieved for Am(III), $D_{\text{Am}}$. For example, in the system with DODOXY, $D_{\text{Am}}$ is 4.2, while with TADPTZ it is 359. The triazine TADPTZ is more branched (the terphenyl DODOXY more linear) and has a slightly larger molar volume, but the difference may also be attributed to the greater basicity (i.e., smaller $K_a$) compared to terphenyl. However, the 100 times larger
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Name/Abbreviation</th>
<th>Name/Abbreviation</th>
<th>Ligand</th>
<th>Name/Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Terpy" /></td>
<td>2,2',6,2''-terpyridine Terpy</td>
<td>13</td>
<td><img src="image" alt="Quinque" /></td>
<td>(4',4'')-di-(4-heptyloxyphenyl)-2,2':6''2''-quinquapyridine DAm Quinque</td>
</tr>
<tr>
<td><img src="image" alt="Tolpy" /></td>
<td>4-tolyl-2,2',6,2''-terpyridine Tolpy</td>
<td>2.8</td>
<td><img src="image" alt="OADPTZ" /></td>
<td>4-octanoyl amino-2,6 di(2-pyridyl) 1,3,5 triazine OADPTZ 287</td>
</tr>
<tr>
<td><img src="image" alt="NitroTolpy" /></td>
<td>4-(4-nitrophenyl)-2,2',6,2''-terpyridine NitroTolpy</td>
<td>2.6</td>
<td><img src="image" alt="TADPTZ" /></td>
<td>4-tetradecanoyl amino-2,6 di(2-pyridyl) 1,3,5 triazine TADPTZ 359</td>
</tr>
<tr>
<td><img src="image" alt="Dodepy" /></td>
<td>4-(4-dodecyloxyphenyl)-2,2',6,2''-terpyridine Dodepy</td>
<td>4.2</td>
<td><img src="image" alt="TADQPTZ" /></td>
<td>4-tetradecanoyl amino-2,6 di(2-quinolyl) 1,3,5 triazine TADQPTZ 0.16</td>
</tr>
<tr>
<td><img src="image" alt="Quater" /></td>
<td>(4',4'')-di-(4,4''')-dilyl-2,2':6''2''-quaterpyridine Quater</td>
<td>490</td>
<td><img src="image" alt="OADQPTZ" /></td>
<td>4-octanoyl amino-2,6 di(2-quinolyl) 1,3,5 triazine OADQPTZ 0.09</td>
</tr>
</tbody>
</table>

**Fig. 4.29** Structure of various oligopyridine and triazine adducts, and distribution ratios (inserts) for Am(III) complexes with these oligopyridines (0.02 M) and 2-bromodecanoic acid (0.00025 M) in tert-butylbenzene and 0.01 M HNO₃. (From Ref. 59.)
extraction by the triazine cannot be explained by the HSAB theory; various explanations are suggested [59]. Steric hindrance can be predicted by modeling the molecular structures and chemical reactions. Advanced programs require mainframe computers, but useful programs are available for desktop computers [49].

4.14 CALCULATION OF EQUILIBRIUM CONSTANTS

Earlier sections presented chemical models for the extraction of acids and metals into organic solvents, and show that these models, expressed mathematically, agree with experimental data at trace metal concentrations and at constant activity coefficients. These models provide a rationale for understanding the chemical principles of solvent extraction.

From plots of the distribution ratio against the variables of the system—[M], pH, [HA]_{org}, [B], etc.—an indication of the species involved in the solvent extraction process can be obtained from a comparison with the extraction curves presented in this chapter; see Fig. 4.3. Sometimes this may not be sufficient, and some additional methods are required for identifying the species in solvent extraction. These and a summary of various methods for calculating equilibrium constants from the experimental data, using graphical as well as numerical techniques is discussed in the following sections. Calculation of equilibrium constants from solvent extraction is described in several monographs [60–64].

4.14.1 Identification of Species

An initial step in data analysis is to develop an equation that represents the experimental data reasonably. Although previous sections dealt with this issue, the approach assumed that certain species are formed. Two alternatives to this procedure are discussed here, both yielding the approximate stoichiometry of the complexes formed in the system. The most elementary is referred to as Job’s method, while the ligand number method, developed by J. Bjerrum, is slightly more advanced.

4.14.1.1 Job’s Method

When a metal M with a ligand A forms an extractable complex of the chemical form M_{n}A_{m}, the extraction is at maximum when the molar ratio of these two in the system is m:a. Similarly, if the extracted species is MA_{n}B_{m}, a plot of the mole ratios of A and B yields a maximum at the ratio a:b. This is illustrated in Fig. 4.2 for the extraction of U(VI) in the TTA-TBP (or TBPO) system. The curves are almost symmetrical around the mole fractions 0.5:0.5, indicating that the extracted species has a 1:1 ratio of TTA to TBP. Because the complex must contain 2 TTA (for electroneutrality), there should also be 2 TBP (or TBPO) molecules in the complex, i.e., MA_{2}B_{2}. 
This method is useful when only one species is extracted, but it has little value for the study of solvent extraction systems that contain several complex species.

4.14.1.2 Ligand Number Method

This method [65–67] is useful for identifying the average composition of the metal species in the system. Consider Eq. (4.36a) for the extraction of $\text{MA}_n$, and assume—for the moment—that only one species, $\text{MA}_n$, exists in the aqueous phase. Taking the derivative of the logarithm of Eq. (4.36) yields

$$
\frac{d \log D}{d \log \left[\text{A}^\text{−}\right]} = z - n
$$

(4.80)

In 1941, J. Bjerrum [65] developed the useful concept of average ligand number, $\bar{n}$, defined as the mean number of ligands per central atom:

$$
\bar{n} = \frac{\sum n \left[\text{MA}_n\right]}{[\text{M}]}
$$

(4.81)

It can be shown [66a–67] that $\bar{n}$ equals $n$ in Eq. (4.79), which can be rewritten

$$
\bar{n} = z - d \log D / d \log \left[\text{A}^\text{−}\right]
$$

(4.82)

For example, in Fig. 4.10 (Example 3), the slope of the plot of $\log D_{\text{Cu}}$ vs. $\log \left[\text{A}^\text{−}\right]$ can be used to conclude what species dominate the system at a given $\left[\text{A}^\text{−}\right]$ value. The relation in Eq. (4.82) indicates an asymptote of slope 2, so the aqueous phase is dominated by uncomplexed $\text{Cu}^{2+}$ ($n = 0$), while for slope 0 the neutral complex $\text{CuA}_2$ dominates the system ($n = 2$). Equation (4.82) shows that any tangent slope of the curve (i.e., $d \log D / d \log \left[\text{A}^\text{−}\right]$) yields the difference $z - n$ in these simple systems.

Example 12: Extraction of Th(IV) by acetylacetone.

Figure 4.30 shows a smoothed curve of measurements of the distribution of Th(IV) from 0.1 M NaClO$_4$ into chloroform containing the extractant acetylacetone (HA) [66a,b]. Taking the derivative of this curve according to Eq. (4.79) the average ligand number is derived as shown in the lower insert. Th(IV) is successively complexed by $\text{A}^\text{−}$ forming $\text{ThA}^2^+$, $\text{ThA}^3^+$, $\text{ThA}^4$, and uncharged $\text{ThA}^+$, which is extracted. At $p\text{A} > 8.5$ the $\bar{n}$-value is zero, i.e., Th is uncomplexed, while at $p\text{A} < 3.5$ the average ligand number of 4 is reached, i.e., Th is fully complexed as $\text{ThA}_4$. See also Example 15.

The average ligand number can be used to obtain approximate equilibrium constants, as described by [65], assuming that at half integer $\bar{n}$-values the two adjacent complexes dominate; e.g., at $\bar{n} = 0.5$ the species $M^{z^0}$ and $\text{MA}^{z^1}$ dominate, while at $\bar{n} = 1.5$ $\text{MA}^{z^2}$ and $\text{MA}^{z^3}$ dominate, etc. The following expression for the stepwise formation constant is approximately valid at

$$
\bar{n} = n - 0.5, \log K_n = -\log \left[\text{A}^\text{−}\right]
$$

(4.83)

This method of obtaining an estimate of the formation constants was done as a first step in the Th(IV)-acetylacetone system in Fig 4.30, where in the lower
**Fig. 4.30** Upper curve: the distribution of Th(IV) between benzene and 0.1 M NaClO$_4$ as a function of aqueous acetylacetonate ion concentration; pA = −log[A$^-$]; the asymptotes have slopes 0 and −4. Lower curve: The average number of ligands per central atom, $\bar{n}$, in same system, as obtained from a derivation of the log $D$(pA) curve. Using the ligand number method, the following equilibrium constants were estimated (with values from graphical slope analysis within parenthesis): log$K_1$ 8.0 (7.85), log$K_2$ 7.6 (7.7), log$K_3$ 6.4 (6.3), and log$K_4$ 5.1 (5.0). Log $K_{D4}$ 2.50 is obtained from the horizontal asymptote. (From Refs. 66a,b.)

figure, $\bar{n}$ is plotted against −log [A$^-$], yielding the preliminary log $K_n$ values given in **Fig. 4.3**. In a similar manner, the adduct formation constants can be determined:

Example 13: The extraction of Zn(II) by β-diketones and phosphoryl adduct formers (cont. of Example 5).

Consider the formation of adducts of the type MA$_a$B$_b$, as described in Example 5 (**Fig. 4.12**). The derivative of Eq. (4.48b) with respect to [B] at constant [A] yields

$$d \log D / d \log [B] = \frac{b}{a}$$

(4.84)

where $b$ is the average number of adduct forming molecules in the molecule at given [B] value. In **Fig. 4.12** the asymptote has a slope of 2, indicating that a maximum of two molecules of TBP (or TOPO) bind to the neutral metal complex. From the lower slopes of the curve, the average number, $\bar{b}$, can be estimated according to Eq. (4.83).
4.14.2 **Graphic Slope Analysis**

For a rational application of slope analysis it is important to measure the variation of the distribution ratio $D$ with one component $x$ at a time while the others, $C$, are kept constant. The solvent extraction equation can then be expressed in the form of a simple polynomial of type

$$y = a_0 + a_1 x + a_2 x^2 + \cdots$$  \hspace{1cm} (4.85)

where $y$ is a function of the distribution ratio $D_{\text{const}}$ and $x$ a function of the variable (e.g., pH, the free ligand ion concentration $[A^-]$, the concentration of free extractant HA or adduct former B in the organic phase, etc.).

### 4.14.2.1 Linear Plots

When the distribution equation can be expressed in the form $y = a_0 + a_1 x$, from a plot of $y$ vs. $x$ the intercept on the $y$ axis yields the $a_0$ parameter and the slope the $a_1$ parameter. This treatment is referred to as the *limiting value method*.

**Example 14:** The extraction of Cu(II) by HTTA (cont. from Example 4).

Example 4 (Fig. 4.11a), is represented by Eq. (4.44), which in logarithmic form is written

$$\log D_{\text{Cu}} = \log K_{\alpha} + 2 \log [HA]_{\text{org}} + 2 \text{pH}$$  \hspace{1cm} (4.86)

For constant $[HA]_{\text{org}}$ (Fig. 4.11a), a plot of $\log D_{\text{Cu}}$ vs. pH yields a line of slope 2, which intercepts pH = 0 at $\log D_{\text{Cu}} = \log K_{\alpha} + 2 \log [HA]_{\text{org}}$. Another plot of $\log D_{\text{Cu}}$ against $\log [HA]_{\text{org}}$ at constant pH yields a line that intersects $[HA]_{\text{org}} = 0$ at $\log D_{\text{Cu}} = \log K_{\alpha} + 2 \text{pH}$ (Fig. 4.11b). In either case, the HTTA system yields $\log K_{\alpha} = -1.25$ for the CHCl$_3$, and $-1.08$ for the CCl$_4$ system. The corresponding values for the IPT system are 1.60 and 0.95, respectively.

**Example 15:** Extraction of Th(IV) by acetylacetone (cont. from Example 12).

In Example 12, it was concluded from Fig. 4.30 that the aqueous phase contained all ThA$_n$-complexes with $0 < n < 4$, and the organic phase only the uncharged ThA$_4$ complex. We can therefore write the distribution of Th(IV) between chloroform and water

$$D_n = \frac{[\text{ThA}_n]_{\text{org}}}{[\text{ThA}_n]_{\text{aq}}} = K_{\alpha} \frac{[\beta']^n}{[\beta][\alpha']}$$  \hspace{1cm} (4.87)

This is rearranged to yield

$$D_n = F_n = \frac{(1 + a_n x^{-1} + a_n^{-1} x^{-2} + a_n^{-2} x^{-3})}{K_{\alpha}}$$  \hspace{1cm} (4.88a)

where $K_{\alpha}$ is the distribution constant of ThA$_n$, $x$ equals $[\alpha]$, and $a_n = \beta_n / \beta_1$.

In a plot of $F_n$ against $x^{-1}$, the intercept becomes $K_{\alpha}$ and the slope is $a_1 / K_{\alpha}$.

In the next step the function $F_1$ is calculated

$$F_1 = (K_{\alpha} D^{-1} - 1)x = a_1 + a_1 x^{-1} + a_1 x^{-2} + \cdots$$  \hspace{1cm} (4.88b)

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A plot of $F_1$ vs. $x^{-1}$ yields $a_1$ at the intercept and $a_2$ as the slope. In third step, $F_2 = (F_1 - a_1) x = a_3 + a_4 x + a_5 x^2$ is calculated, yielding $a_3$ and $a_4$, etc. Using this technique all four $a_n$ values are obtained, from which one can deduce the $\beta_n$ values [actually the $K_n$ values in Eq. (3.5)] and the $K_{DC}$ value.

Dyrrsen and Sillén [68] pointed out that distribution ratios obtained by conventional batchwise techniques are often too scattered to allow the determination of as many parameters as used in Examples 15 and 16. They suggested a simplified graphic treatment of the data, based on the assumption that there is a constant ratio between successive stability constants, i.e., $K_n/K_{n+1} = 10^b$, and that all distribution curves can be normalized so that $N^{-1} \log \beta_n = a$, where $N$ is the number of ligands $A^{-}$ in the extracted complex. Thus, the distribution curve $\log D_n$ vs. $\log [A^-]$ is described by the two parameters $a$ and $b$, and the distribution constant of the complex, $K_{DC}$. The principle can be useful for estimations when there is insufficient reliable experimental data.

4.14.2.2 Nonlinear Plots

It is not possible to obtain simple linear relations between $D$ and the variables when both the aqueous or organic phase contain several metal species. Instead a double polynomial such as

$$D = Y = \frac{b_0 + b_1 y + b_2 y^2 + b_3 y^3 + \cdots}{a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \cdots} = \frac{\sum b_y}{\sum a_x}$$

is obtained for which there is no simple solution.

Example 16: Extraction of U(VI) by acetylacetone.

Fig. 4.31 shows the extraction of U(VI) by acetylacetone (HA) from nitric acid solutions, $D_{U}$, as a function of $pA = -\log [A^-]$ at six different total concentrations of HA. A comparison with Fig. 4.3 indicates that we can expect complexes of the type $MA_n(OH)_p(HA)_r$, which formally is equivalent to $H_r^p M A_n$. The extraction reaction is of the type Eq. (4.86), as one expects a series of self-adduct complexes $MA_n(HA)$, in the organic phase, and one or two series of stepwise complexes $MA_n$ and $M(OH)_p$ in the aqueous phase. Thus the extraction reaction is of the type Eq. (4.89) with a ratio of several polynomials. Even in this case, a graphic extrapolation technique was useful by determining a set of intermediary constants for each constant $[HA]_{org}$ from $\log D_{U}$ vs. $pA$. Plotting these intermediate constants vs. $[HA]_{org}$, a new set of constants were obtained, from which both the stepwise formation constants $\beta_n$ and the adduct formation constants $K_{ad,1}$ and $K_{ad,2}$ for the reaction $UO_2A_n(H_2O)_{n+} + nHA \leftrightarrow UO_2A_n(HA)_{n+}$ in the organic phase. A more detailed analysis also allowed the determination of formation constants for $UO_2(OH)_p$ ($p = 1$ and 2). There may be other explanations to the extraction results. However, with the model used and the constants calculated, $\log D_0$ could be correctly predicted over the whole system range $[U]_{tot}$ 0.001–0.3 M, pH 2–7, and $[HA]_{org}$ 0.01–1.0 M. See also Example 17.
Fig. 4.31  Extraction of U(VI) by acetylacetone (HA) from 0.1 M NaClO₄ into chloroform as a function of pH at different total concentrations of HA. (From Ref. 69.)
4.14.3 Numerical Methods

The most complicated equations presented in this chapter are of the types shown by Eq. (4.89), where a series of complexes are formed in the organic phase and, at the same time, one or a series of complexes in the aqueous phase. More complicated equations would be obtained if mixed complexes and/or polynuclear complexes are present, and if varying activity factors are introduced, but these cases are not discussed here. Thus the solvent extraction equations can be expressed by Eq. (4.89), where \( x \) and \( y \) are independent variables and \( a_n \) and \( b_n \) are unknown independent parameters. The polynomial in the denominator refers to the formation of aqueous phase complexes; in the case that the metal forms several series of complexes with different ligands \( A^- \), \( L^- \), etc., the denominator contains several polynomials: \( c_0 + c_1z + \cdots \), etc. The polynomial in the numerator always refers to the formation of organic phase complexes.

There is no exact numerical solution to Eq. (4.89) when both \( x \) and \( y > 0 \). In practice, therefore, one variable must be kept constant (or zero), while the value of the other changes. This was described for Example 16. Thus, if \( x \) is kept constant, the double polynomial is reduced to a simple one

\[
y = C_x \sum \beta_j y^j \quad \text{(4.90)}
\]

where \( C_x \) is a constant at constant \( x \). The problem is therefore reduced to the determination of the parameters of a simple polynomial, to which many numerical methods have been applied with varying degrees of success. The main requirement is that all computed parameters should be positive numbers (or zero).

In order to solve an algebraic system of \( n \) parameters, only \( n \) equations are needed (a minimum with no error estimates). When the solvent extraction reaction can be described by Eq. (4.90), there are as many equations as there are experimental points. Commonly, in solvent extraction 10–50 points are needed to cover the whole concentration range of interest, while the number of unknown parameters in simple cases is \(<5\). In evaluating the parameters, it is important to use the complete suite of experimental data, as that gives greater significance to the \( a_n \) or \( b_n \) values.

There are several ways to solve a large number of polynomials like Eq. (4.90) for the \( a_n \) parameters, e.g., by minimizing the sum of the residuals, the least square method (LSQ) being the standard procedure. It is an objective regression analysis method, which yields the same results for a given chemical system, independent of method of investigation, provided there are no errors in the technique or fundamental chemical assumptions. Because the method may be applied in somewhat different ways, it may sometimes give slightly different results. Therefore, in judging a set of equilibrium constants, it is useful to learn how an author has applied the minimization technique.

In Eq. (4.91) \( x \) is usually the free ligand concentration \([A^-]\), or concentration \([B]\) of the adduct former, while \( y \) is a simple function of the distribution
The least square method requires that $S$ (the weighted squared residuals) in expression Eq. (4.91) is minimized

$$S = \sum_{i=1}^{L} w_i \left( \sum_{n=0}^{N} (a_n x_i^n) - y_i \right)$$

(4.91)

where $N + 1$ is the number of parameters, and $L$ the number of experimental points; $N + L - 1$ is referred to as the number of degrees of freedom of the system; each point has a value $x_i / y_i$. Because experiments are carried out over a large range of $D$, $[A]$ and/or $[B]$ values, the points carry different algebraic weight (e.g., the value 1000 obscures a value of 0.001). Therefore, in order to use the LSQ technique properly, each point must be correctly weighted, $w_i$. This can be done in several ways, the most common being to weight it by $y_i$, or by $\sigma_i^2$, or by a percentage value of $y_i$; $\sigma_i$ is the standard deviation in the measurement of $y_i$. The difference $a_n x_i^n - y_i$ (the residual) is not zero, because the difference is to be taken between a measured value, $y_i$ (meas.), and the corresponding calculated value, $y_i$ (calc.), by the $a_n x_i^n$ function [i.e., $y_i$(calc.) $- y_i$(meas.)], using the actual $a_n$ values at the time of the operation.

The principle of the LSQ technique is to compute the set of positive $a_n$ values that give the smallest sum of the residuals; Eq. (4.91) reaches the $S_{\text{min}}$ value. If the residuals equal zero (which rarely occurs in practice), $S_{\text{min}}$ would be zero, and there would be a perfect fit between the experimental points and the calculated curve.

There are several mathematically different ways to conduct the minimization of $S$ [see Refs. 70–75]. Many programs yield errors of internal consistency (i.e., the standard deviations in the calculated parameters are due to the deviations of the measured points from the calculated function), and do not consider external errors (i.e., the uncertainty of the measured points). The latter can be accommodated by weighting the points by this uncertainty. The overall reliability of the operation can be checked by the $\chi^2$ (chi square) test [71], i.e., $S_{\text{min}} / (L + N - 1)$ should be in the range 0.5–1.5 for a reasonable consistency between the measured points and the calculated parameters.

Example 17: Extraction of Pm(III) by acetylacetone.

In Example 7, it was concluded that a number of self-adducts PmA$_3$ (HA)$_b$ were formed in the organic phase ($0 < b < 2$) in addition to the PmA$_n$ complexes in the aqueous phase ($0 < n < 4$); some extraction curves are given in Fig. 4.14. Equation (4.55) is of the same form as Eq. (4.89); rewriting Eq. (4.55b)

$$Y = D_{\text{org}} \Sigma \beta_i [A]^i / \beta_i [A]^i = K_{\infty} (1 + K_{\text{eq}} [HA]_{\text{aq}} + \cdots)$$

(4.92)

which can be subdivided into

$$Y_{\text{org}} = C \cdot K_{\infty} (1 + K_{\text{eq}} [HA]_{\text{aq}} + \cdots)$$

(4.93a)
and

\[ Y_{HA_{org}} = C_1 D_{org} \sum \beta_n [A]^n \]  

(4.93b)

\( Y_{HA_{org}} \) contains the measured \( D_{org} \), the [A] values, and the \( \beta_n \) values. It can thus in principle be treated as an Example 16 to yield the \( \beta_n \) values and the \( C_2 \) values (one for each \( [HA]_{org} \)), remembering that \( a_0 = 1 \). Because \( Y_{HA} / C_1 = Y_{HA_{org}} / C_2 = Y' \), a second plot of \( Y' \) against \( [HA]_{org} \) yields the \( K_{D1} \) and \( K_{D2} \) values. The analysis of the system yielded \( K_{D1} = 0.008, K_{d1.1} = 7 \) and \( K_{d1.2} = 3 \). In these calculations, a SIMPLEX program was used [75].

In comparisons of equilibrium constants collected from the literature (e.g., Fig. 4.22 or [47]), or correlations of data for a large number of systems (e.g., Figs. 4.20–4.23), it is desirable to present both the statistical uncertainty of each “point,” which is often given by the standard deviation (one or several \( \sigma \)'s) of the point, and the general reliability (statistical significance) of the whole correlation [76], for which the chi-square test offers a deeper insight into the reliability of the experimental results [77]. More advanced statistical tests for systems of our kind have been described by Ekberg [78].

### 4.15 EXPERIMENTAL DETERMINATION OF DISTRIBUTION RATIOS

The studies described above have the purpose of identifying the reacting species in a solvent extraction process and developing a quantitative model for their interactions. The fundamental parameter measured is the distribution ratio, from which extraction curves are derived. Solvent extraction work can still be carried out with simple batchwise (or point-by-point) technique, but continuous on-line measurements give faster and more accurate results.

#### 4.15.1 Stirred Cell Semicontinuous Techniques

Each point-by-point experiment requires a complete set of mixing, separation, sampling, and analysis. This usually leads to scattered results, though it may not be critical, if the \( D \) values cover a limited range from 0.1–10. However, the more the \( D \) values deviate from 1, the more accurate must be the measurements; also the number of points required for a reliable extraction curve usually increases. To reduce the uncertainty and labor involved with the batch technique, the stirred cell technique has become popular.

Figure 4.32 shows a typical thermostated stirred cell. The liquid volumes are commonly 50 + 50 mL. The stirrer may consist of a single paddle at the interface, or a double paddle, one in the center of each phase. The cell may contain baffles, etc., to improve the mixing. Stirring may be violent, completely destroying the interface and producing very small (\( \approx 1 \) mm) droplets, or slow
Fig. 4.32  A thermostated double jacket (1) cell for solvent extraction studies (heavier phase 8, lighter phase 9) under nonoxidizing conditions, using a hydrogen gas inlet (6) to a Pd-black catalyst (11), pH glass electrode (3), magnetic stirrer (10), connections for additions (5). Alternative constructions contain rotating paddles and fixed pipings connected to the two phases for frequent sample withdrawals.

in order not to destroy the interface. The stirring rate is optimized to the time for reaching equilibrium and complete phase separation. The experiments are either carried out with intermittent violent stirring, in which case samples are withdrawn after each complete phase separation, or with mild stirring during which it is possible to continuously withdraw samples. Equal volumes are sampled each time, commonly <1 mL. The simple stirred cell has been improved by introducing phase discriminating membranes in the sampling outlet [79]. This is particularly advantageous for kinetic experiments and is further described in Chapter 5. The sampling of the stirred cell can be automated, so that at regular intervals pH and temperature are recorded, and samples withdrawn for automatic analysis of concentration of interesting species in more or less standard fashion. It is also possible to use ion-sensitive probes in one of the phases instead of sampling.

4.15.2 Centrifugal Extraction-Separation Systems

A different approach to solvent extraction experimentation, referred to as the AKUFVE principle, was developed in the 1960s [80a–d]. The AKUFVE is
illustrated in Fig. 4.33. Efficient mixing of the two phases and their additions is achieved in the mixing vessel and at the inflow into the phase separator, which consists of a continuous flow centrifuge, which in a special separation chamber and at very high rotational velocity (5,000–50,000 rotations per minute) separates the mixture into two very pure phases, containing <0.01% of entrainment of one phase in the other phase. The H-centrifuge may be made of Pd-stabilized

**Fig. 4.33** The AKUFVE solvent extraction apparatus: Efficient mixing is achieved in the separate mixing vessel, from which the mixture flows down into the continuous liquid flow centrifugal separator (the H-centrifuge, hold-up time <1 s). (From Refs. 83a,b.) The outflow from the centrifuge consists of two pure phases, which pass on-line detectors, AMXs, for on-line detectors or continuous sampling. (From Refs. 80a–80d, 81.)

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Ti, or PEEK (polyether ether ketone) to allow measurements under very corrosive conditions. The separated phases pass AMX gadgets for on-line detection (radiometric, spectrophotometric, etc.) or phase sampling for external measurements (atomic absorption, spectrometric, etc.), depending on the system studied. The aqueous phase is also provided with cells for pH measurement, redox control (e.g., by reduction cells using platinum black and hydrogen, metal ion determination, etc.) and temperature control (thermocouples).

The AKUFVE technique allows a large number of points (50–100) to be determined in a one-day experiment over a \( D \)-range of better than \( 10^3 \) to \( 10^{-3} \), not counting time of preparation. In a special version of this technique (LISOL for LIquid Scintillation On Line) [82], the \( D \) range \( 10^{-5} \) to \( 10^4 \) has been accurately covered, as for the Pm-acetylacetone system, Example 7 and Fig. 4.14.

The centrifugal separator of the AKUFVE system is also used for phase separation in the SISAK technique [84]. SISAK is a multistage solvent extraction system that is used for studies of properties of short-lived radionuclides, e.g., the chemical properties of the heaviest elements, and solvent extraction behavior of compounds with exotic chemical states. In a typical SISAK experiment, Fig. 4.34, radionuclides are continuously transported from a production

![Fig. 4.34](image)

**Fig. 4.34** A typical SISAK setup used for studies of \( \alpha \)-decaying nuclides, e.g., trans-actinides. (From Ref. 84.)
site in an accelerator or a research reactor to the SISAK equipment via a gas-jet transport system. The nuclides are dissolved in an aqueous phase that is fed into a centrifuge battery comprising 1–4 solvent extraction steps. The product solution leaving the last step is pumped, e.g., to a nuclear radiation detection system. The transport time from the target site to the detection system depends on the centrifuge size, number of centrifuge steps, and flow rate. For a one-step chemistry, i.e., dissolution step and a single centrifuge extraction, and maximum flow rates, the overall transport time is around 2.5 s. This fast transport has allowed detailed $\gamma$-spectroscopic studies of radionuclides with half-lives around 1 s. Recently the SISAK equipment was successfully applied to studies of the heaviest elements, and solvent extraction data were obtained for element 104 Rf [85]. Fast chemical separation systems have been developed for quite a large number of elements [86].

Centrifugal extractors have been designed for a number of industrial uses (see succeeding chapters). In some cases they have been scaled down to laboratory size but mainly been used for developing industrial multistage processes.

4.15.3 Liquid Partition Chromatography

In liquid partition chromatography a solute distributes itself between a mobile liquid phase and an immobile solvent attached to a solid matrix (in the earliest experiments a claylike *kieselguhr*). It is outside the scope of this chapter to discuss this technique, which, however, is briefly described in Chapter 15.

4.16 CONCLUSION AND FINAL COMMENTS

The solvent extraction process is usually described by a single net reaction, defined by the extraction constant $K_{ex}$. Variations in $K_{ex}$ caused by modifications of the solvent system, such as changes in the temperature or aqueous ionic strength, or by replacing one solvent by another, or making substitutions in the extractant molecule, may be explained by careful consideration of the parameters of the system. However, such studies are difficult and not always sufficient for predicting new systems. A better foundation for understanding the extraction process is to consider the steps in the process contributing to the net extraction reaction, particularly when these steps are governed by regularities. Knowledge of these regularities helps in interpreting systems as well as in predicting new ones. Extension of these distribution data to thermodynamic constants is likely to give benefits in increased chemical knowledge of the behavior of solutes in different solvent systems. Advanced quantum chemistry calculations and computer modeling of extraction processes can help us in designing new, selective solvent extraction systems, as well as in interpreting extraction phenomena (see Chapter 16).
REFERENCES

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