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THEORY AND PRACTICE IN SOLVENT EXTRACTION STUDIES

by

A.W. Ashbrook*

ABSTRACT

The theory of the extraction and separation of metals by the technique of solvent extraction is discussed, followed by its application to practical or industrial metal extraction processes.

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Direction des mines
Circulaire d'information IC 308

LA THÉORIE ET LA PRATIQUE DES ÉTUDES EN EXTRACTION PAR SOLVANT

par
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RÉSUMÉ

L'auteur discute la théorie de l'extraction et de la séparation des métaux par la technique d'extraction par solvant ainsi que l'application de cette technique aux procédés pratiques ou industriels d'extraction des métaux.

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TABLE OF CONTENTS

Page

ABSTRACT.......... i

RESUMÉ.......... ii

INTRODUCTION.......... 1

The Solvent Extraction Process.......... 4

The Practical Process of Solvent Extraction.......... 5

The Theory of Solvent Extraction.......... 7

Systems Involving Compound Formation.......... 11

- Chelating Extractants.......... 11
- Acidic Extractants.......... 44

Systems Involving Ion Association.......... 49

Systems Involving Solvation.......... 58

Practical Considerations.......... 61

- Extraction Coefficient.......... 62
- Extractant Concentration.......... 66
- Effect of pH.......... 69
- Aqueous Phase Composition.......... 77
- Metal Ion Concentration.......... 81
- Solvent Loading Capacity.......... 83
- Use of $pH_{1/2}$ Values.......... 86
- Scrubbing.......... 88
- Stripping.......... 90
- Solvent Pre-Treatment.......... 92
- Kinetics of Extraction.......... 95

DISCUSSION..........101

Page

REFERENCES.. 108

APPENDIX I.. 112

APPENDIX II....................................... 118

APPENDIX III...................................... 119

TABLES

No. Page

1 Theoretical Decrease in $pH_{1/2}$ as a Function of n and i Values.................................. 43

2 Some Extractable Metal-TBP Species.................. 60

3 Effect of Metal Concentration on the Extraction Coefficient of Uranium 82

FIGURES

No. Page

1 The General Process of Solvent Extraction.......... 6

2 Some of the Equilibria Involved in the Extraction of a Metal.. 19

3 Extraction of Nickel From Ammonium Sulphate Solution with 0.5 M Versatic 911............... 34

4 Effect of Extractant Concentration on the Extraction of Mn(II) by Oxine........................... 39

5 Some Equilibria Involved in the Extraction of Cobalt from a Chloride System using a Tertiary Amine.. 55

No. Page

6 Effect of A/O Ratio on Metal Extraction............. 63

7 pH for the Separation of Two Metals in a Single Stage................................. 65

8 Variation of Extraction Coefficient of Uranium With TBP Concentration......................... 67

9 Effect of Extractant Concentration on Metal Extraction.................................... 68

10 Effect of Metal Oxidation State on the Extraction Coefficient................................... 71

11 General Effect of pH on Metal Extraction............ 76

12 Effect of Sulphate on the Extraction of Co and Ni with D2EHPA................................... 78

13 Effect of Various Anions and Anion Concentration on the Extraction of Uranium by a Tertiary Amine.. 78

14 Extraction of Uranium by Diethyl Ether in the Presence of Various Metal Nitrates............. 80

15 Extraction of Cobalt by D2EHPA as a Function of D2EHPA Concentration........................... 85

16 Effect of $[(NH_4)_2SO_4]$ on $pH_{1/2}$ Values in the Extraction of Cobalt with Versatic 911......... 87

17 Model of LIX-65N-Cu^{2+} Complex $[C_6H_5C{=}NHOC_6H_3C_9H_{19}O]_2Cu \cdot 2H_2O$.................100

INTRODUCTION

Just over one hundred years have passed since Berthelot and Jungfleisch(1) first enunciated a law governing the distribution of a metal species between two immiscible phases. Since that time the technique and theory of solvent extraction have advanced as the theories and knowledge of solutions and metal complexes have progressed. Almost all of our present-day knowledge of this process has derived from analytical chemistry, in which discipline considerable use of the technique is now made.

In the 1940's the need for the separation and recovery of radioactive materials saw the introduction of solvent extraction to large scale operations, and from this the technique has been applied to metallurgical processing largely as a result of the interest shown in hydrometallurgical routes for the treatment of complex ore bodies.

The large amount of continuing work on both reagents and systems has resulted in the adoption of solvent extraction as a unit process in hydrometallurgical operations for the recovery of a number of non-ferrous metals.

As the number of studies and publications in the field of solvent extraction increase, it has become apparent that there are essentially two approaches being taken by workers in the field; a more fundamental (academic) approach and a phenomenistic (industrial) approach. Unfortunately there appears to be little in the way of an intermediate position in which a coalescence of these extremes obtains. Thus, for example, solvent extraction processes are developed and put into operation with little or no understanding of the chemistry of the system and as a result, when problems occur, considerable time and money can be lost in overcoming or understanding the causes of the problems. On the other hand a large amount of data is available in the literature on the theoretical and more fundamental aspects of metal extraction and separation by solvent extraction, most of which is never applied to real systems. The position is rapidly approaching the point -- if it has not been reached already -- where a systematic examination of all the data would be a formidable task indeed. Much of the theory of solvent extraction is to be found only in analytical chemistry texts or scattered in the literature. Many of the practical aspects of solvent extraction are buried in descriptions of processes or are not to be found in published form. There appears, therefore, to be a need for an amalgamation of the theory and practice of solvent extraction as applied to the extraction of metals, and this monograph is an attempt at such an amalgamation by discussing first the theory of solvent extraction followed by its application to real (or industrial) extraction processes.

It is intended mainly to point out to the more practically minded investigators that the application of theory to solvent extraction processing has something to offer in understanding metal extraction processes, and in predicting from theory, chemistry and known data what a particular system is likely to offer or achieve. It should also be of interest to those who are entering the field of solvent extraction of metals in hydrometallurgical processing.

Also, it is hoped this monograph will be of use to those involved in the more fundamental aspects of solvent extraction in applying their investigations towards real processes.

The treatment has no pretentions of being exhaustive, but rather aims to develop the more important aspects of theory and how they can be applied to understanding real processes.

The Solvent Extraction Process

The process of solvent extraction (or liquid-liquid extraction as it is sometimes called) as applied in metallugical processing is an equilibrium process which can be described quite simply by an equation such as

$$M + \overline{E} \rightleftharpoons \overline{ME} \qquad [1]$$

In the first step the metal, M, is transferred from an aqueous phase to an organic phase $\overline{E}$ (extraction stage) as some complex ME, in which case the process requires that the equilibrium position in this equation be shifted to the right. The second step is the reverse of the first, that is, the metal is transfered from the organic phase to an aqueous phase (stripping stage) in which case this process requires that the equilibrium position be shifted to the left.

So basically, the solvent extraction of metals is a simple operation requiring only a shift in the equilibrium between the extraction and stripping processes. This basic simplicity is a particular attraction for its use in metallurgical, and also in other processes. Indeed, little or nothing need be known about the chemistry of a solvent extraction process in order to develop a commercially feasible operation for the extraction of a metal (or metals) and its recovery in a pure form.

In attempting an understanding of the mechanisms of metal extraction systems the situation can become very complex depending on several factors, among which the type of extractant and the composition of the aqueous phase are the most important. Thus the theory of metal extraction into and out of an organic medium involves essentially the chemistry of metal complexes in both aqueous and organic media.

Let us then try to develop the theory as applied to this process, and then see how this relates to investigations into the development of commercial processes. But first, it will be instructive to have a somewhat better idea of the solvent extraction process as applied commercially in the treatment of metal-bearing solutions, and become acquainted with some of the nomenclature used. A complete list of solvent extraction nomenclature is given in Appendix I.

The Practical Process of Solvent Extraction

The general solvent extraction circuit is shown schematically in Figure 1. The metal-bearing aqueous feed solution and solvent are fed, usually in a counter-current manner, into a contactor in which the two phases are mixed. In this stage the metal of interest is transfered from the aqueous to the organic phase. After settling, the aqueous phase or raffinate is separated and treated for the recovery of other metals, recycled to some point upstream or downstream from the solvent extraction circuit, or goes to waste.

From the extraction stage, the loaded solvent may go to another contactor where it is scrubbed with a suitable aqueous solution to remove small amounts of metals or impurities

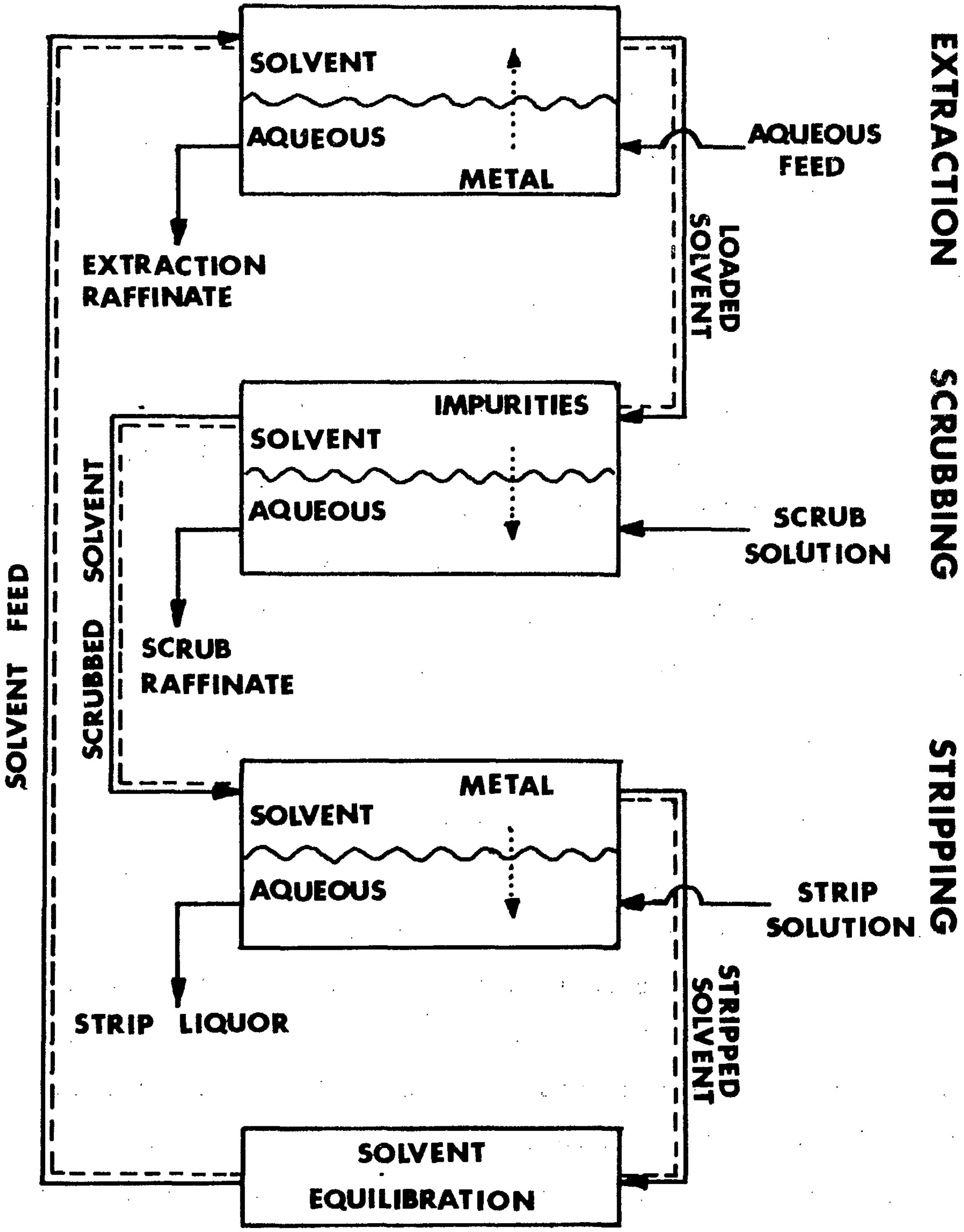


Figure 1: The General Process of Solvent Extraction.

co-extracted in the extraction stage. The scrub raffinate (aqueous) may then be recycled to a stage upstream from the SX circuit, for example to the leaching stage, or to the aqueous SX feed tank.

After scrubbing, the loaded solvent passes to a third stage in which the metal is stripped from the organic phase by some suitable aqueous solution producing (usually) a fairly concentrated solution of the metal salt, which then goes to further processing for metal production.

The stripped solvent is recycled back to the extraction stage; if necessary it is treated (equilibrated) prior to entering the extraction stage.

Each of the three stages described -- extraction, scrubbing and stripping -- may involve several contactors in each stage. Thus the extraction of uranium from acid sulphate liquors using a tertiary amine as the extractant may require three contactors for extraction, one for scrubbing, and two for stripping.

With this brief outline of solvent extraction processing, and some of the nomenclature involved, we will now proceed to develop some of the theory of solvent extraction as applied to metal extractions.

The Theory of Solvent Extraction

When a metal-containing aqueous phase is shaken with an organic phase into which the metal is extracted it will be distributed between the two phases. The distribution may be chemical or physical in nature, depending on the system. Physical processes are those involving the extraction of simple, uncharged covalent molecules such as the halides of arsenic(III), antimony (III), germanium (III) and mercury (II) into organic solvents such as carbon tetrachloride. In such cases the Nernst distribution law$^{(2)}$ is usually valid, and the distribution coefficient, K_D, is independent of both the total solute (metal) concentration and the phase ratio (ratio of the volumes of the aqueous and organic phases). Thus K_D is simply the ratio of solute concentration in the two phases:

$$K_D = (\bar{S})/(S) \qquad [2]$$

where the bar represents the organic phase.

Thus the Nernst law depends only on the solubility of the metal species in the solvent phase. No chemical interactions between the metal species and the organic phase take place, that is, the solute is of identical chemical form in both phases.

Except for systems similar to those noted above, chemical reactions are involved in the extraction of metals, and occur between the metal species present in the aqueous phase and one or more components of the organic or solvent phase. As a result, the Nernst distribution law does not hold in such systems, although it will be seen that the basic equation used in practical solvent extraction studies (extraction coefficient) resembles very closely the Nernst distribution equation.

Normally a metal ion exists in aqueous solution as a hydrated ion, with little or no tendency to transfer to an organic phase. Thus in order to achieve the required transfer the metal ion has to be modified in some way. To convert a metal ion to an extractable specie its charge requires neutralisation (except for the case noted above) and some or all its water of hydration has to be replaced by some other molecule or ion. These are the major requirements and can be met by complexing the ion with an ion of opposite charge to form a neutral specie, which at the same time replaces some or all of the water of hydration around the metal ion; by formation of ion-association complexes which also provide for the formation of a neutral specie with the extractant; and by replacing the water of hydration with molecules of a solvent. We can consider the overall process as one of converting a hydrophilic specie into a hydrophobic specie.

Complexation of a metal ion can be viewed as a process in which the hydrated water molecules are replaced by other usually more complex molecules, or ligands as they are usually called. All complexing reactions are then, strictly, substitution reactions.

The nature of the extractable metal species is therefore of fundamental importance in metal extraction systems and it is logical to classify extraction systems on this basis. Accordingly, the classes of systems considered in this monograph are:

(i) those which involve compound formation

(ii) those which involve ion association

(iii) those which involve solvation of the metal ion.

This method of classification is not meant to imply that these systems are mutually exclusive, but rather to simplify discussions of the various systems. Indeed, some extractants can belong to more than one class, depending in large measure on the experimental conditions.

The theory of solvent extraction as we know it today is based essentially on that used in analytical chemistry, and because most metal extraction systems in this field involve metal chelate complexes, most of the theory concerns such complexes.

A considerable amount of information is available on metal chelate (and other) complexes(3,4), and a more than passing knowledge of modern inorganic chemistry is necessary in order to understand in a more complete way the theory and reactions involved in solvent extraction processes. Because of our knowledge of the chemistry of metal-organic complexes, our understanding of solvent extraction processes involving for example metal chelates, is much greater than for systems involving other metal complexes involving, say, ion association. It will be instructive, therefore to consider first those metal extraction systems employing chelation and compound formation, and then the more complex ion-association and solvation systems.

In the past, much of the theory relating to metal chelate extraction has been applicable only in analytical studies, but with the recent introduction of chelating extractants for use on a commercial scale (5-7), together with their rather spectacular successes in this area undoubtably most, if not all, future extractants will be of this type. Therefore we will not be wasting our time in considering the theory of such metal extractions.

Systems Involving Compound Formation

Chelating Extractants

The simplest equation we can write to illustrate the extraction of a metal ion, M^{n+}, by an extractant, HA, is

$$M^{n+} + \overline{nHA} \rightleftharpoons \overline{MA_n} + nH^+ \qquad [3]$$

which formally resembles equation [1] and also the process of solid-liquid ion exchange, in which HA is equivalent to ion-exchange resins. It is not surprising then that solvent extraction is also referred to as liquid ion exchange. Thus systems employing chelating and acidic extractants are cation-exchange systems, while those employing amine extractants are anion-exchange systems. Again it is emphasised that we are dealing with an equilibrium process, and as we shall see later, this is of prime importance in any consideration of solvent extraction processing since the size of plant is dependent, among other things, on the position of the equilibrium as described by equations such as [3], and on the rate at which equilibrium is reached in the extraction and other stages.

One point which should be stressed before we go any further is that really we should be considering the activities of the various species involved in metal extraction, rather than concentrations. Provided the concentrations of the metal are low, activity and concentration may be regarded, for all normal purposes, as being the same. However, in practical applications (for example leach liquors) where salt concentrations are high (> 0.1 M) substantial differences between activity and concentration will undoubtably occur. Our knowledge of the variation of activity with concentration in such solutions is very limited, but one way around the problem is to maintain the ionic strength of a particular system constant. In this way at least the experimental results will be relative. The problem of activity and concentration will arise when data determined from studies employing extractants at very low metal and salt concentrations are used to predict their use in practical processes. It is important to remember this point. Actually most practical studies employ real or simulated aqueous feed solutions, and provided these remain of essentially the same composition, the data obtained can be compared without much problem. In the following discussions we shall use concentrations, simply because this makes the equations much less cumbersome to deal with.

Equation [3] tells us that the extraction of a metal described by this equation is heavily dependent on the equilibrium pH of the aqueous phase. Thus, as the pH is decreased, (hydrogen ion concentration increased) metal extraction will decrease since the equilibrium will be shifted towards the left. Conversely, as the pH is increased, metal extraction will increase. Of course, a limit is imposed here by the pH at which the metal hydrolyses. The extraction is also dependent on the stability of the extractable metal complex formed, which is a function (in part) of the extractant, but more of this later.

We can see, then, that for systems where the extraction involves only very low metal concentrations, for example tracer or ppm quantities (as in analytical chemistry) the amount of hydrogen ion formed will be small, and will change the equilibrium pH of the system very little. On the other hand, the extraction of larger amounts of metal, as in a commercial process, will produce correspondingly larger amounts of hydrogen ion.

For example, in the extraction of copper by a monobasic reagent HA the extraction of one mole of copper will produce 2 moles of hydrogen ion:

$$CuSO_4 + 2\overline{HA} \rightleftharpoons \overline{Cu(A)_2} + H_2SO_4 \qquad [4]$$

and in the extraction of ferric iron, 3 moles of hydrogen ion will be produced for every mole of Fe(III) extracted:

$$Fe_2(SO_4)_3 + 6\overline{HA} \rightleftharpoons 2\overline{Fe(A)_3} + 3H_2SO_4 \qquad [5]$$

In order to achieve high metal loading of the solvent, the hydrogen ion produced must therefore be neutralised in some way, and examples will be given later as to how this is achieved.

Now the degree to which a metal is extracted by a solvent can be determined simply by an analysis of the aqueous phase. Let us consider the extraction of copper as illustrated by equation [4]. If we shake together an aqueous solution of copper sulphate of known concentration with a volume of, say, 8-hydroxyquinolihe (oxine) solution at a suitable pH, then at equilibrium we will have the condition:

$$\mathrm{CuSO_4} + \overline{\mathrm{2HOx}} \rightleftharpoons \overline{\mathrm{Cu(Ox)_2}} + \mathrm{H_2SO_4} \qquad [6]$$

The amount of copper extracted is determined simply by analysis of the aqueous phase (raffinate) after shaking. Since we know the initial copper concentration we can calculate the concentrations of copper in the organic phase (assuming no volume change in the phases occurs on shaking). Thus, under the experimental conditions used, we can readily calculate the ratio of copper in the two phases, which gives us a good indication of the extent to which the equilibrium in equation [6] is shifted to the right. The statement above is underlined to emphasize that only under the experimental conditions used will the ratio of concentrations of metal be valid; as we shall see later, even small changes in experimental conditions can change dramatically the resultant ratio.

This analytically determined distribution of a metal between an aqueous phase and an organic phase is known as the extraction coefficient, designated E, or the distribution coefficient, D (we shall use the former here), and is defined as:

$$E = \frac{\text{concentration of metal in the organic phase}}{\text{concentration of metal in the aqueous phase}} \qquad [7]$$

Metal concentrations are determined analytically, and are total concentrations of metal, *in whatever form*, in each phase. This very simple relationship is basic to all solvent extraction studies, and provides much of the data on which solvent extraction processes are based. One really need know no other relationships in order to carry out experimental work in developing a solvent extraction process, and it is probably safe to say that several operating processes have been developed with little or no more mathematical or theoretical knowledge.

As defined, E is independent of the phase ratio of the aqueous and organic phases. However, it should be evident that the phase ratio will influence the *amount* of metal extracted since, for example, at a given concentration of extractant, [HA], the amount of extractant available for extraction purposes is given by its concentration multiplied by the phase volume:

$$\text{Total amount of HA} = \overline{[\text{HA}]}\ \overline{v} \qquad [8]$$

where $\overline{v}$ is the volume of the organic phase.

We shall see that from a theoretical point of view the volumes of aqueous and organic phases are not of much concern because we are concerned only with *concentrations* of metal ions, whereas in practical investigations volumes of phases are of importance because here we are concerned with the *transfer of amounts* of metals from one phase to the other.

The equilibrium constant (K_E) for the system described by equation [3] is given by:

$$K_E = \frac{[\overline{MA_n}]}{[M^{n+}]} \cdot \frac{[H]^n}{[\overline{HA}]^n} \qquad [9]$$

which is a mathematical expression for the Law of Mass Action. This law, due to Guldberg and Waage$^{(8)}$ states that the velocity of a chemical reaction is proportional to the active masses of the reacting substances. For our discussions, active mass will be taken as concentration.

If we apply this law to a simple reversible reaction at constant temperature, such as:

$$A + B \rightleftharpoons C + D \qquad [10]$$

then the rate, or velocity, at which A and B react is proportional to their concentrations, and thus we can write:

$$V_f = k_f[A][B] \qquad [11]$$

where V_f is the velocity of the forward reaction which produces the reaction products C and D, and k_f is the proportionality constant. In the same way we can write the reverse reaction, in which the products of equation [10] react to form the initial reactants A and B, as:

$$V_r = k_f[C][D] \qquad [12]$$

Now at equilibrium, $V_f = V_r$ since the equilibrium here is dynamic and so:

$$k_f[A][B] = k_r[C][D] \qquad [13]$$

or

$$\frac{[C][D]}{[A][B]} = \frac{k_r}{k_f} = K_E \qquad [14]$$

where K_E is defined as the equilibrium constant for the reaction at constant temperature.

Notice the similarity between equation [9] and [14]. What does this equation tell us. Well, the first thing is that it obviously says nothing about the kinetics of the process, that is, the rate at which equilibrium is attained. It does tell us, however, that if one of the reactant or product concentrations is changed the equilibrium will adjust itself so as to maintain K_E constant. For example, if in a solvent extraction process we were to increase the concentration of metal ion in the aqueous phase, then the amount of metal extracted would increase to compensate and maintain K_E constant. This assumes, of course, that there is sufficient free extractant available in the solvent to extract more metal. If this were not so, K_E would not be maintained constant. This effect is prevalent in solvent extraction processes in which the solvent is loaded to near its maximum; an increase in metal concentration in the feed cannot be extracted and hence reports in the raffinate.

Returning now to equation [9], since we know that E is given by the first part of this relationship (equation [7]) then:

$$K_E = E\left(\frac{[H]}{[\overline{HA}]}\right)^n \qquad [15]$$

$$\text{and so } E = K_E\left(\frac{[\overline{HA}]}{[H]}\right)^n \qquad [16]$$

We see then that the extraction coefficient E, which is what we determine experimentally (equation [7]) is proportional to the equilibrium constant, to the nth power of the extractant concentration in the solvent phase, and is inversely proportional to the nth power of the hydrogen ion concentration in the aqueous phase. Thus K_E can be readily calculated from experimental data.

We see also from equation [16] that E is independent of the total metal concentration, and thus the extraction should be independent of the total amount of metal present. Consequently, this equation should hold for both high and low (tracer) concentrations.

It is possible to simplify equation [16] still further by including the condition that the concentration of the extractant be sufficiently high that extraction of a metal does not change its concentration by any significant amount. Thus $[\overline{HA}]$ can be regarded as a constant, and if we include this with the constant K_E, we have:

$$E = \frac{K^*}{[H]^n} \qquad [17]$$

where $K^* = K_E[\overline{HA}]$.

Under these conditions E is a function only of $[H]^n$. This is a useful equation to employ in some investigations because of its (relative) simplicity, and we will see an example of its use later on.

Of course, the reactions involved in the solvent extraction of metals are not usually as simple as indicated above, and especially not so if we are dealing with actual plant solutions such as leach liquors. Let us consider some of these reactions and their effects on metal extraction. Also, by making certain assumptions regarding a system we can eventually arrive back at equation [17].

Some of the equilibria involved in the system described by equation [3] are shown in Figure 2. First, we have the ionisation of the extractant in the aqueous phase, the equilibrium constant being:

$$K_i = \frac{[H^+][A^-]}{[HA]} \qquad [18]$$

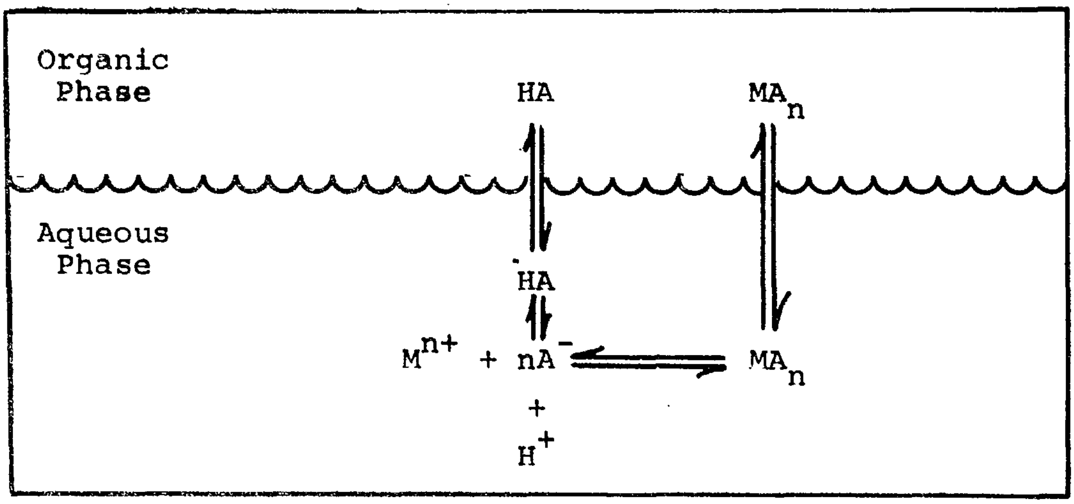


Figure 2: Some of the Equilibria Involved in the Extraction of a Metal.

This is followed by formation of the extractable metal complex, which is a stepwise series of reactions usually written in the following manner:

$$\begin{array}{lll}
M^{n+} + A^- \xrightleftharpoons{k_1} MA^{(n-1)+}; & k_1 = \dfrac{[MA^{(n-1)+}]}{[MA^{(n-1)}][A^-]} & \\
MA^{(n-1)+} + A^- \xrightleftharpoons{k_2} MA_2^{(n-2)+}; & k_2 = \dfrac{[MA_2^{(n-2)+}]}{[MA^{(n-1)+}][A^-]} & \\
\cdot \qquad\qquad \cdot & \cdot & \\
\cdot \qquad\qquad \cdot & \cdot & [19] \\
\cdot \qquad\qquad \cdot & \cdot & \\
MA_{(n-1)}^{+} + A^- \xrightleftharpoons{k_n} MA_n; & k_n = \dfrac{[MA_n]}{[MA_{(n-1)}^{+}][A^-]} &
\end{array}$$

for which the overall formation constant K_f, is:

$$K_f = k_1 k_2 \ldots k_n \qquad [20]$$

For the distribution of the extractant between the two phases we have:

$$K_{ex} = \frac{\overline{[HA]}}{[HA]} \qquad [21]$$

and this value will depend essentially on the solubility of the extractant in the aqueous phase. It should be noted that the value of K_{ex} can vary considerably depending on the salt concentration, temperature and pH of the aqueous phase.

The other equilibrium condition shown in Figure 2 is that for the metal-extractant species between the aqueous and organic phases (K_{MA_n}):

$$K_{MA_n} = \frac{\overline{[MA_n]}}{[MA_n]} \qquad [22]$$

Other reactions which may be operative, but not shown in Figure 2, are those involving metal complexation in the aqueous phase such as acid hydrolysis:

$$\begin{array}{ccccc} M(H_2O)_n^{n+} & \rightleftharpoons & M(H_2O)_{m-1}(OH)^{(n-1)+} & + & H^+ \\ \vdots & & \vdots & & \vdots \qquad\qquad [24] \\ M(H_2O)_{m-(n-1)}(OH)_{n-1}^{n-(n-1)+} & \rightleftharpoons & M(H_2O)_{m-n}(OH)_n & + & H^+ \end{array}$$

and complexation involving an anionic component of the aqueous phase:

$$\begin{array}{ccccc} M^{n+} & + & X^- & \rightleftharpoons & MX^{(n-1)+} \\ \vdots & & \vdots & & \vdots \qquad\qquad [24] \\ MX_{n-1}^{+} & + & X^- & \rightleftharpoons & MX_n \\ MX_n & + & X^- & \rightleftharpoons & MX_{n+1}^{-}, \text{ etc.} \end{array}$$

An example of the latter is ion association (or outer-sphere complexation) such as:

$$Co(H_2O)_6{}^{2+} + SO_4{}^{=} \rightleftharpoons \{Co(H_2O)_6{}^{2+}\cdot SO_4{}^{=}\} \qquad [25]$$

and such equilibria are dependent largely on the anion concentration in the aqueous phase.

If we now make the assumption that the only metal species in the organic phase is the fully complexed MA_n, that is, that the intermediate species in equation [19] are not extracted (generally a reasonable assumption) then the distribution of the metal between the two phases is, as before, given by:

$$E = \frac{[\overline{M}]}{[M]} \qquad [26]$$

and substituting the various reactions as undergone by the metal ion the formation of non-extractable species (equations [19], [23] and [24]), then:

$$E = \frac{\overline{[MA_n]}}{[M^{n+}] + [MA^{(n-1)+}] \ldots [MA_{n-1}{}^{+}] + \sum_i [M(OH)_i{}^{n-i}] + \sum_j [MX_j{}^{n-j}]} \qquad [27]$$

which is simply an expression for the distribution of a metal between the organic and aqueous phases as a function of extractable and non-extractable species, the overall effect of the formation of non-extractable species being given by the value of E which, as we noted previously, is simply an analytically determined ratio.

If we are not concerned with the individual effects of metal complexation in the aqueous phase, but merely in the total effects as they affect the extraction of a metal or metals, we need only concern ourselves with values of E determined for the particular experimental conditions in which we are interested. In order to determine the individual effects, and investigate how they influence or affect a particular system, we shall have to go further.

As we have seen, the formation and concentration of an extractable metal species is dependent on the various equilibria involved. If only the fully complexed (electrically neutral MA_n) specie is extractable, then metal extraction will be considerably influenced by the equilibria involved in the formation of MA_n. To take this into account, we will have to include equation [20] in our overall equation describing the system. Thus substituting equation [20] into equation [27], and also including the distribution of the extractable species (MA_n) between the two phases (equation [22]) we obtain an expression for E of the form:

$$E = \frac{K_f K_{ex} [A^-]^n}{1 + k_1[A^-] + k_1k_2[A^-]^2 + \ldots + K_f[A^-]^n \cdot 1 + \left(\dfrac{\sum\limits_i [M(OH)_i^{\,n-i}] + \sum\limits_j [MX^{n-j}]}{[MA_n]} \right)} \qquad [28]$$

Further substitution to include the ionisation of the extractant, upon which the extractable metal species depends (equation [18]), and the distribution of the extractant between the two phases (equation [21]) gives:

$$E = \frac{K_f K_{MA_n} K_i^{\,n}}{K_{ex}^{\,n}} \left[\left(\frac{[H^+]}{[HA]} \right)^n + \frac{k_1 K_i}{K_{ex}^{\,n}} \left(\frac{[H]}{[HA]} \right)^{n-1} + \ldots \right. \qquad [29]$$

$$+ \frac{k_1 k_2 \ldots k_{n-1} K_i^{\,n-1}}{K_{ex}^{\,n-1}} \cdot \frac{[H^+]}{[HA]} + \frac{K_f K_i^{\,n}}{K_{ex}^{\,n}} \left\{ 1 + \sum_i [M(OH)_i^{\,n-i}] \right.$$

$$\left. \left. + \sum_j [MX_j^{\,n-j}]/[MA_n] \right\} \right]^{-1}$$

This rather formidable equation can be simplified by making reasonable assumptions (educated guesses?) regarding the system, or in experimental work by judicious adjustment of conditions to eliminate certain species.

Let us consider what happens to this equation when the following assumptions are made:

(i) that the concentration of extractable metal species in the aqueous raffinate is neglibible. This is a reasonable assumption if we consider, from the practical point of view, that unless this were the case a commercial solvent process would not be an economical proposition because of the loss of extractant (as a soluble metal-extractant complex) to the raffinate. Because of the cost of extractant, which can be as much as $5 per lb, only a few (< 10) ppm loss can be tolerated, both from an economical and an environmental point of view.

(ii) that hydrolysis of metal does not occur (equation [22]). In many systems the pH of the aqueous phase is sufficiently low to inhibit hydrolysis problems, and in basic (ammoniacal) systems most, if not all, hydrolysable metals will be precipitated and removed prior to extraction.

(iii) that ion-association or outer-sphere complexation (equation [25]) does not occur. While this may be true of many analytical methods which employ solvent extraction, this type of complexation may be quite prevelant in commercial solvent extraction systems, arising from the high salt concentration in many feed solutions. For example, in the leaching of ores and concentrates, strong acid concentrations may be required which will produce a solution high in salt concentration. This effect will be considered later, but it must be borne in mind in any investigation into commercial SX processes.

(iv) that adduct formation between metal complexes and undissociated extractant, diluent or modifier does not occur. This condition is not usually obvious, but any synergism exhibited by the system may suggest that such a condition exists.

(v) that the concentrations of intermediate metal complex species are negligible (equation [19]). This is a reasonable assumption if the concentration of extractant is much greater than the metal ion concentration. However, in systems involving metal complexation with ammonia (ammine formation) for example, this assumption is almost certainly invalid because of the small differences between the formation constants for the concurrent metal ammine species. An example of this will be given later.

On the basis of these assumptions, equation [29] is greatly simplified to:

$$E = \frac{K_f K_{MA_n} K_i^n}{K_{ex}^n} \left\{ \frac{[\overline{HA}]}{[H^+]} \right\}^n \qquad [30]$$

and by combining the various constants then:

$$E = K_T \left[\frac{[\overline{HA}]}{[H]} \right]^n \qquad [31]$$

which is identical in form to equation [16].

Thus the extraction of a metal in these systems is heavily dependent on the concentration of the extractant in the organic phase and on the pH of the aqueous phase, when the assumptions made above are taken into account. Also, metal extraction is independent of the total metal ion concentration.

Equation [30] shows that the value of E is dependent on several factors other than the extractant concentration and pH. These are the stability of the extracted metal complexes (K_f), the distribution of the extractable metal complex between the two phases and the ionisation of the extractant on which E is directly dependent, and which is inversely dependent on the solubility of the extractant in the aqueous phase. This latter condition is the reverse of that required in a practical process, as indicated previously. However, the necessity for the extractant to be distributed between the two phases, which suggests that the extractable metal complex is formed in a homogeneous reaction in the aqueous phase and then transfers to the solvent phase, is a matter more of opinion than fact. The other alternative is a heterogeneous reaction occurring at the interface of the organic and aqueous phases, in which the ionic moiety of the extractant molecule is situated in the aqueous phase and the non-polar moiety in the organic phase, and complexation occurs essentially at the boundary. The uncharged complex thus formed is then soluble in the organic phase. Intuitively, these two extremes should be differentiable by extraction rate studies, since the latter phenomenon will depend (at least to a large extent) on the interfacial area. Other factors, such as interfacial tension, etc., will also have an effect. However, such studies are complicated by the fact that both physical (stirring and mixing) and chemical (rate controlling step) effects will influence the extraction rate.

Now we have seen that metal extraction by compound-forming extractants is very dependent on the pH of the system. If we do some tests on the extraction of metals by a particular extractant, at various pH values, we will arrive at an order of extraction of metals which is a function of the equilibrium pH. And if we use several extractants we will find that this order is remarkably constant even with similar but different extractants. Why is this so? The answer lies basically in the magnitude of the stability constants of the various metal complexes which, for any given extractant, is a function of the metal ion. Metal stability constants often follow the so-called

Irving-Williams series(9), which for divalent metal ions is Mn < Fe < Co < Ni < Cu > Zn, and which is remarkably independent of the nature of the complexing ligand. This same order is generally found for the extraction of metal complexes.

It is not surprising to find also that the general order of metal extraction follows the order of metal acid ionisation constants or hydrolysis constants (pK_a values):

$$M(H_2O)^{n+} \overset{K_{hydrol}}{\rightleftharpoons} M(OH)^{(n-1)+} + H^+ \qquad [32]$$

$$\text{where } pK_a = -\log K_{hydrol} \qquad [33]$$

The hydrolysis of metal ions is a fundamental importance in many processes, including solvent extraction. The formation of $M(OH)^{(n-1)+}$ complexes in the aqueous phase invariably gives rise to olation as the pH is increased:

$$2M(OH) \rightleftharpoons MOM + H_2O \qquad [34]$$

which is the formation of polynuclear hydroxy complexes of various forms, and which eventually leads to precipitation. Once precipitated, the metal hydroxide species have little tendency to react with a metal extractant because they are quite stable.

Thus we see that while an increase in pH favors the extraction of a metal species, a pH is reached at which hydrolysis and olation occur, resulting in a decrease in the metal ion available for complexation with the extractant and hence in a decrease in metal extraction. These effects give rise to the well used statement that 'metals extract best at a pH just below that at which they hydrolyse'. The order of acid ionisation constants for some metals (pK_a values) is: $Fe^{3+} < Cu^{2+} < Zn^{2+} \sim Co^{2+} < Fe^{2+} < Ni^{2+} \sim Mn^{2+}$(10), which is the general order of extraction of these metals by the extractants being considered here. Of course, other factors may alter this order, especially between metals for which the pK_a differences are small, such as complex formation in the aqueous phase.

Referring again to equation [30] or [31], increasing the concentration of extractant or decreasing the hydrogen ion concentration in the aqeuous phase (increasing pH) results in an increase in the extraction coefficient (E). These two effects are not independent when extraction involves a reaction as shown in equation [3]. This is because, as the extraction of metal increases, the hydrogen ion liberated increases in concentration in the aqueous phase, resulting in a decrease in E. Obviously at low metal ion concentrations this effect will be minimal, but in studies on SX processes, where metal concentrations in the organic phase can exceed 20 kgm m^{-3}, the increase in aqueous phase pH is significant. It is imperative, therefore, that in such studies the pH of the aqueous phase be determined <u>after</u> the system has reached equilibrium, and that this equilibrium pH be the one reported. This most important point will be considered more fully below.

As an example of a fairly complex metal extraction system involving the formation of intermediate metal complex species, let us look at the extraction of a metal, for example copper, from an ammonium sulphate solution (pH > 7) by a carboxylic acid. Generally, extraction of metals by carboxylic acids can be represented by a form of equation [3], thus:

$$M^{n+} + \overline{nRCOOH} \rightleftharpoons \overline{M(RCOO)_n} + nH^+ \qquad [35]$$

and in the case of cupric ion, then

$$Cu^{2+} + \overline{2RCOOH} \rightleftharpoons \overline{Cu(RCOO)_2} + 2H^+ \qquad [36]$$

If now the aqueous phase contains ammonium ions (NH_4^+) arising from the ionisation of ammonium sulphate then, at sufficiently high pH values, hydrolysis of ammonium ion will occur to give free ammonia (NH_3):

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad [37]$$

for which the dissociation constant is:

$$K_{NH_4^+} = \frac{[NH_3][H^+]}{[NH_4^+]} \qquad [38]$$

The free ammonia so formed will complex with metal ions capable of forming ammine complexes, the formation of which, as we have seen before, will be governed by the equilibria:

$$Cu^{2+} + NH_3 \overset{k_1}{\rightleftharpoons} Cu(NH_3)^{2+} \qquad k_1 = \frac{[Cu(NH_3)^{2+}]}{[Cu^{2+}][NH_3]}$$

$$\begin{array}{llll} Cu(NH_3)^{2+} + NH_3 \overset{k_2}{\rightleftharpoons} Cu(NH_3)_2{}^{2+} & & k_2 = \dfrac{[Cu(NH_3)_2{}^{2+}]}{[Cu(NH_3)^{2+}][NH_3]} & \\ \cdot \quad \cdot \quad \cdot & & \cdot & \\ \cdot \quad \cdot \quad \cdot & & \cdot & [39] \\ \cdot \quad \cdot \quad \cdot & & \cdot & \\ Cu(NH_3)_{i-1}{}^{2+} + NH_3 \overset{k_i}{\rightleftharpoons} Cu(NH_3)_i{}^{2+} & & k_i = \dfrac{[Cu(NH_3)_i{}^{2+}]}{[Cu(NH_3)_{i-1}{}^{2+}][NH_3]} & \end{array}$$

where i is the metal coordination number, in this case 4, and the overall formation constant is given by:

$$\begin{aligned} K_{Cu(NH_3)_i{}^{2+}} &= \frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4} \\ &= k_1k_2k_3k_4 \end{aligned} \qquad [40]$$

Again we make various (reasonable) assumptions regarding the conditions existing in this system, namely, that the formation of metal ammines affects the extraction of metal only as a result of decreasing the concentration of the extractable metal ions in the aqueous phase (that is, the metal ammines are not extracted), and that the only metal species in the organic phase is $Cu(RCOO)_2$ (equation [36]). The expression for E is then:

$$E = \frac{\overline{[Cu(RCOO)_2]}}{\sum\limits_{0}^{i}[Cu(NH_3)_4{}^{2+}]} \qquad [41]$$

and by substituting equations [16], [22], [38] and [40] into [41] we obtain:

$$E = \frac{K_E \cdot [\overline{RCOOH}]^2}{\sum_{o}^{4} K_{Cu(NH_3)_4{}^{2+}} \cdot K_{NH_4{}^+}{}^{4} \cdot [\overline{RCOOH}]^{4} \cdot [H]^{2-4}} \qquad [42]$$

or in general:

$$E = \frac{K_E \cdot [\overline{HA}]^n}{\sum_{o}^{i} K_{M(NH_3)_i{}^{n+}} \cdot K_{NH_4{}^+}{}^{i} \cdot [\overline{HA}]^{i} \cdot [H]^{n-i}} \qquad [43]$$

From equation [43] we again see that E is independent of total metal concentration, and depends largely on the extractant concentration and pH. If now the extractant concentration is made sufficiently large with respect to the metal concentration, then it will change very little as metal is extracted and may be considered to be constant, and can be combined with K_E as another constant, say K*. Further, at constant ammonium ion concentration $[NH_4]^+$ may also be considered to be constant.

Now if the average number of ammonia ligands per metal atom in the aqueous phase is j, then by taking logarithms of equation [43] and differentiating with respect to pH, we obtain:

$$\left(\frac{\partial \log E}{\partial pH}\right)_{[NH_4]^+} = n - j \qquad [44]$$

A plot of log E versus pH will have the shape of a parabola (at constant ammonium ion concentration), the slope of which at any point will be determined by j, the average number of ammonia ligands coordinated to the metal ion in the aqueous phase.

Since the value of $K_{NH_4^+}$ for ammonium sulphate is known, the values of $K_{Cu(NH_3)_i^{2+}}$ for copper ammine complexes are available from the literature(11), (as they are for many metals forming soluble ammine complexes) and K_E and K* can be readily determined by experiment, we can use equation [43] in studying the effects of the formation of non-extractable copper ammines on the extraction of this metal from ammonium sulphate solutions.

This approach has been taken in several studies on the extraction of metals from ammonium sulphate solutions(12-15), and generally it is found that the experimental extraction data fit well with theoretically derived data (Figure 3). Complications occur in the case of cobalt, since in ammoniacal solution cobalt(II) is readily oxidised to cobalt(III), and unless this is taken into account in the calculations, deviations occur between calculated and theoretical data.

Solvent extraction studies on ammoniacal systems are of particular significance from a practical point of view because of the fact that metals such as copper, nickel and cobalt can be, and are, leached from ores and concentrates by ammonia-ammonium salt solutions, and the separation and recovery of these metals from such liquors is of great economic importance.

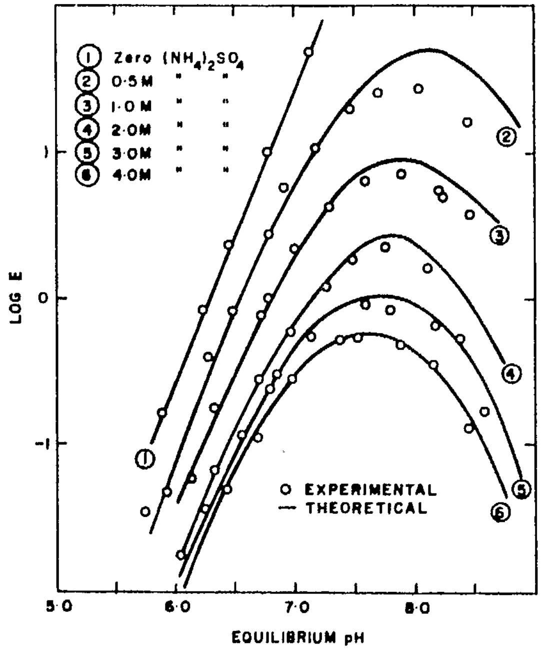


Figure 3: Extraction of Nickel From Ammonium Sulphate Solution with 0.5 M Versatic 911.

Let us now consider further the relationships which exist between the various parameters involved in the solvent extraction of metals. Taking logarithms of equation [16] we obtain:

$$\log E = \log K_E + n \log [\overline{HA}] - n \log [H] \qquad [45]$$

Thus by plotting log E versus pH at constant $[\overline{HA}]$, we should obtain a curve whose slope is equal to n. Further, if we write this equation as:

$$\log E = \log K_E + n(\log [\overline{HA}] + pH) \qquad [46]$$

then plots of log E versus $(\log [\overline{HA}] + pH)$ will give a straight line of slope n and an intercept equal to log K_E. Such plots are useful in getting around the problem of having to reproduce extractant concentrations and identical pH values in experimental studies. By suitable manipulation we see that we can obtain an expression involving - log [H], that is, pH. So multiplying by $\frac{1}{n}$ we have:

$$\frac{1}{n} \log E = \frac{1}{n} \log K_E + \log \overline{[HA]} - \log [H] \qquad [47]$$

or,

$$- \log [H] = pH = \frac{1}{n} \log E - \frac{1}{n} \log K_E - \log \overline{[HA]} \qquad [48]$$

Now if we have the situation where (for an A/O ratio of 1, that is, where $v = \overline{v}$), 50 percent of the metal is extracted into the organic phase, then we know that $E = 1$ from our definition of E in equation [7]. This is a unique situation because we can see immediately that log E is now 0. Thus putting $E = 1$ in equation [47] eliminates E, and so:

$$0 = \frac{1}{n} \log K_E + \log \overline{[HA]} - \log [H] \qquad [49]$$

and by rearranging:

$$- \log [H] = pH = - \frac{1}{n} \log K_E - \log \overline{[HA]} \qquad [50]$$

The pH given by equation [50] is that at which 50 percent of the metal is extracted, and is known variously as pH_{50}, $pH_{0.5}$ or $pH_{1/2}$. We shall use the latter designation here.

Now the percent metal extracted (P) will vary with variation in the A/O ratio:

$$P = \frac{100\ E}{E + v/\bar{v}} \qquad [51]$$

where v and $\bar{v}$ are the volumes of the aqueous and organic phases respectively. For the case where $v = \bar{v}$, then $v/\bar{v} = 1$, but for all other cases the equation for P has to be normalised, thus:

$$P = \frac{100(E\cdot v/\bar{v})}{(E\cdot \bar{v}/v) + 1} \qquad [52]$$

Rearranging equation [51] and equating in terms of the equilibrium constant for equation [16], we have:

$$E = \frac{P}{100 - P} = K_E \frac{\overline{[HA]}^n}{[H]^n} \qquad [53]$$

and taking logarithms we have:

$$\log E - \log (100-P) = \log K_E + n \log \overline{[HA]} - n \log [H] \qquad [54]$$

Equation [54] thus represents a family of sigmoid curves obtained by plotting P versus pH, and the position of each curve on the pH axis will depend only on K_E and $\overline{[HA]}$. We can, again, derive an equation for $pH_{1/2}$ from equation [54].

Deviations from the theoretical slope n in such plots will indicate that the extraction is not as simple as described, for example, by equation [3], but may involve metal complexation in the aqueous phase, adduct formation or polymerisation in the organic phase, and so on.

Elimination of the term for the concentration of extractant in equation [16] can be brought about by taking $\overline{[HA]}$ sufficiently large and the metal ion concentration sufficiently small that extraction of the metal will involve only a small amount of the total extractant. Thus we can consider $\overline{[HA]}$ as being constant, and can combine this with K_E to produce another constant, say K*, then:

$$pH_{1/2} = -\frac{1}{n} K^* \qquad [55]$$

This approach is useful only in fundamental studies, and makes calculations somewhat easier since it eliminates one variable. In practical studies where maximum use of the extractant, that is maximum metal loading, is required as an aid to achieving maximum economy of the process, this approach cannot be used.

The difference in $pH_{1/2}$ values for two metals having the same values of n (same oxidation states) can be used as a measure of the degree of separation of the metals. For example, if we require > 99 per cent extraction of metal M_1 from metal M_2, with < 1 per cent mutual contamination in a single extraction using equal aqueous and organic volumes, we have the situation:

$$M_1/M_2 = 10^2/10^{-2} = 10^4$$

thus $(pH_{1/2}M_1 - pH_{1/2}M_2) > 4$. For the best separation of these metals, a pH intermediate between the $pH_{1/2}$ values would be required. Similarly in selective stripping operations, using an aqueous solution of 2 pH units lower than the higher $pH_{1/2}$ would, theoretically at least, allow separation of a metal from an extract containing both metals. We can arrive at this same conclusion using values of E for two metals. Thus E_1/E_2, which is usually known as the separation factor (SF), becomes:

$$SF = E_1/E_2 = 10^2/10^{-2} = 10^4 \qquad [56]$$

As far as practical solvent extraction studies are concerned, one rarely has the situation described above, that is, > 99 per cent metal extraction in a single stage. Thus the use of $pH_{1/2}$ values in this context is rarely used. Separation factors have seen more use in practice, and more will be said about this later.

What other information can we obtain from equation [50]? First, we see that an increase in extractant concentration will result in a decrease in $pH_{1/2}$. Thus by increasing the extractant concentration tenfold, the $pH_{1/2}$ is shifted to a lower value by 1 pH unit. Second, the higher the value of E the lower will be the value of $pH_{1/2}$, and the whole extraction isotherm will shift to lower pH values.

These effects are illustrated in Figure 4 which shows the extraction of manganese(II) by oxine (10^{-1} and 10^{-2} M) in chloroform(16). Thus at 10^{-2} M oxine, $pH_{1/2}$ is 6.66, while at 10^{-1} M it is 5.66, a change of 1 pH unit, and the whole curve is shifted to the left on the pH axis.

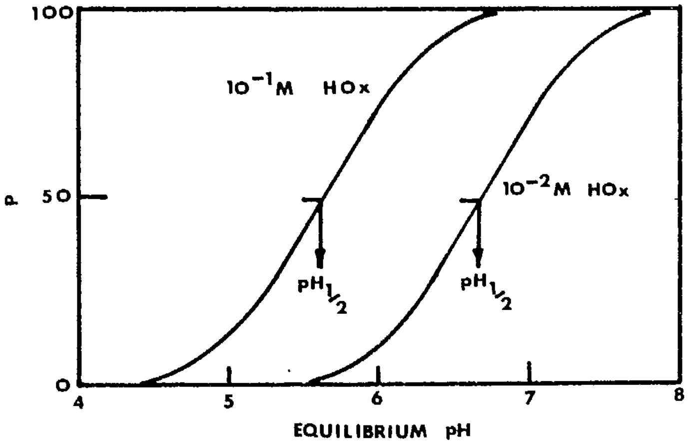


Figure 4: Effect of Extractant Concentration on the Extraction of Mn(II) by Oxine.

Again taking equation [16] for the equilibrium constant of a reaction of the type:

$$M^{n+} + \overline{nHA} \rightleftharpoons \overline{MA_n} + nH^+ \qquad [3]$$

by introducing expressions for the ionisation constant (K_i) of the extractant (equation [18]), the distribution of the extractant (K_{ex}) between the two phases (equation [21]), and the overall stability constant β_n ($\beta_n = k_1k_2 \ldots k_n$, the individual or stepwise stability constants) of the extracted metal complex ($\overline{MA_n}$), we arrive at:

$$K_E = E\beta_n \frac{K_i{}^n}{K_{ex}{}^n} \qquad [57]$$

and by taking logarithms and multiplying by $-\frac{1}{n}$ in the usual way we have:

$$-\frac{1}{n}\log K_E = pK_i + \log K_{ex} - \frac{1}{n}\log \beta_n E \qquad [58]$$

which we can equate with $pH_{1/2}$ as before. From this equation for $pH_{1/2}$ we can draw the following conclusions; that the more easily ionised -- lower pK_i or the more acidic -- is the extractant, the lower will be the $pH_{1/2}$ value; the greater the stability constant (β_n) of the extracted metal complex, the lower will be the $pH_{1/2}$ value; in other words the lower will be the pH at which the metal complex will be formed and thus extracted; and, as we have seen before, the higher the concentration of extractant, the lower will be the $pH_{1/2}$ value.

As was shown previously, the order of metal extraction with compound-forming extractants generally follows the same order irrespective of the extractant. This is also concluded from an examination of equation [58] as a result of the magnitude of the metal-complex stability constant. Thus the extraction of a series of metals by a particular extractant will normally be in the order of decreasing β_n values, thus $\beta_{n_1} > \beta_{n_2} > \beta_{n_3}$ ... etc. for metals 1, 2, 3 ...., or, in terms of $pH_{1/2}$ values, $pH_{1/2^1} < pH_{1/2^2} < pH_{1/2^3}$ ... etc. Thus metal 1 having the highest β_n will extract at the lowest $pH_{1/2}$. Under similar experimental conditions the order of $pH_{1/2}$ for the extraction of a single metal by various extractants will then indicate the order of metal-extractant stability, or the order of the basicity of the extractant.

We can modify equation [50] to take into account adduct formation in the solvent phase. Adducts referred to here are metal complexes in which some water of hydration is replaced by molecules of the extractant, that is, solvation of the complex by the solvent. For example in the extraction of some metals by oxine, adducts of the type shown below have been reported(16).

$Co(Ox)_2 \cdot 2HOx$

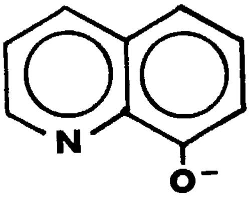
$Zn(Ox)_2 \cdot 2HOx$

$Cd(Ox)_2 \cdot 2HOx$

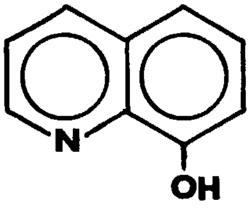
$Ag(Ox) \cdot HOx$

$Sc(Ox)_3 \cdot HOx$

where Ox =



HOx =



Metals such as Cu^{2+}, Ni^{2+}, Fe^{3+} and Mn^{2+} do not form adducts, and are extracted as $M^{n+}(Ox)_n$ complexes.

Now referring to equation [50], we note that E was defined as a function of the nth power of $[\overline{HA}]$, where n can be considered as the number of molecules of extractant involved in the metal complex (for monobasic extractants). In the case of adduct formation, the number of extractant molecules associated with the metal complex will be greater than n, say n + i. It should be noted that while the hydrogen ion concentration in equation [50] is also raised to the power n, it will remain so in the case of adduct formation because here the neutral extractant molecule is adducted and not its anionic moiety.

Thus equation [50] can be re-written:

$$E = K_E \frac{\overline{[HA]}^{n+i}}{[H]^n} \qquad [59]$$

and using this to derive an equation for $pH_{1/2}$ we obtain:

$$pH_{1/2} = -\frac{1}{n}\log K_E - \frac{n+i}{n}\log \overline{[HA]} + \frac{1}{n}\log E \qquad [60]$$

This equation tells us that if $n > 0$, an increase in extractant concentration will have a larger effect on the decrease in $pH_{1/2}$ values. The theoretical values of $pH_{1/2}$ for various values of n and i are shown in Table 1.

So systems in which the change in $pH_{1/2}$ as a function of extractant concentration changes by more than 1 pH unit for a tenfold change in $\overline{[HA]}$ would suggest that adduct formation is involved.

Other factors can affect $pH_{1/2}$ values, such as metal complexation in the aqueous phase. This has been shown, for example, in the case of extraction of copper, nickel and cobalt from ammonium sulphate solutions, using a carboxylic acid(12-15). Here, increasing the salt concentration shifts the $pH_{1/2}$ values to higher values; thus changing the ammonium sulphate concentration from 0 to 4 M gives an increase in $pH_{1/2}$ values for cobalt, nickel and copper of approximately 0.95, 1.2 and 1.2 pH units, respectively. This shift in $pH_{1/2}$ can be used to determine the association constant of a metal-anion association complex$^{(17)}$.

TABLE 1

Theoretical Decrease in $pH_{1/2}$ as a Function of n and i Values

n	i	Decrease in $pH_{1/2}$ Value
1	0	1
1	1	2
2	0	1
2	1	3/2
2	2	2
3	0	1
3	1	4/3
3	2	5/3

This effect of salt concentration on $pH_{1/2}$ values indicates the necessity of ensuring that in any comparison of such values the experimental conditions under which they were obtained should be identical. This need for similar experimental conditions when comparing solvent extraction data is very important, and more will be said on this matter later.

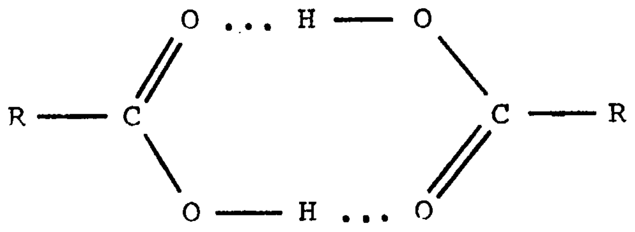
Acidic Extractants

Extraction mechanisms involving acidic extractants are more complicated to describe, in a general way, than with chelating extractants. While the same qualitative considerations apply, such as the influence of pH, extractant and metal ion concentration, factors affecting the order of metal extraction and so on, the composition of the extracted species is much less predictable.

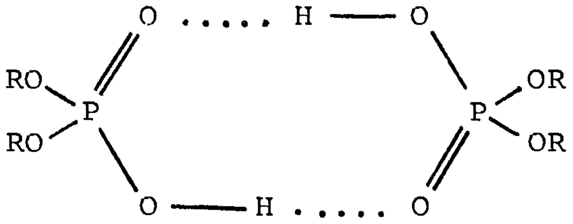
Extraction of metals by organophosphorus, carboxylic, and sulphonic acids is affected more by the solvent phase properties than it is for chelating extractants. Thus both organophosphorus and carboxylic acids often form dimers or polymers (self association) in the organic phase, mainly as a result of hydrogen bonding, which may affect considerably their extractive properties. Solvation of the extracted species is also a factor to be considered.

It will be useful to consider some of these properties of the acidic extractants, and see how the equations involved differ from those for extraction by chelating reagents.

Carboxylic acids usually, but not always (19), form dimers in non-polar organic liquids as a result of (intermolecular) hydrogen bonding, and are considered to be of the type:



where the dotted lines indicate the hydrogen bonds. The possibility also exists for hydrogen bonding between the extractant and diluent; thus propionic acid has been reported to hydrogen bond to chloroform, the bonding occurring between the hydrogen of the chloroform and the propionic acid molecule(18). Di-(2-ethylhexyl) phosphoric acid, (D2EHPA), $(RO)_2POOH$, forms dimers in most organic liquids(19):



For the cases where dimer- or polymerisation of the extractant occurs, the equilibrium or mass action equation must be modified. Thus in the case of a carboxylic acid which forms dimers in an organic diluent:

$$M^{n+} + \frac{m}{2}\,(\overline{H_2A_2}) \rightleftharpoons (\overline{MA_n(m-n)HA}) + nH^{+} \qquad [61]$$

where H_2A_2 represents the dimeric form of the extractant, and m is the total number of extractant molecules in the extracted species. This equation also indicates that the amount of hydrogen ion generated in the extraction is the same as would be generated in a similar extraction system in which dimerisation did not occur.

Proceeding in the usual manner, then:

$$\log E = \log K_E + npH + \frac{m}{2}\log[\overline{H_2A_2}] \qquad [62]$$

where K_E is the equilibrium constant as before, Equation [62] is thus of the same form as, for example, equation [45], and in the same way we can obtain an expression for $pH_{1/2}$:

$$pH_{1/2} = -\frac{1}{n}\log K_E - \frac{m}{2n}\log [\overline{H_2A_2}] \qquad [63]$$

which resembles closely equation [60] which described $pH_{1/2}$ as a function of adduct formation.

According to equation [63] then, the $pH_{1/2}$ value should vary directly as the concentration of the dimeric extractant species in the organic phase, and so a plot of $pH_{1/2}$ versus log $[\overline{H_2A_2}]$ should give a slope of $-m/2n$ from which the value of m can be determined.

The concentration of metal ion can affect the value of E as we have seen. The effect of polymerisation of the extracted complex in the solvent phase can also affect E, and may result in an increase in E as the metal ion concentration is increased, or in a decrease as a result of polymerisation or complexation in the aqueous phase.

If we consider the former case, then we shall have to modify our equilibrium expression. Thus, for example, we can write:

$$M^{n+} + \frac{m}{2}[\overline{H_2A_2}] \rightleftharpoons \frac{1}{p}[\overline{(MA_n \cdot (m-n)HA)_p}] + nH^+ \qquad [64]$$

in which p represents the average number of units, MA_n, in the polymer complex.

In this situation we no longer have the condition that the concentration (molarity) of the metal in the solvent phase is equal to the concentration of the extracted species (as was generally the case for chelating extractants) because of the polymerisation. To account for this effect in describing E we must again make some modifications to our general expression, namely:

$$E = \frac{\overline{[M]}}{[M]} = \frac{\dfrac{\overline{[M]}^{1/p}}{p} \cdot [M]^{\frac{p-1}{p}}}{{[M]\,\frac{1}{p}}^{1/p}} \qquad [65]$$

It can then be shown by suitable substitution (which we will not go into here) that at $pH_{1/2}$, where $[M] = M_{Total/2}$, the rate of change of $pH_{1/2}$ with total metal ion concentration is equal to $-(p-1)/np$, and so p can be determined from a plot of $pH_{1/2}$ versus log M_{Total}, the slope of the line being equal to p.

This type of general approach can be taken for any system in which dimer or polymer formation occurs.

Studies on metal extractions using D2EHPA as the extractant have indicated two extreme situations depending on the metal ion concentration. At low metal loading (tracer levels), metal extraction is considered to occur according to the equation

$$M^{n+} + n\overline{(HA)}_2 \rightleftharpoons \overline{M(A\cdot HA)} + nH^+ \qquad [66]$$

whereas at higher metal loading the available evidence supports the view that extraction occurs according to:

$$M^{n+} + \overline{nHA} \rightleftharpoons \overline{MA_n} + nH^+ \qquad [67]$$

which suggests that the effects of dimerisation of the D2EHPA are apparent only with low metal concentrations, and that perhaps the dimerisation effects are destroyed as the metal loading increases. The same situation probably obtains with carboxylic acids, and thus the binuclear complexes reported in the extraction of copper, nickel and cobalt by naphthenic acid may be the result of low metal loading in these studies (20). The extracted species reported here were $Cu_2A_4 \cdot 2HA$, $Ni_2A_4 \cdot 4HA$ and $Co_2A_4 \cdot 4HA$.

The order of metal extraction by acidic extractants is essentially the same as for chelating extractants, for the same reasons. Some reversals in this order between adjacent metals can be achieved, usually as a result of complexation in the aqueous phase.

Metal-metal exchange between metal-extractant complexes can be achieved quite readily with acidic extractants. For example:

$$2Fe^{3+} + \overline{3CuA_2} \rightleftharpoons \overline{2FeA_3} + 3Cu^{2+} \qquad [68]$$

in which a copper-carboxylic acid complex in an organic phase is contacted with a ferric ion solution to extract the ferric ion and replace it in the aqueous phase with copper. Thus for a series of metal extractions by an acidic extractant, a metal can be displaced from the solvent phase by a metal to its left in the series. This type of exchange has been used in a Russian process for the separation of cobalt and nickel using a carboxylic acid extractant(21).

Of course, stripping of a metal from a solvent phase by acids is a well known example of this exchange, in which case hydrogen ion plays the role of a metal ion.

This same metal-metal exchange principle has been used for pH control in the separation of cobalt and nickel(22). The use of the sodium salt of D2EHPA as the extractant, in which exchange of sodium for cobalt occurs at pH 5-6, produces the sodium salt of the anion used in the system, which is essentially neutral and hence does not affect the pH of the system as would the formation of hydrogen ion if the acid form of D2EHPA were used. This is then a metal-metal exchange rather than a metal-hydrogen ion exchange.

Sulphonic and alkyl sulphuric acids have not been used as extractants in commercial solvent extraction operations. Like the carboxylic acids, they tend to have high solubility in the aqueous phase, and aggregate in the solvent phase.

Systems Involving Ion Association

Systems employing ion association are much more difficult to analyse than those previously discussed. This difficulty arises as a result of our lack of understanding of species in concentrated solutions, that is, solutions of greater than about 0.1 M ionic strength. Thus the usually accepted equivalence of concentration with activity at low concentrations of salts cannot be applied, and the quantitative expressions derived for chelate and acidic extractant system become essentially qualitative in ion-association systems. Accordingly, much of the work done on such systems from a more practical point of view is invariably empirical in nature.

It will be instructive to discuss, albeit briefly, what we mean by ion association, or outer-sphere complexation as it may be termed. This phenomenon results from physical attractive forces between oppositely charged species. For example, the association of ions A^+ and B^- to form an ion-association complex $A^+ \cdot B^-$:

$$A^+ + B^- \rightleftharpoons (A^+ \cdot B^-)^0 \qquad [69]$$

for which the association constant, K_{ass}, is given by:

$$K_{ass} = \frac{[(A^+ \cdot B^-)]}{[A^+][B^-]} \qquad [70]$$

Much of the theory of ion-association complexes is due to Bjerrum(23) who related the formation of such complexes to the various parameters involved by the equation:

$$K_{ass} = \frac{4\pi N e^2}{10^3 \varepsilon k t} \cdot Q(b) \qquad [71]$$

in which

$$b = \frac{e^2}{a \varepsilon k T} \qquad [72]$$

and a is a parameter interpreted as the distance between the charge centers of oppositely charged ions when in contact, ε is the dielectric constant (DEC) of the solvent, and the other symbols have their usual meaning. Thus ion-association is largely dependent on DEC, and will increase with a decrease in the DEC of the solvent. The high DEC of water (78.5 at 25°C) would then tend to inhibit ion-association, but as the ionic concentration is increased the DEC decreases. In solvents of low DEC, ion association would tend to be the rule.

Ion association also increases with temperature in solvents of high DEC since DEC decreases significantly with increasing temperature and εT (equation [71]) decreases. Conversely, with solvents of low DEC, ion association decreases with increasing temperature since ε does not change much, hence εT increases.

Ion-association constants vary significantly; for example, K_{ass} for $Co(NH_3)_6{}^{3+}\cdot Cl^-$ is 74, for $Co(NH_3)_6{}^{3+}\cdot I^-$ is 17, for $Co(NH_3)_6{}^{3+}\cdot SO_4{}^{2-}$ is 2.2×10^3, all at 25°C.

It should be evident then that for solvent extraction systems employing high ionic concentrations in the aqueous phase, considerable ion association between metal complexes and other ions will occur, the compositions of which will vary depending on many factors.

Let us now consider the organic phase and the problems associated in trying to understand reactions occurring between it and the aqueous phase components.

Commercial processes involving ion-association systems employ long chain aliphatic primary (RNH_2), secondary (R_1R_2NH), tertiary ($R_1R_2R_3N$) amines, or quaternary ammonium salts ($R_1R_2R_3R_4N^+ \cdot X^-$) as the extractant. All these reagents, when dissolved in a diluent, aggregate to a greater or lesser extent. Because of this aggregation the number of equilibria involved is a largely unknown factor, and especially so when we include the equilibria involved in the aqueous phase. Thus the number of equilibria required to describe the ion-association extraction of metals is many times that involved in, say, a chelate extraction system.

As mentioned above, a major complication in amine extraction systems is the molecular association of amine salts into dimers, trimers, etc.:

$$R_3NH^+ \cdot X^- \rightleftharpoons (R_3NH^+ \cdot X^-)_2 \rightleftharpoons \ldots \rightleftharpoons (R_3NH^+ \cdot X^-)_n \qquad [73]$$

and one of the more important factors affecting aggregation is the nature of the diluent used.

Extraction of a metal M^{n+}, which forms anionic complexes with an anion A^- in the aqueous phase, by an amine salt R_3NHA can be represented as an anion exchange process such as:

$$MA_n^{(n-m)+} + \overline{(m-n)(R_3NHA)} \rightleftharpoons \overline{((R_3NH)_{m-n}MA_n)} + (m-n)A^- \qquad [74]$$

In order to achieve this exchange the amine must first be converted to an appropriate salt to provide an anion to exchange with the metal specie:

$$\overline{R_3N} + HX \rightleftharpoons \overline{R_3NH^+ \cdot X^-}$$

that is, the amine in the solvent phase when contacted with an aqueous acid (HX) solution extracts the acid to form an amine salt or polar ion-pair, $R_3NH^+ \cdot X^-$, in the solvent phase. Thus on contacting this solvent with an aqueous solution containing an anionic metal species $\overline{MY}^-$, exchange can occur according to:

$$\overline{R_3NH^+ \cdot X^-} + MY^- \rightleftharpoons \overline{R_3NH^+ \cdot MY^-} + X^- \qquad [75]$$

It has been shown that it is not absolutely necessary to have anion exchange occur in order to extract an anionic metal species. Thus in the extraction of uranium, which is usually represented as the extraction of a uranyl sulphate anion ($UO_2(SO_4)_3{}^{4-}$), the neutral uranyl sulphate species can also be extracted(24):

$$\overline{(R_3NH)_2SO_4} + UO_2SO_4 \rightleftharpoons \overline{(R_3NH)_2UO_2(SO_4)_2} \qquad [76]$$

The degree to which either the extraction of an anionic or neutral uranium species is involved then depends on the uranium species present in the aqueous phase, which in turn depends on the sulphate concentration and pH of the aqueous phase. In acid sulphate systems the importance of pH becomes more pronounced than for nitrate or chloride systems as a result of the dibasic nature of sulphuric acid, which gives rise to the sulphate-bisulphate equilibria:

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \qquad [77]$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^= \qquad [78]$$

Thus at high acid concentrations (low pH), bisulphate is the major anionic species present, whereas, as the acid concentration is decreased, the sulphate ion will be the predominant specie.

The use of high bisulphate concentrations results in a decrease in uranium extraction presumably because uranyl bisulphate is not extracted. Conversely, at pH values which produce high sulphate concentrations, the amine does not easily form the sulphate salt (is present as free amine) and thus does not extract the anionic uranyl sulphate complex. As a result, the pH range over which uranium extracts from a sulphate system is limited by these conditions.

Uranyl nitrate shows little tendency to form anionic nitrate complexes, and thus the extraction of this metal from nitrate systems by amines is not popular. The mechanism of uranium extraction in this case has also been suggested to involve the extraction of a neutral species(25):

$$\overline{R_3N} + HNO_3 \rightleftharpoons \overline{R_3NH{\cdot}NO_3}$$

$$\overline{2R_3NH{\cdot}NO_3} \rightleftharpoons \overline{(R_3NH{\cdot}NO_3)_2} \quad \text{(dimer)} \qquad [79]$$

$$UO_2(NO_3)_2 + \overline{2R_3NH{\cdot}NO_3} \rightleftharpoons \overline{(R_3NH{\cdot}NO_3)_2UO_2(NO_3)_2}$$

$$UO_2(NO_3)_2 + \overline{2(R_3NH{\cdot}NO_3)_2} \rightleftharpoons \overline{\{(R_3NH{\cdot}NO_3)_2\}_2UO_2(NO_3)_2}$$

The extraction of anionic metal chloro complexes by amines is used in commercial operations such as the separation of cobalt from nickel$^{(26)}$. It is known that nickel has little tendency to form anionic chloro complexes, whereas cobalt has. Thus cobalt can be extracted from nickel in high chloride (> 200 kgm m^{-3}) solution by a tertiary amine. This can be represented by an equation of the type:

$$\mathrm{CoCl_4^{=}} + \overline{\mathrm{2R_3NH^{+}\cdot Cl^{-}}} \rightleftharpoons \overline{\mathrm{\{(R_3NH^{+})_2\cdot CoCl_4^{=}\}}} + \mathrm{2Cl^{-}} \qquad [80]$$

Some of the equilibria involved are shown in Figure 5.

In general, the ease of extraction of complex metal anion species from chloride media by amines follows the order: quaternary > tertiary > secondary > primary.

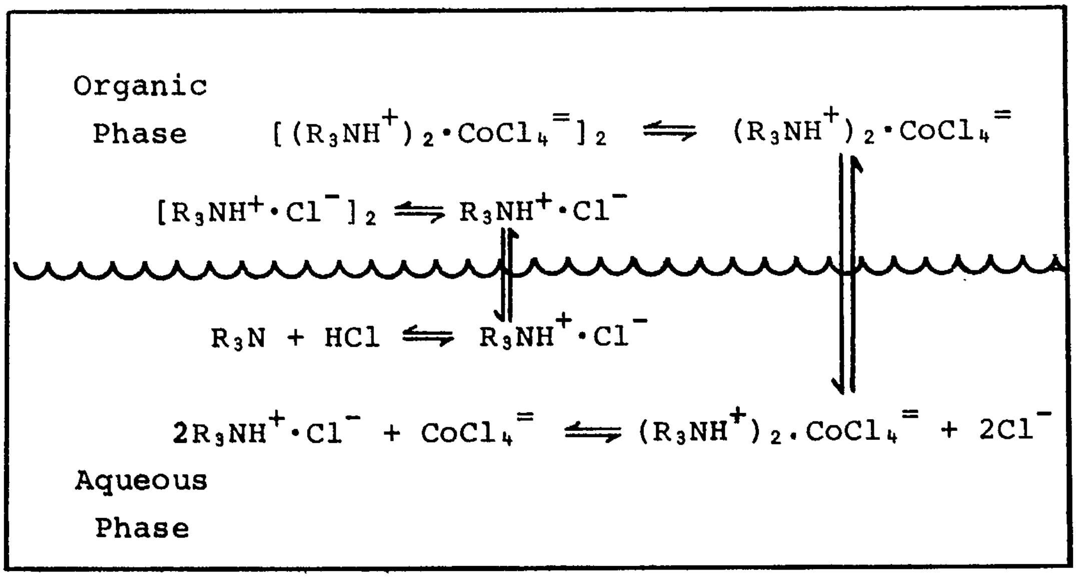


Figure 5: Some Equilibria Involved in the Extraction of Cobalt from a Chloride System using a Tertiary Amine.

If we take as example the extraction of cobalt from a chloride system, and use the equilibria shown in Figure 5, we can write an expression for E in terms of these equilibria, namely:

$$E = \frac{\overline{[(R_3NH^+)_2\ CoCl_4^=]_2} + \overline{2[\{(R_3NH_2^+)\cdot CoCl_4^=\}_2]}}{\sum\limits_{i=2} [CoCl_i^{(2-i)+}] + [(R_3NH^+)_2\cdot 2CoCl_4^=]} \qquad [81]$$

This equation by no means includes all the equilibria and complexes involved in this extraction system, hence we can see that it is indeed a very complex system. What we see by determining E is the overall effect of all the individual effects occurring under the conditions at which E was determined. It is for such reasons that metal extraction systems of this type are not understood, and we cannot apply much in the way of theory because there really isn't much to apply.

What we can say about the order in which metals extract from chloride systems is that those metals which readily form anionic chloro complexes will extract more readily at lower chloride concentrations than those which do not readily form anionic chloro complexes. Thus the order of metal extraction as a function of increasing hydrochloric acid concentration is: Zn > Pb > Fe(III) > Cu > Co(III) > Mn(II) > Cr(III) > Ni, and as a function of chloride concentration is: Mo(VI) > Zn > Fe(III) > Sn(II) > Cu > Co(II) ≃ Fe(II) > Mn(II) > Cr(III) ≃ Ni(II).

Metal extractions by amines from hydrochloric acid solutions exhibit a maximum in the extraction curves, which is seen to occur at about 8 M hydrochloric acid. Decrease in extraction above this acid concentration is considered to be due mainly to the preferential extraction of acid, probably HCl_2^-. For this reason it is generally observed that metal extraction is greater from alkali chloride solutions than from hydrochloric acid solutions at the same chloride concentration.

Another factor which influences metal extractions by amines is the nature of the carbon chain, and the number of carbon atoms, in the amine molecule. Normally, aliphatic amines are the best extractants, since aromatic radicals, especially when attached to the amine nitrogen, weaken the extractive properties probably as a result of the influence of the electron density of the aromatic ring.

In many ways the problems encountered with the use of amines as metal extractants are similar to those involving acidic extractants, namely salt effects, aggregation of the extractant in the solvent phase, third phase formation, solubility and so on. Thus salt effects generally decrease metal extraction by amines in the order: $ClO_4^- > NO_3^- > Cl^- > SO_4^= > F^-$, which is the order of the complexing ability of these anions.

We can, therefore, say very little about the theoretical aspects of metal extraction in ion-association systems, consequently much of the work on such systems has to rely heavily on experimental data, without the opportunities for understanding or predicting the behaviour of such systems.

Systems Involving Solvation

Another important group of extraction systems is that based on the power of oxygen-containing organic extractants to solvate inorganic molecules or complexes. By such solvation the solubility of the inorganic species in the organic phase is greatly increased.

There are two main groups of extractants in this area; those containing oxygen bonded to carbon such as ethers (C-O-C), esters (-COOR), alcohols (C-OH) and ketones (C=O), and those containing oxygen bonded to phosphorus such as alkyl-phosphate esters (≡P=O).

One distinguishing feature between these extractant types involves the role played by water. The strongly polar organophosphorus compounds compete favorably with water and can replace water molecules in the first hydration sphere of a metal atom. With ethers and ketones water is a necessary part of the complex, probably forming bridges between the organic and metal components of the complex through hydrogen bonding. These extractants can, by virtue of solvation, extract both acids and metal complexes.

One marked feature of extractants containing C-O bonds is the high degree of metal hydration that occurs in the solvent phase. For example, in the extraction of ferric chloride into ether, five molecules of water are associated with the extracted metal complex in the solvent phase. Solvation numbers as high as 12 have been reported which makes the existance of solvates of specific composition questionable. This, combined with the fact that these systems exhibit strong non-ideality in the organic phase, even at low concentrations, makes a general theoretical treatment almost impossible.

The most well known and most used of the organophosphorus esters is undoubtedly tri-n-butyl phosphate (TBP). Because of its wide use in the processing of nuclear materials, an almost bewildering amount of data is available on it and on similar reagents. But despite this, general equations for metal extractions cannot be given. These systems are complex, with few easily definable species formed, and with few direct similarities between different systems.

As a general rule-of-thumb, we can say that the extractive power of phosphorus-containing extractants increases with increase in the number of carbon-phosphorus bonds over the series: phosphate-phosphonate-phosphine oxide. The solubility of neutral organophosphorus compounds in water decreases in the order: phosphine oxides > phosphinates > phosphonates > phosphates. This is a result of the increasing polar nature of the phosphonyl group. On the other hand, the solubility of these reagents in acid solution is not so predictable; generally at low acid concentrations the solubility is low but as the acid concentration is increased solubility increases, in some cases to prohibitive values.

Neutral organophosphorus extractants have the ability to extract acids, and here again considerable work has been done to understand the mechanism without much success. Acid extraction depends in part on the diluent used and on the concentration of extractable metal ions. For example, the extraction of nitric acid by TBP is decreased as the amount of uranium is extracted from a nitric acid solution(27).

Extraction of metals by TBP from various acidic media appears to involve generally two molecules of TBP in the extracted species, and some proposed extracted species are given in Table 2.

TABLE 2

Some Extractable Metal-TBP Species

System	Extracted Species	Reference
$UO_2(NO_3)_2$-TBP	$UO_2(NO_3)_2 \cdot 2TBP$	28
UCl_4-TBP	$UCl_4 \cdot 2TBP$	29
Mo(VI)-HCl-TBP	$MoO_2Cl_2 \cdot 2TBP$	30
NbF_5-TBP	$NbF_5 \cdot HF \cdot 3TBP$	31
TaF_5-TBP	$TaF_5 \cdot HF \cdot 2TBP$	31
V(V)-HCl-TBP	$HVO_5Cl_2 \cdot TBP$	30

The effect of acid concentration on the extraction of metals by TBP is similar to that with amines. Thus as the acid concentration is increased, the extraction of metal increases, but above a certain point the extraction falls off. This is due to the perferential extraction of acid and to the formation of anionic metal species in the aqueous phase.

Extractants containing C-O bonds are electron donating compounds, but the alcohols, being amphoteric, exhibit both donor and acceptor properties and resemble water in many ways. Alcohols have been used mainly in processes for the extraction of phosphoric acid from solutions resulting from the dissolution of phosphate rock(32,33).

Only one ketone appears to have been used commercially for the extraction of metals, namely methyl isobutyl ketone (MIBK), and processes employing this extractant are limited to the separation of zirconium and hafnium(34), and niobium and tantalum(35).

As a result of the complexity of solvent extraction systems which employ solvating extractants, we cannot readily apply a theoretical approach. Consequently, as with ion-association systems, most of the data available are empirical.

Practical Considerations

Having digested the theoretical aspects of the extraction of metals by solvent extraction, we can now have a look at what these might mean to someone involved in studies on the extraction of metals in the development of commercially useful processes, and point out some of the aspects which must be understood and appreciated in reporting data, comparing different systems, etc.

Extraction Coefficient

The extraction coefficient, E, is a measure of how well a solvent will extract a metal, that is, a measure of the overall driving force of the solvent extraction system, and is thus concentration dependent. As defined by equation [7], E is a number, has no units, and is not a constant. The value of E depends on many factors, such as the phase (A/O) ratio, extractant concentration, temperature, pH, metal complexation in the aqueous and organic phases, and metal concentration in the aqueous phase.

Let us look at the variation of E as a function for example, of A/O ratio. This is illustrated graphically in Figure 6 for the extraction of cobalt from an acid solution (pH 6) using D2EHPA as the extractant(22). In these experiments the same cobalt concentration in the feed, the same extractant concentration in the solvent, and the same equilibrium pH were maintained. Only the A/O ratio was varied. Values of E are seen to vary from about 100 at an A/O ratio of 1/2 to about 1.9 at an A/O ratio of 10/1. Similar wide variations can result from changes in the other factors noted above.

By itself, a value of E has really no meaning, simply because it is dependent on the variables noted above. Thus to say that an extraction system is good because the extraction coefficient is high, without giving the conditions under which the result was obtained, is of little value to anyone. Similarly, comparisons of different systems using only E values is again an exercise in futility. It cannot be emphasised too strongly that values of E are unique to a particular system, and comparisons of different systems should be done only when the experimental conditions are identical for each. Thus any comparisons of systems must usually be made with considerable caution.

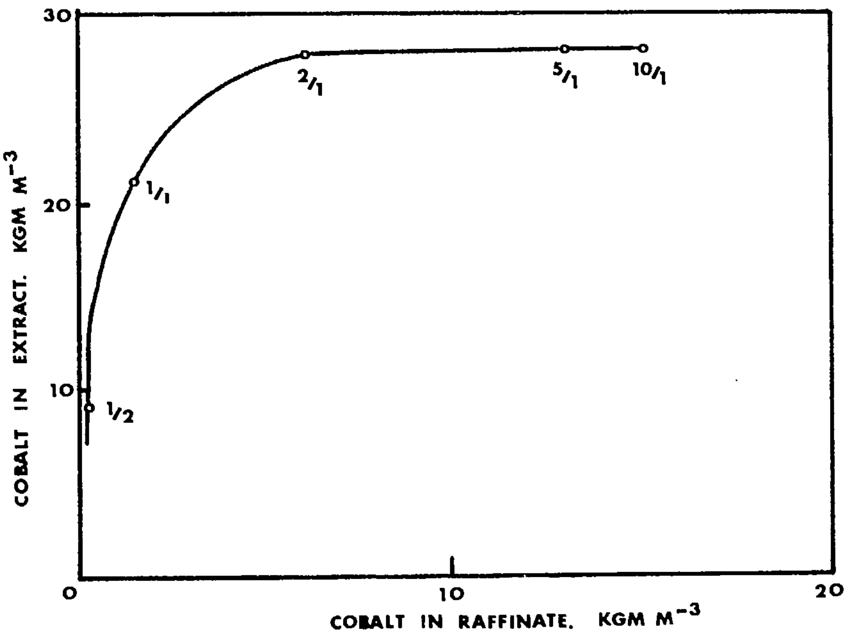


Figure 6: Effect of A/O Ratio on Metal Extraction.

In spite of these restrictions, the extraction coefficient, or log E, is the most used parameter in solvent extraction studies. Together with the loading capacity of a solvent it is basic to the design of a solvent extraction process.

As we have seen (p. 36) the per cent metal extraction is related to E by equation [53]. For the situation where the separation of two metals is to be made (from the same solution) a useful indication as to whether this can be achieved is given by the so-called separation factor. This was defined, in terms of the extraction coefficients for each of the two metals in similar systems, by:

$$SF = E_A/E_B \qquad [82]$$

where E_A and E_B refer to the E value for metals A and B respectively.

Separation factors of greater than one indicate that the two metals can be separated, but this gives no indication of the ease of separation or the number of stages which may be required. For example, the separation factor for the extraction of cobalt from an aqueous phase containing both cobalt and nickel at pH 5-6, using D2EHPA as the extractant, is about 1.6. It has been estimated that to obtain a cobalt-nickel ratio of 100 in the loaded solvent, something of the order of 50 contact stages are required(36). Generally, the higher the separation factor, the less the number of stages required to achieve a given metal ratio in the loaded solvent.

Two metals having the same oxidation state, that is having similar slopes for log E versus pH plots, can be separated (for all practical purposes) in a single extraction stage if there is a pH (pH_s in Fig. 7) where log E for metal B is -2 when log E for metal A is +2. This is shown in Figure 7. The minimum separation of these two curves must then be 4/n. For two metals where the extraction curves are not of the same slope, this approach does not hold. However, in this case an arbitrary value of E may be used as a reference, and a convenient reference is the $pH_{1/2}$ value.

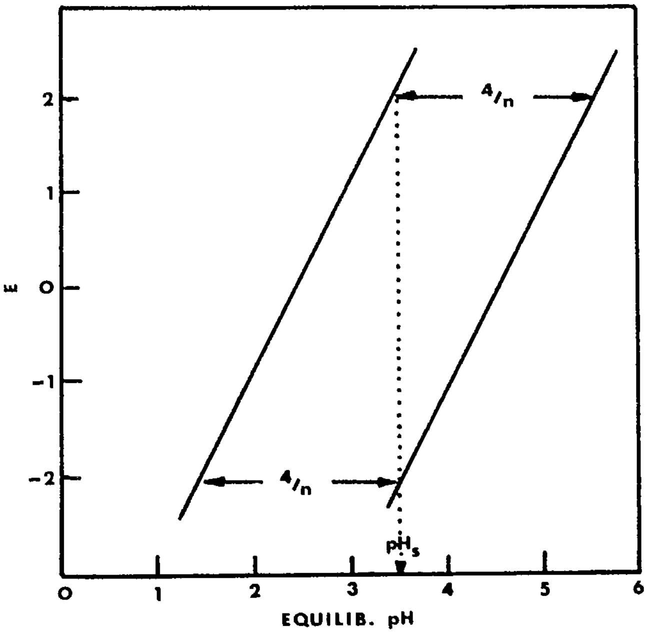


Figure 7: pH for the Separation of Two Metals in a Single Stage.

It is evident that for metals having an oxidation state of +4, the difference in pH required to afford separation is 1 pH unit, but for oxidation states of +1 the difference required is 4 pH units. Application of this type of approach in considering metal separations, prior to doing experimental work, can provide a good idea of whether the approach to be taken is likely to give the desired result.

In using separation factors as a basis for comparisons of different systems one must again be aware of the limitations of this approach. What was stated about the use of E values in system comparisons also applies here. Even small variations in the ratios of metals in the aqueous feed solution can give rise to substantial differences in separation factors, even when all other conditions are fixed.

These problems in comparisons occur again and again in solvent extraction studies, and since so much depends on the particular system, equipment, and so on, it is extremely difficult to make valid comparisons.

Extractant Concentration

For a given metal ion concentration in the aqueous phase the extraction coefficient will increase with an increase in extractant concentration, other factors being constant. And naturally, the converse is true. This is evident from equation [16] and is illustrated in Figure 8 for the extraction of uranium by tributyl phosphate.

As the extractant concentration increases, then the distribution curve for a metal, as a function of pH, will shift towards lower pH values as predicted by equation [50], and we have seen that we can calculate this shift for the general cases (Table 1). Thus for a fixed metal ion concentration, pH and phase ratio, the amount of metal extracted will increase with an increase in extractant concentration, the resulting effect being one of shifting the distribution curve as illustrated in Figure 9. Let us assume that the system has a $pH_{1/2}$ of 3.5 and that the E - pH plot is as indicated by the solid line, giving a value of E = 1 under these conditions. Increasing the extractant concentration will result in the extraction of more metal, and since the amount of metal in the system is fixed, then E must increase at this pH. This gives us, say, a point at E = 5. Now for the second system (high extractant), this point must fall on a new curve which we would obtain under the experimental conditions given, and which is represented by the dotted line. Conversely, a decrease in extractant concentration will shift the curve towards higher pH values.

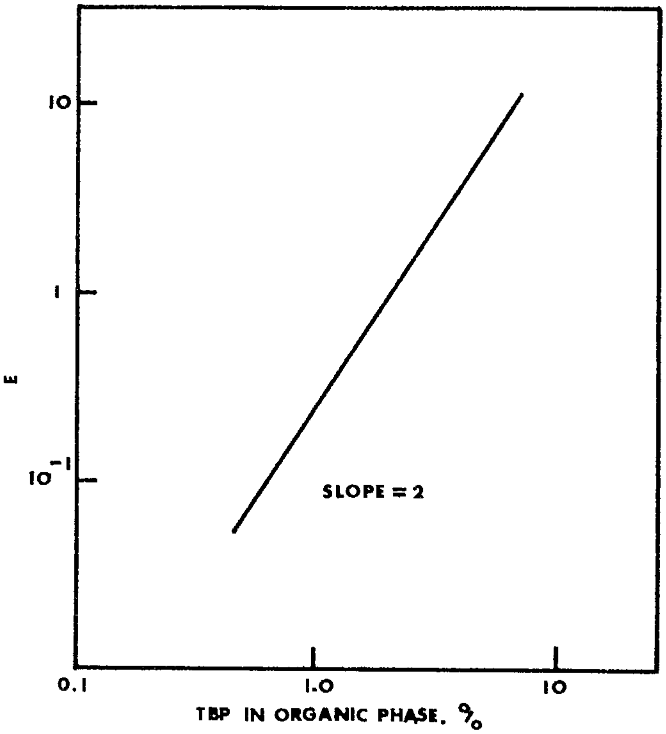


Figure 8: Variation of Extraction Coefficient of Uranium With TBP Concentration(28).

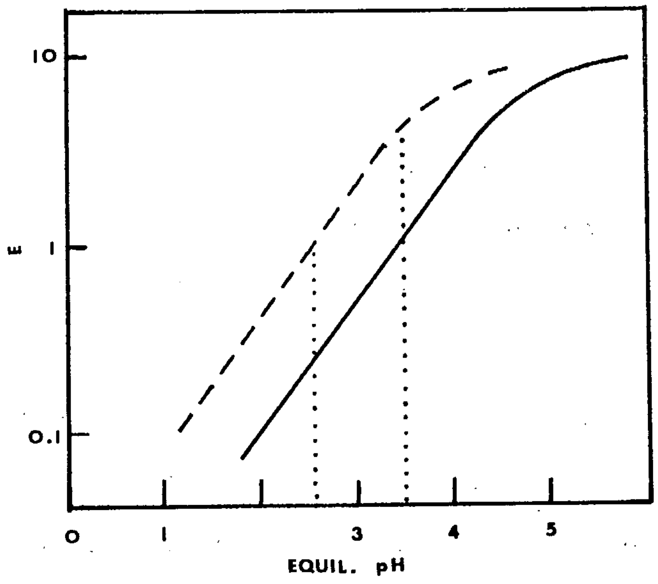


Figure 9: Effect of Extractant Concentration on Metal Extraction.

This illustrates again the dependency of E on the experimental conditions under which it is determined. Obviously, any value of E (within reason) can be obtained by variation of conditions, and thus, as was pointed out before, comparisons of systems by using values of E are of little value unless all the experimental conditions are given.

If we know the oxidation state of a metal ion involved in the extracted specie we can calculate the shift in pH expected on changing the extractant concentration. Some of these were given in Table 1 for a tenfold change in concentration.

Plots of extractant concentration versus E generally show a linear relationship provided that the concentration of metal is not too high. The slope of the line is equal to the number of extractant molecules, n, associated with the metal atom in the extracted species. This number may or may not be an integer; the latter case may arise, for example, when the extractant solvates the extracted species.

That the slope of extractant concentration versus E gives the value of n is shown by the following:

$$M^{n+} + \overline{nHA} \rightleftharpoons \overline{M \cdot nA} + nH^{+} \qquad [83]$$

$$K_E = \frac{[\overline{M \cdot nA}]\,[H]^n}{[M^{n+}]\,[\overline{HA}]^n} \qquad [84]$$

At constant pH;

$$K_E = \frac{E}{[\overline{HA}]^n} \qquad [85]$$

$$\text{and } E = K_E[\overline{HA}]^n \qquad [86]$$

Taking logarithms;

$$\log E = n \log [\overline{HA}] + \text{constant} \qquad [87]$$

which is the equation of a straight line of slope n.

Effect of pH

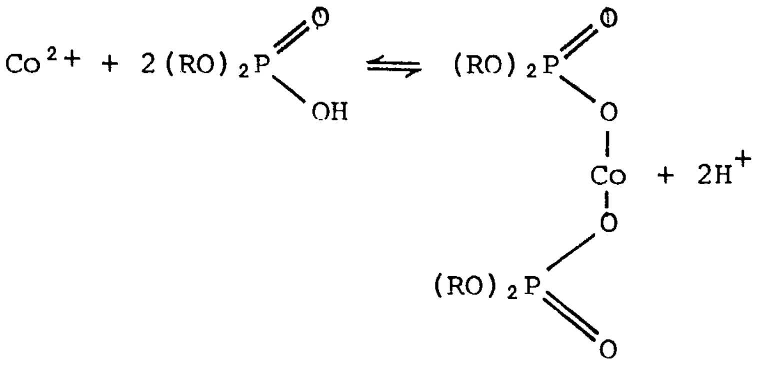
As indicated by equation [3], all extractants of the chelating or acidic types used in solvent extraction processes liberate hydrogen ion on the extraction of a metal, and the greater the amount of metal extracted (that is the higher the solvent loading) the more hydrogen ion is produced. This results in a decrease in pH of the system and consequently a decrease in the amount of metal extracted (the reverse reaction in equation [3]).

From equation [50] it follows that the higher the equilibrium pH of the system, the lower will be the extractant concentration needed to achieve a given per cent metal extraction, and vice versa. At constant extractant concentration E will increase as the pH is raised unless, of course, other factors such as metal complexation or hydrolysis occur in the aqueous phase.

For example, at a phase ratio of 1, increasing the pH by one unit will increase E by an order of magnitude for n = 1. For n = 2 an increase of 10 orders of magnitude is predicted, and so on. This is shown in Figure 10 for metal ions having values of 1 to 4. The curves each have a linear portion, the slope of each being equal to the number of hydrogen ions released in the formation of the extractable species.

It should be pointed out here that the number of hydrogen ions and molecules of extractant involved in the formation of extractable species depends on the type of extractant. All commercially available extractants of the chelating or acidic type available today are monobasic in nature, and thus release one hydrogen ion for every molecule which combines with a metal. The number of molecules of extractant involved in the formation of an extracted specie depends on the oxidation state or coordination number of the metal ion, and the number of places at which bonding can occur to the extractant. A few examples will illustrate this.

Let us consider first D2EHPA. This is a monobasic extractant which forms ionic-type complexes with metals atoms, such as:



[88]

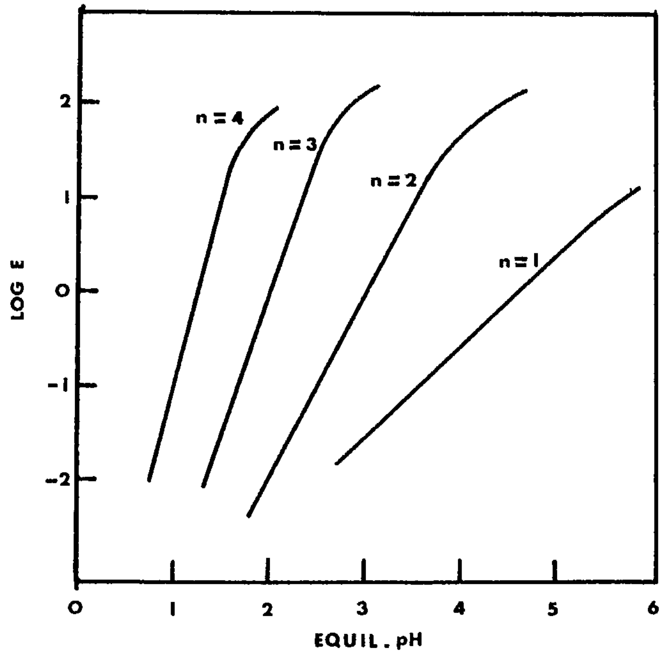
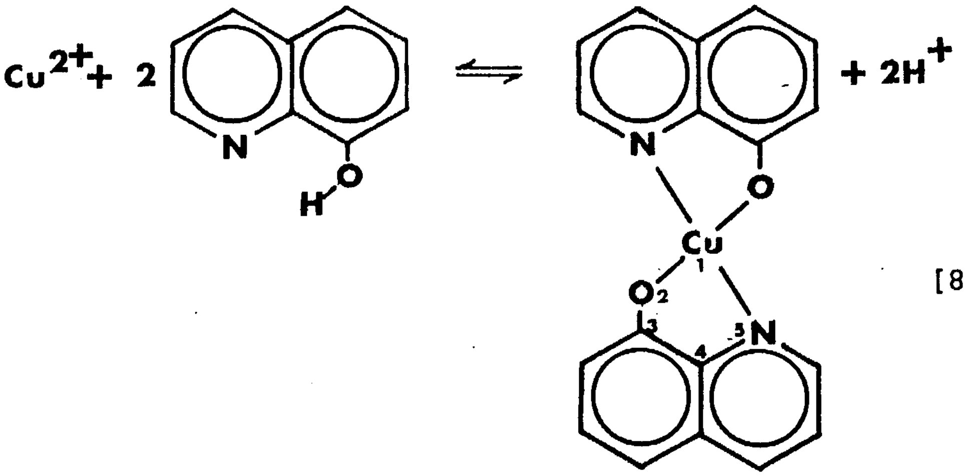


Figure 10: Effect of Metal Oxidation State on the Extraction Coefficient.

and these complexes depend on the oxidation state of the metal ion. Thus for Co^{2+}, 2 molecules of D2EHPA are involved; for Fe^{3+}, 3 molecules are involved; for Th^{4+}, 4 molecules are involved, producing electrically neutral species.

The situation may be similar or different with chelating extractants, depending on the extractant. Chelating extractants presently available commercially are monobasic in nature since they involve the ionisation of a hydrogen atom prior to complex formation. Bonding to a metal ion occurs through two atoms of the extractant (oxygen and nitrogen) in these cases, forming a ring structure which includes the metal atom, thus:



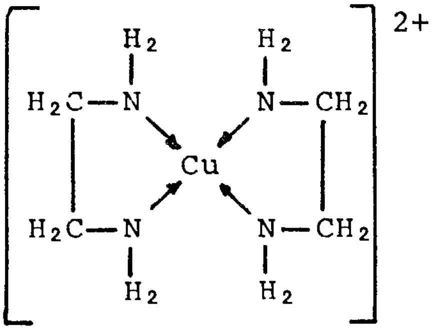
[89]

Cupric Oxinate

in which the cupric oxinate involves two 5-membered rings as indicated. This is the reason for naming such complexes chelates, the word being derived from the Greek for claw (for example a crab's claw).

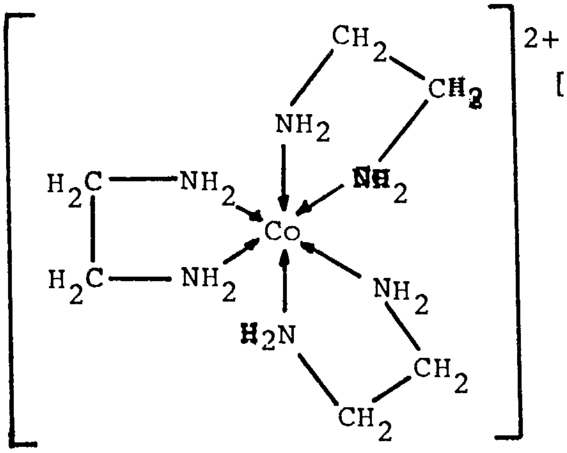
Complex formation occurs also between metal ions and chelating reagents which do not contain ionisable hydrogen atoms. For example:

$Cu^{2+} + 2H_2NCH_2CH_2NH_2 \rightleftharpoons$
ethylenediamine



[90]

$Co^{2+} + 3H_2NCH_2CH_2NH_2 \rightleftharpoons$



[91]

In these cases a neutral complex is not formed because ethylenediamine is not ionised, and the complex results from electron donation from each nitrogen atom to the copper or cobalt atom to form the (coordination) bonds. It will also be noted that two molecules of ethylenediamine are used to form the copper complex, whereas three are required for the cobalt complex, even though both metals are in the same oxidation state. This is because the complex formed depends in such cases on the coordination number of the metal ion, which for

Cu^{2+} is normally 4, and for Co^{2+} is six. Complexes of this type can only be isolated as salts, for example:

$$\{Cu(NH_2CH_2CH_2NH_2)_2{}^{2+}\cdot 2Cl^-\}$$

and

$$\{Co(NH_2CH_2CH_2NH_2)_3{}^{2+}\cdot SO_4{}^{=}\}$$

in which an anion neutralises the charge on the complex (en = ethylenediamine).

Thus we can see why it is advantageous in solvent extraction to use chelating extractants which result in the formation of neutral complexes rather than charged complexes, since one of the conditions pointed out earlier for extraction of a metal complex is charge neutralisation.

This digression into metal complex chemistry indicates the point that, without a knowledge of the chemistry of metal complexes, it is difficult or impossible to appreciate what is occurring during the extraction of a metal, or to assess or predict what might be expected in the extraction of metals by a particular solvent system.

The pH of the system affects both the metal ion and the extractant. Thus if the pH is increased, the metal will eventually hydrolyse and will not extract. Decrease in pH -- increase in hydrogen ion concentration -- may result in the formation of non-extractable metal species as a result of complexation with components of the aqueous phase. This occurs, for example, in systems which involve sulphuric acid due to equilibria between $SO_4^=$, HSO_4^- and H_2SO_4, resulting in the formation of metal complexes with these anions. The extraction of uranium from sulphate solution with amines is a case in point. We have seen how variation of pH in an ammonium sulphate system can affect the formation of non-extractable metal ammines, and how one can predict the extractability of metals such as Cu, Ni, and Co from such systems from a knowledge of the stability constants of the metal ammines.

All extractants suffer protonation as the pH of the system decreases.

$$A^- \overset{H^+}{\rightleftharpoons} HA \overset{H^+}{\rightleftharpoons} H_2A^+ \ldots \qquad [92]$$

If the extractant is unable to ionise as a result of the concentration of hydrogen ion, it will not be able to form a complex with a metal ion and hence extraction will not occur.

The general effect of pH is illustrated in Figure 11 for the extraction of a metal. At low pH values, extraction decreases as a result of protonation of the extractant, and at high pH values, extraction decreases as a result of hydrolysis of the metal. It was noted earlier that a metal extracts best at a pH just below that at which it hydrolyses. Thus, in general, one can draw a series of curves of the type shown in Figure 11 in which the pH range over which the extraction is expected to occur by a chelating or acidic extractant will increase as the pH at which the metal hydrolyses becomes higher.

This generalisation does not hold for ion-association or solvating extractants because these are not primarily dependent on pH for metal complex formation, but rather on factors such as anion concentration in the aqueous phase.

It should be apparent that pH is of prime importance in many solvent extraction systems, and affects other variables significantly. But the pH value of fundamental importance is the equilibrium pH of the system, and this fact should never be forgotten.

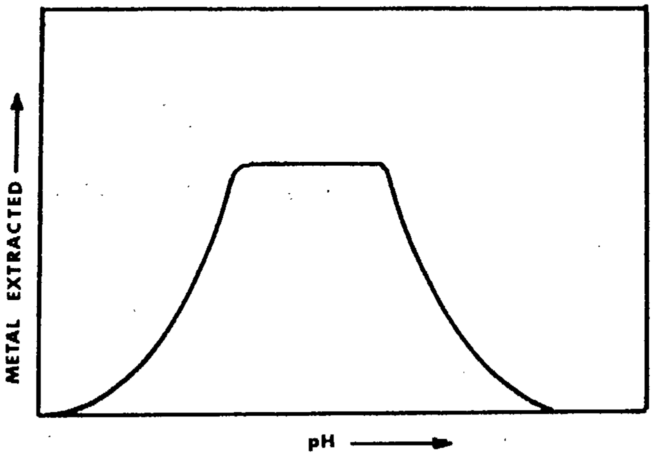


Figure 11: General Effect of pH on Metal Extraction.

Aqueous Phase Composition

The type and concentration of anionic species present in the aqueous phase affects the extraction of metals, as we saw in the theoretical section. It can generally be expected that where a metal complex in the aqueous phase has a stability greater than that of the metal-extractant complex, it will not be extracted. For example, hydrolysed and ion-associated metal species can drastically affect the extraction of a metal by some extractants. This is illustrated in Figure 12 where the extraction of cobalt and nickel by D2EHPA from ammoniacal solution is shown to be affected by the concentration of sulphate ion in the aqueous phase. Presumably the formation of ion-association complexes, such as $Co(NH_3)_6 \cdot SO_4^+$, inhibits metal extraction because the stability of such complexes is greater than those of the extractable cobalt and nickel complexes. This particular effect is reversible so that, if the anion concentration is decreased by dilution, metal extraction is increased(36).

Similar effects of salt concentration in the aqueous phase have been reported for the extraction of metals by carboxylic acids, as shown in Figure 3 for the extraction of nickel from ammonium sulphate solutions using Versatic 911 as the extractant(13). This particular system was discussed on p. 33.

Again, in the extraction of uranium from acid sulphate solution by a tertiary amine (tri-n-octylamine), uranium extraction decreases with increasing concentration of other anions, and the effect varies with the anion(37). This is shown in Figure 13.

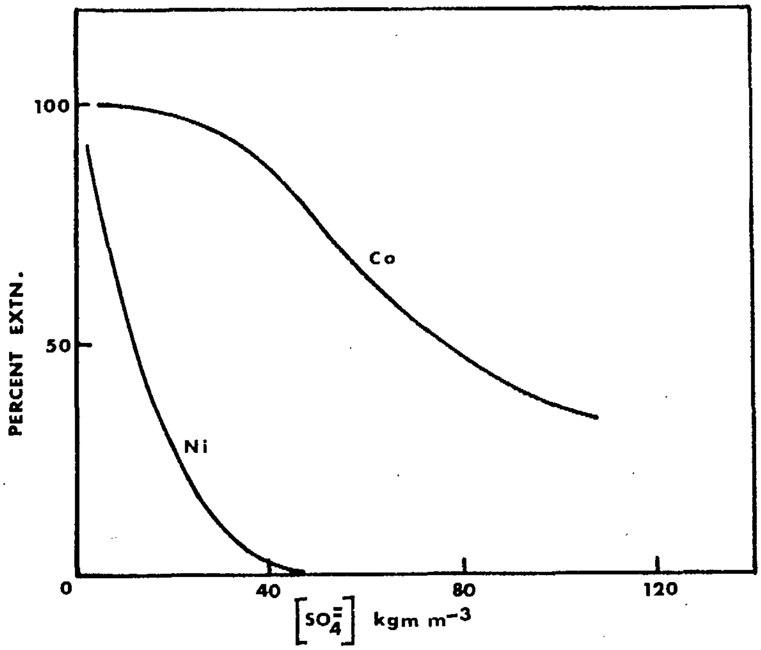


Figure 12: Effect of Sulphate on the Extraction of Co and Ni with D2EHPA$^{(22)}$.

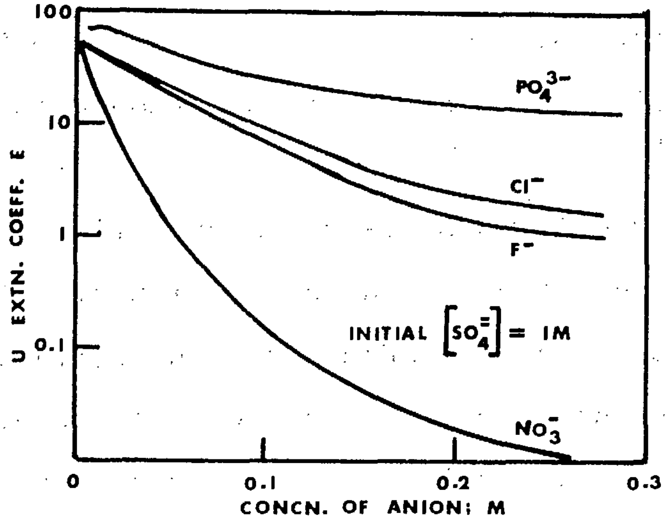


Figure 13: Effect of Various Anions and Anion Concentration on the Extraction of Uranium by a Tertiary Amine$^{(37)}$.

On the other hand, extraction of metals by neutral extractants can be enhanced by increasing the salt concentration, probably as a result of a salting-out effect in which the dissociation of the extractable neutral species (to form charged species) is depressed. An example is shown in Figure 14 for the extraction of uranium by diethyl ether in the presence of various metal nitrate salts (38).

Complexation of a metal in the aqueous phase can be used to advantage in the separation of metals. In a process for the separation of zirconium and hafnium, the neutral metal thiocyanate complexes are formed by the addition of ammonium thiocyanate, which allows the extraction of hafnium from zirconium by methyl isobutyl ketone. The separation of cobalt from nickel in ammoniacal solution, by such as Versatic 911, results from the fact that the formation constants for nickel ammines are higher than for cobalt ammines. Thus the nickel is preferentially complexed in the aqueous phase as non-extractable ammine complexes and the cobalt, which is present as the uncomplexed ion, extracts.

The extraction of metals by amines (anionic exchange) generally requires the formation of anionic metal species in the aqueous phase, which is achieved by the use of high salt or acid concentrations.

In general, if complexation of a metal in the aqueous phase produces a neutral species it will not be extracted by an anionic or cationic extractant, and the formation of a non-extractable metal-anion or ion-association complex in the aqueous phase is dependent on the anion and on its concentration. For this reason, extraction data on synthetic leach solutions may be significantly different from those obtained using an actual plant leach liquor, and this should be borne in mind in the development of any solvent extraction process.

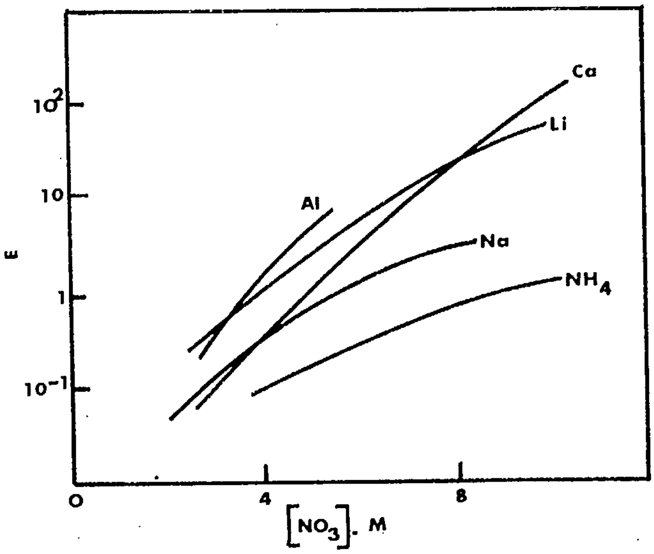


Figure 14: Extraction of Uranium by Diethyl Ether in the Presence of Various Metal Nitrates$^{(38)}$.

Conversely, if the metal species in the aqueous phase is electrically neutral then extraction by neutral or solvating extractants is probably likely. However, increasing the concentration of diverse ions may seriously affect the extraction, either by the formation of stable metal complexes, or by the formation of unextractable charged species:

$$M^{n+} + nX^{-} \rightleftharpoons MX_{n} + X^{-} \rightleftharpoons MX^{-}_{n+1} + X^{-} \rightleftharpoons MX^{2-}_{n+2} \cdots \qquad [93]$$

where MX_n is the extractable species, and the non-extractable species MX^{-}_{n+1}, $MX^{=}_{n+2}$, etc., are formed as a result of high concentrations of the anion X^{-}.

Metal Ion Concentration

The concentration of free extractant at equilibrium, $[HA]_F$, is given by:

$$[HA]_F = [HA]_T - [M{\cdot}nA] \qquad [94]$$

where $[HA]_T$ represents the total concentration of extractant and $[M{\cdot}nA]$ the concentration of extractant associated with the extracted species. If now the metal ion concentration in the system is increased, all other conditions remaining constant, $[M{\cdot}nA]$ will increase with the result that $[HA]_F$ will decrease with a relative decrease in E. An example of this effect is shown in Table 3. For the extreme situation where extraction of a metal results in complete, or almost complete loading of the solvent, it is evident that for the same system and conditions, increasing the metal ion concentration will result in a decrease in the value of E because the concentration of metal in the solvent will remain almost constant, whereas that in the aqueous phase will increase. This is perhaps intuitively obvious, but it should be appreciated that E is seen, once more, to be very dependent on the experimental conditions.

TABLE 3

Effect of Metal Concentration on the Extraction Coefficient of Uranium

$[UO_2(NO_3)]$ Molar	E
0.04	5.7
0.21	2.6
1.68	0.4

40 vol per cent TBP; 2 M HNO_3

We have noted, early in the theoretical discussions, that equations for E can be written which are independent of the metal ion concentration. But it must be emphasised that this obtains only under controlled conditions. For example, E is equal to the equilibrium constant multiplied by the ratio of extractant and hydrogen ion concentrations (equation [16]). In assuming that E is then independent of metal ion concentration also assumes that K_E remains constant. Whether this is so would have to be determined experimentally, but it is unlikely, especially if high (> 0.1 M) concentrations were involved, because really we should be using activities rather than concentrations, and activities can change substantially with increasing concentration of reactants.

This problem does not occur to the same extent when low concentrations, say 10^{-3} M, of metal are used, and for this reason it is much easier to obtain consistent data for these systems than it is for practical systems. This is one of the reasons that fundamental studies on the extraction of metals are carried out using low concentrations of reactants, or concentrations which result in a decrease in the number of variables in the system.

Solvent Loading Capacity

Of major importance in commercial solvent extraction processing is the limiting portion of E or log E - pH plots as shown, for example, in Figure 9. The extent of the limiting portion of such curves depends on factors, such as the pH at which hydrolysis or complexation of the metal ion occurs in the aqueous phase, solubility of the extractable species in the solvent phase or loading capacity of the solvent.

Many solvent extraction processes are operated in this region simply because this is where maximum utilisation of the solvent occurs under the particular set of conditions used. While it is not absolutely necessary, nor indeed possible (for example,as a result of high viscosity of the solvent) to operate at the point of maximum solvent loading, doing so ensures that a minimum solvent flow rate is required, which is of considerable economic importance.

It should be pointed out that for a single stage process (of which there are very few) the above comments apply directly. In a multi-stage process, and most commercial operations are of this type, we are talking about the last stage of the extraction circuit, and the stages prior to this will have lower solvent utilisation.

For a system involving the separation of two metals where the separation factor is small, it is usually best to operate under maximum solvent loading conditions consistent with low metal loss to the raffinate in order to inhibit coextraction of the metal having the lower E value.

The maximum loading obtainable by a solvent depends, among other things, on the total available or free extractant and on the solubility of the metal-extractant species, rather than any limit in the extent of extraction. The solubility of an extractable species depends in large part on the diluent used in the solvent, and also on the modifier if present.

Poor solubility of an extracted species results in many cases in the formation of a third phase intermediate in density between the diluent and the aqueous phase. To inhibit third phase formation a modifier is usually added to the solvent to increase the solubility of the extracted species.

Extraction of a metal by a particular solvent does not necessarily increase linearly with increase in the extractant concentration in the solvent. An example is shown in Figure 15 for the case of extraction of cobalt with D2EHPA. The deviation from linearity may be due to dimer- or polymerisation of the extractant, or a decrease in solubility of the extractable cobalt complex without the formation of a third phase.

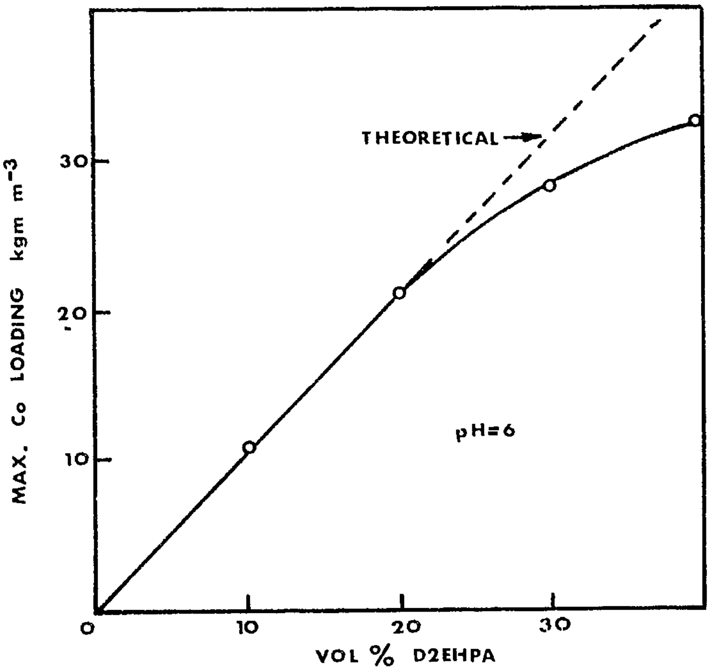


Figure 15: Extraction of Cobalt by D2EHPA as a Function of D2EHPA Concentration.

An approximate idea of the loading capacity of a particular solvent can be calculated knowing the composition or structure of the extracted species, and the concentration of the extractant in the solvent. For example Kelex 100, a substituted 8-hydroxyquinoline, forms a 1:2 metal:extractant complex with cupric ion (Cu^{2+}). Thus a 0.5 M solution of Kelex 100 in an inert diluent should have a maximum loading capacity of 0.25 M copper, that is, 0.25 X 63.5 = 15.9 kg Cu m^{-3}. This agrees well with the experimentally determined loading of such a solvent, namely 15.0 kgm Cu m^{-3}. Similarly, Kelex 100 forms a 3:1 complex with ferric ion (Fe^{3+}), thus the same solvent should load $\frac{0.5}{3}$ X 55.8 = 9.3 kgm Fe m^{-3}.

Generally, then, the greater the ratio of extractant to metal in the extractable species, the lower will be the loading capacity of a given solvent unless, of course, the atomic weight of the metal is sufficiently high to reverse this.

Theoretical loading capacities of solvents are usually attained in practice only for those which contain low extractant concentrations. The higher the extractant concentration, the greater is the deviation from theoretical, in most cases, for the reasons given above.

Use of $pH_{1/2}$ Values

The $pH_{1/2}$ values obtained from extraction data are useful in comparing the dependence of the extraction of a metal on pH, on salt concentration, and in the determination of the relative acidities of different extractants. The shift in the extraction pH of a metal as a function of salt concentration in the aqueous phase is shown in Figure 16, where $pH_{1/2}$ values for the extraction of cobalt by Versatic 911 are plotted as a function of ammonium sulphate concentration in the aqueous phase(12). The relationship is seen to be linear. This variation of pH would be difficult to determine if other variables were used, such as the pH at which 100 per cent metal extraction occurs; such values are at best only approximate since it is very difficult to determine the exact pH at which 100% metal is extracted.

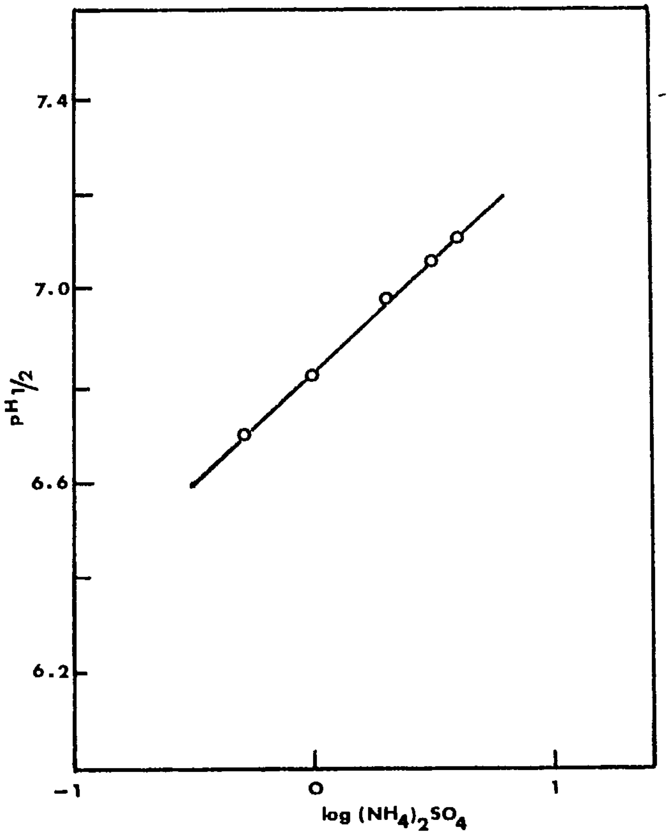


Figure 16: Effect of $[(NH_4)_2SO_4]$ on $pH_{1/2}$ Values in the Extraction of Cobalt with Versatic 911(12).

The use of $pH_{1/2}$ values in indicating the relative acidities of different extractants has been demonstrated for the LIX extractants and Kelex 100(40). The order of $pH_{1/2}$ values found is: LIX-63 > LIX-64 > LIX-64N > LIX-70 > Kelex 100, that is, the acidity of these reagents increases from LIX-63 through Kelex 100. Thus, Kelex 100 will extract copper at a pH lower than any of the other reagents. The order of metal-extractant stability is then the reverse of this order. This series may also be inferred, of course, from the structures of these reagents.

As with many of the other parameters of solvent extraction discussed above, $pH_{1/2}$ values are dependent on several variables, and care must be taken when using them for comparative purposes.

Scrubbing

Scrubbing usually refers to the removal of unwanted co-extracted species in the loaded solvent from the extraction stage of a process. There are many instances of the use of this technique in analytical chemistry, but relatively few in solvent extraction processes, and little has been published on this technique. Another well used method is to remove co-extractable metals from the solution prior to solvent extraction, and a case in point here is iron, which can in many cases be precipitated.

The specificity of an extractant for a particular metal depends on many factors, including pH, kinetics, complexation in the aqueous phase, metal and extractant concentrations, and so on.

No extractant is entirely specific for one metal, hence co-extraction of other metals will occur to some extent, together with anionic species or acids. Co-extraction may be physical or chemical in nature. For example, entrainment of aqueous phase in the loaded solvent, especially if the feed contains high metal concentrations, would show as co-extraction from analysis of the loaded solvent. However, this situation can usually be overcome by scrubbing the loaded solvent with water, or some suitable solution.

Purification of the loaded solvent by scrubbing is more of a problem if the co-extraction is chemical in nature. There are essentially two ways of approaching this type of situation: use of an acidic solution at a pH which is just sufficient to strip the unwanted metal and leave the metal of interest in the solvent phase, or use of a solution of a salt of the metal of interest which, by contacting with the loaded solvent, replaces the co-extracted unwanted metal by the metal required.

The former case is one of selective stripping, and this was discussed in the theoretical section. Calculation of the theoretical pH required for the scrub solution, based on distribution data for the co-extracted metals, can be made and used in this situation. It should be noted that invariably some of the metal of interest is also removed from the solvent, but provided that this is small, and the concentration of the metal in the solvent phase is not depleted to any great extent, the process is viable since the scrub liquor can be recycled to some upstream stage in the process.

The latter case noted above is essentially a metal exchange process, similar to those discussed under carboxylic acids. For example, the co-extraction of nickel and cobalt using D2EHPA at pH 5-6 can produce a Co/Ni ratio in the loaded solvent of about 20. If the loaded solvent is then contacted with a cobalt salt solution containing, say 20 kgm m^{-3} of cobalt, the Co/Ni ratio in the scrubbed solvent can reach as high as 900. This process is illustrated by equation [95]$^{(22)}$:

$$\overline{((RO)_2POO)_2Ni} + CoSO_4 \rightleftharpoons \overline{((RO)_2POO)_2Co} + NiSO_4 \qquad [95]$$

This results from the fact that for the system in question, cobalt extraction occurs at a pH slightly lower than does nickel, and this fact is used in the scrubbing process.

Of course, the Co/Ni ratios obtained in the solvent in this process are dependent in large part on the Co/Ni ratio in the feed, and also on whether the continuous phase is the aqueous or the solvent phase. This high Co/Ni ratio in the feed would produce higher ratios in the solvent than if the reverse were the case. Similarly, the A/O ratio in the scrub stage would also influence the Co/Ni ratio obtained.

The scrubbing technique thus provides a powerful technique for improving the quality of a loaded solvent prior to recovery of a metal by stripping, and can be understood in terms of the effects of pH and metal concentrations, that is, mass transfer.

Stripping

Stripping, as we have noted before, is the reverse reaction to extraction. Thus considered from the point of view of equation [3], it is really just the application of the law of mass action. In this reaction, the only variable which can be changed to reverse the reaction once the metal is extracted, is the hydrogen ion concentration in the aqueous phase. Consequently, stripping in such cases requires the use of an acid solution of a concentration sufficiently high to shift the equilibrium far to the left of equation [3] to drive the metal into the aqueous phase. With ion-association and solvating systems, where high salt or acid concentrations are required for metal extraction, stripping with water usually results in shifting the equilibrium to the left.

The stability of the extracted species will govern the type and concentration of strip solution required. For example, it should be evident that the lower the pH at which metal extraction occurs, the higher must be the acid concentration of the strip solution.

Problems can occur when the stability of the extracted complex is so great that even concentrated acids will not allow the metal to be stripped. This occurs, for example, in the case where cobalt is extracted by LIX extractants from ammoniacal solutions, and undoubtably results from the oxidation of cobaltous ion to cobaltic ion. If we look at the stability constants (K_f) of cobaltous and cobaltic ammines, we see that for the former, log $K_6 = 10^{4.4}$, whereas for the latter, log $K_6 = 10^{35.2}$(11), which is about 30 orders of magnitude higher. Thus cobaltic ammines are very stable complexes and are not readily decomposed by strong acids. The stability constants of cobaltic-LIX complexes would thus appear to be higher than those for cobaltic ammines, and hence are not amenable to stripping by acids.

One way in which cobalt has been stripped from such extracts is by precipitating it with H_2S(41) as CoS, the solubility product of which is 1.9 X 10^{-27} in aqueous solution and is presumably less than the solubility product of the cobalt-LIX complex.

Solvent Pre-Treatment

We have already seen that pre-treatment or pre-equilibration of a solvent is necessary in some cases in order to provide the ions necessary to exchange with metal species, for example in the case of amine extractants. Most solvents require some pre-equilibration prior to entering the extraction stage of an extraction process. In some cases this is accomplished in the stripping stage, and the stripped solvent is then recycled directly to the extraction stage. In other cases the solvent requires additional treatment after stripping prior to recycle to extraction.

Examples of the former case are to found with acidic or chelating extractants which require that they be in the acid form for metal extraction. Thus the LIX extractants can be recycled directly after the stripping stage, as can amines. For a monobasic extractant we have:

$$CuSO_4 + \overline{2HA} \overset{\text{extraction}}{\rightleftharpoons} \overline{CuA_2} + H_2SO_4 \qquad [96]$$

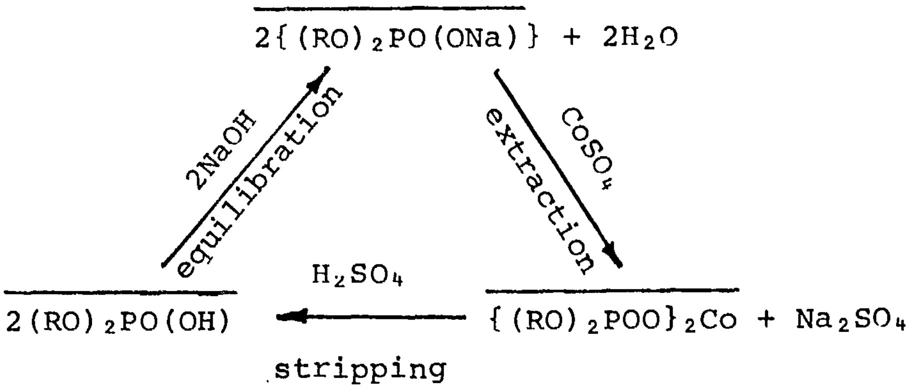
$$\overline{CuA_2} + 2HX \overset{\text{stripping}}{\rightleftharpoons} CuX_2 + \overline{2HA} \qquad [97]$$

and for a tertiary amine:

$$UO_2(SO_4)_3{}^{4-} + 2(R_3NH)_2SO_4 \overset{\text{extraction}}{\rightleftharpoons} [(R_3NH)_4UO_2(SO_4)_3] + 2SO_4{}^{=} \qquad [98]$$

$$\overline{[(R_3NH)_4UO_2(SO_4)_3]} + H_2SO_4 \overset{\text{stripping}}{\rightleftharpoons} UO_2(SO_4)_3{}^{4-} + \overline{2(R_3NH)_2SO_4} + 4H^+ \qquad [99]$$

Other systems in which the solvent requires additional treatment after stripping are those, for example, in which metal-metal or similar exchange is involved in the extraction stage. Thus for the system where the sodium salt of D2EHPA is used as the extractant for the extraction of cobalt, we have:

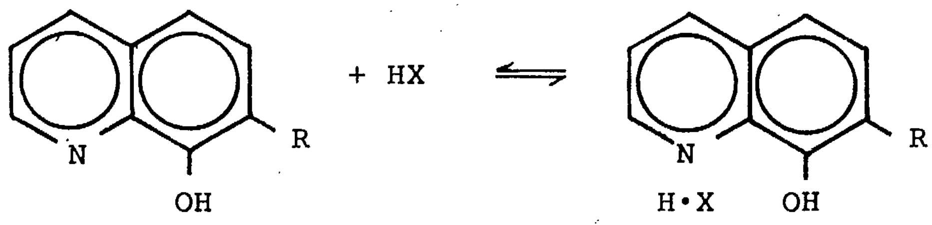


[100]

which involves an additional equilibration stage. Systems such as this one are particularly useful for maintaining an essentially constant pH in the extraction stage, since sodium ion is liberated rather than hydrogen ion, which forms a neutral sodium salt in the aqueous phase rather than an acid.

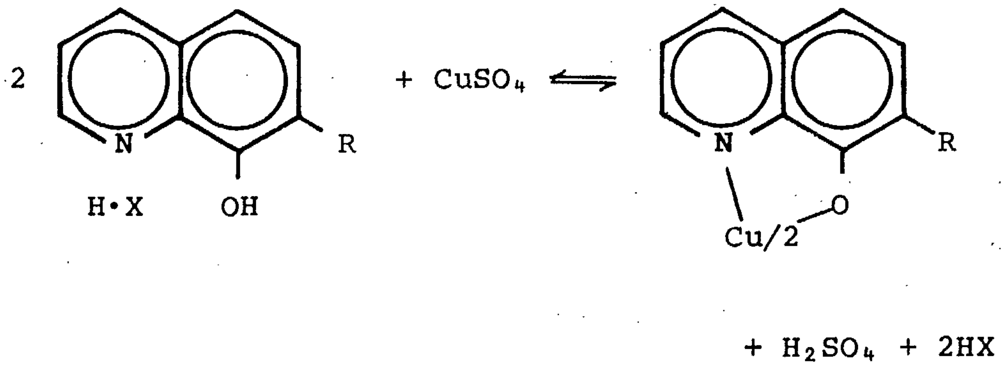
Equilibration of a solvent can also be accomplished in the extraction stage, although this technique is not usually very efficient. Thus in the extraction of zirconium from hafnium using TBP as the extractant from a high (10 M) nitric acid solution, the stripped TBP solvent can be recycled to the extraction stage - in this case a column - and equilibrated in the bottom section of the contactor where there is little or no zirconium since here the aqueous solution is essentially the raffinate. Of course, this approach means that sufficient acid must be present in the aqueous phase at the bottom of the column to accomplish the required equilibration at the bottom.

Extractants which extract acid in an acid strip stage, which would result in problems in the extraction stage, have to be treated to remove most or all of this acid. A case in point is Kelex 100 which, because of its basic nitrogen atom, can form acid salts just like an aliphatic amine:



[101]

Since the acid molecule (HX) would have to be displaced prior to the formation of a metal complex it may slow the reaction rate and also increase the acid concentration in the aqueous phase in the extraction stage. Thus:



[102]

in which twice the acid concentration is produced compared with that produced if the HX acid molecule were not present. This could have a considerable effect on the extraction of copper for, as we know, the greater the hydrogen ion concentration in the aqueous phase the lower will be the loading of the solvent.

To overcome this, and similar situations, a water treatment after stripping will usually suffice.

Kinetics of Extraction

We have noted earlier that solvent extraction is an equilibrium process, and our discussions have reflected this. However, the rate at which equilibrium is reached is also an important factor, and in solvent extraction processing the kinetics of the system governs, amongst other things, the throughput of the process. Thus with slow kinetics the retention time in the extraction stages must be greater than for a system involving fast kinetics. Very fast kinetics of extraction, for example, allows the use of contactors which have retention times in the order of seconds (such as centrifuges) and which allow for high flow rates.

Generally, metal extraction is governed by mass transfer and diffusion rates which are, on the whole, fairly rapid. Most chemical reactions involving ionic-type reactions are rapid, whereas the rates of reactions involving chelate formation can vary over a considerable range.

Other factors affecting extraction rates are viscosity of the phases, amount of agitation, and the temperature of the system.

In a heterogeneous system such as we have in solvent extraction the rate of extraction of a metal will depend, in large measure, on the surface area of the dispersed phase. We should note that in a contactor one phase will be dispersed (the dispersed phase) in the other (the continuous phase), and this depends essentially on the conditions initially present at the start of agitation of the phases.

The surface area of the dispersed phase will depend on the amount of agitation, that is, on the energy input to the system. However, it should not be thought that the greater the agitation the greater the rate of metal extraction. Too much energy input can result in the formation of stable or semi-stable emulsions. Furthermore, decreasing the bubble size of the dispersed phase can result in making the bubbles resemble rigid spheres. In this condition there is no internal movement within the spheres, no new surfaces are produced, and the extractant within the sphere can not get to the surface to react with metal ions. Consequently, the extraction rate is slow.

As with all reactions the slowest step in the process is rate determining, that is, it controls the overall rate of the system. For example, the formation of an extractable complex may be much slower than the rate at which the complex is extracted into the organic phase:

$$M^{n+} + n\overline{HA} \xrightleftharpoons{\text{slow}} \overline{MA_n} + nH^+ \qquad [103]$$

$$\mathrm{MA}_n \overset{\text{fast}}{\rightleftharpoons} \overline{\mathrm{MA}}_n \qquad [104]$$

thus the rate determining step is equation [103].

Another example of a rate determining step in metal extractions is that of desorption of surface-active extractants such as amines from the organic-aqueous interface. This effect reduces the rate of transfer of metallic species apparently as a result of "mechanical blocking", especially if the interfacial area is large due to excessive mixing. Thus extraction with excessive mixing may be significantly different from that obtained with more gentle mixing with the same system because equilibrium is not attained in the former case. It does not necessarily follow, then, that increasing the energy to mixing will increase the rate of extraction.

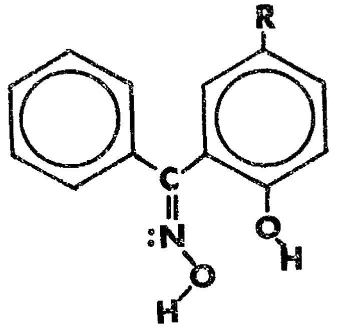
The rate at which equilibrium is attained between two phases which are initially not at equilibrium depends on the degree or extent to which the concentrations in the two phases initially differ from those attained at equilibrium. This is fixed by the extraction coefficient for that particular system; in other words, it depends on the chemical potential of the metal in the two phases.

In many cases the chemical reactions involved in the extraction process are rapid, whereas in other cases a chemical reaction may be the rate determining step. In the extraction of metal chelates the rate of dissociation of the chelating reagent and the rate of metal-chelate formation are rate determining. Generally, extraction rates for metal extraction using chelating extractants are slower than for the acidic extractants where ionic mechanisms are involved. In chelates involving keto-enol isomerism, this sets the rate of complex formation, which is generally slow. Variation of extraction rate with concentration of the extractant in the aqueous phase indicates that the rate determining step is that of metal-extractant formation.

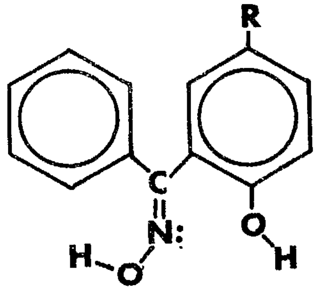
The rate of metal extraction may also be a function of the inertness of the hydrated metal ion to substitution, that is, to the replacement of water of hydration by a complexing reagent. If we consider metal complexation rates in these terms, the rate at which the waters of hydration are replaced by other water molecules should give some indication as to the rate at which complexation with reagents other than water will occur. The rate constants for water exchange for some metals follow the order: $Cu^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Fe^{3+} > Cr^{3+}$. Thus it is not surprising that ferric complexes are, on the whole, only slowly extracted by solvents, whereas Cu^{2+} and Mn^{2+} are usually extracted very rapidly. This kinetic effect is certainly a major reason why specificity for copper over iron can be achieved using chelating extractants such as Kelex 100 or the LIX reagents.

Other reasons for slow extraction kinetics are steric rearrangement between species in the formation of an extractable complex, or strongly hydrolysed or otherwise complexed metal in the aqueous phase which results in slow reversibility of such complexes to ones amenable for complexation with the extractant.

A timely example of steric inhibition is shown by the syn isomers of LIX extractants. These are substituted o-hydroxy benzophenone oximes, and can exist in two isomeric forms, syn and anti:

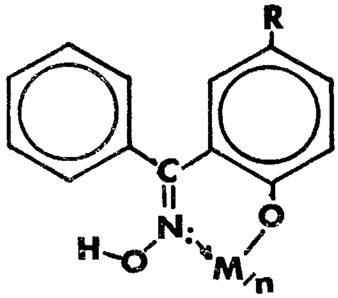


syn isomer



anti isomer

Only the anti isomer forms metal complexes at any appreciable rate, the syn isomer doing so only slowly. This is a result of the spacial orientation of the electron pair on the nitrogen atom in the anti isomer being advantageously situated for complexation with a metal atom:



whereas in the syn isomer it is oriented in a direction unsuitable for metal complexation.

It may be of interest to the reader to see the differences between the structure of a metal complex drawn in two dimensions and a photograph of a three-dimensional model of the same complex. The photograph is shown in Figure 17, and the drawing immediately below, for the copper(II) complex of LIX-65N

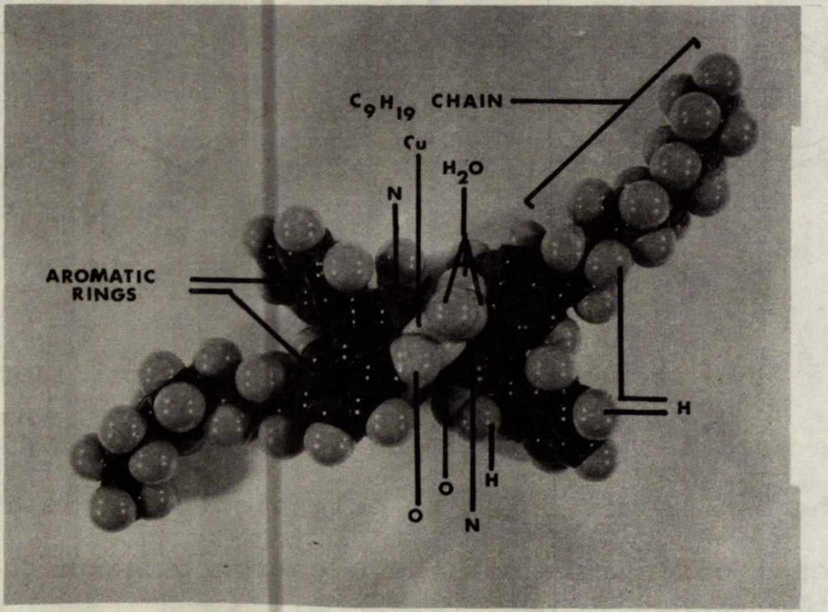
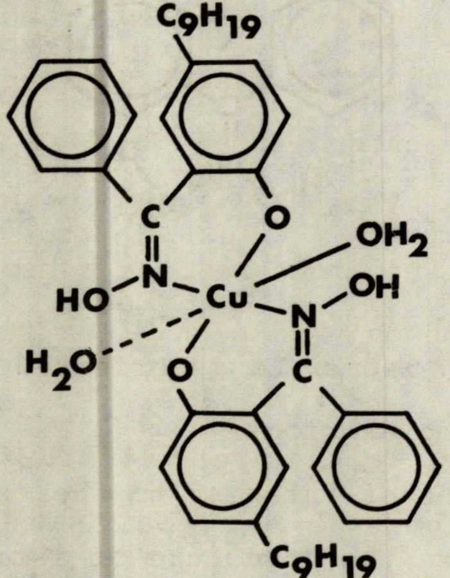


Figure 17. Model of LIX-65N-Cu^{2+} Complex
$[C_6H_5C{=}NHOC_6H_3C_9H_{19}O]_2Cu\cdot 2H_2O$



The two long tails in Figure 17 are the nonyl groups (C_9H_{19}); the aromatic rings are also evident, and it is seen that they are not coplanar.

Returning to our subject it should be apparent that commercial solvent extraction systems must have overall extraction rates of the order of not more than a few minutes. Information available on such systems, and even on other systems such as are used in analytical chemistry, is not very great. Because of this, and because of the many factors which influence the kinetics, it is difficult to make any generalizations regarding this subject. But whatever the reasons, the kinetics of metal extraction are important in solvent extraction processes.

DISCUSSION

Perhaps the one thing which becomes apparent in discussing the solvent extraction of metals is that the process hinges to such a large extent on the composition and chemistry of the aqueous phase. It is somewhat surprising, therefore, that so little attention is paid to this phase, and so much to the solvent phase. Indeed, in much of the published literature on solvent extraction processes, the aqueous phase assumes a minor role, and the only concern shown it is when the pH needs adjusting.

Actually, we know very little about the species existing in solutions of high salt and metal concentrations such as leach liquors. In aqueous systems where information is available on metal complexes, such as metal ammines in ammonium sulphate solutions, we can make very good predictions concerning the extraction of metals from them. For example, the extraction of metals such as copper, nickel, cobalt and zinc from ammonia-ammonium sulphate solutions by extractants such as carboxylic acids is undoubtably controlled by the reactions occurring in the aqueous phase, and not by the extractant-metal ion reaction. Thus for all such extractants it can be confidently predicted that the order of metal extraction as a function of pH is a function primarily of the metal ammine stability constants.

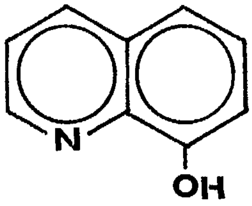
Similarly in acidic systems, the order of metal extractability by chelating and acidic extractants almost always follows the order of the metal hydrolysis constants, which are controlled by conditions existing in the aqueous phase. Deviations from this order may result as conditions in the aqueous phase change; for example, metal hydrolysis constants vary with change in ionic strength, and a particular ionic strength may reverse the order of the hydrolysis constants of two metals which are very similar. Again, steric and kinetic effects may predominate giving rise to changes in this order. But on the whole, few changes are found, thus this a fair generalization.

Metal extraction is heavily dependent on pH, and adjustment of the aqueous phase pH can be used as a means of increasing or decreasing extraction, separating metals, and so on. Again, the aqueous phase effects essentially control the metal extraction.

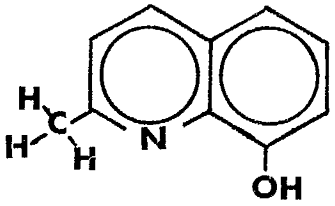
Aqueous phase composition is of greater importance when ion-association or solvating extractants are used for metal extraction. In such systems, where high acid or salt concentrations are mandatory, the problems associated with attempting to understand the mechanisms of metal extraction become very difficult, or even unsurmountable, because we really know very little about such systems, and at these concentrations, solution theory breaks down. Accordingly, much of the data on such systems are phenomenistic in nature - we know the overall effect, but not the individual effects which comprise it. Thus we cannot predict nearly as much as we can for systems involving complexation, except for such as the extraction of metals from high chloride systems where we know which metals form extractable anionic chloro complexes, and their stabilities. For example, nickel has little tendency to form anionic chloro complexes whereas cobalt does ($CoCl_4^{2-}$), hence cobalt can be extracted from nickel by amines at high chloride concentrations in the aqueous phase. Here again, we see that the reactions in the aqueous phase are the predominant factors in metal extractions. Similar examples can be given for systems employing solvating extractants.

Of course, reactions between metals and extractants do have an effect on metal extractions. These are concerned more with organo-metallic interactions which can occur only if the conditions in the aqueous phase allow them. However, to be fair, even if the conditions in the aqueous phase allow the presence of metal ions suitable for complexation with an extractant, the reaction may not necessarily occur, for several reasons. For example, the reaction between a metal ion and an extractant may be kinetically slow. It is well known that some metal ions are very inert - that is, the exchange rate between the ligands (such as water) in the first hydration sphere is very slow; chromium(III) is probably the best known example. Thus for some metals, complex formation and hence extraction is very slow, and for others it is fast. The specificity of Kelex 100 for copper over iron is a result of the fact that the copper-Kelex reaction is kinetically fast, whereas that with ferric iron is kinetically slow.

Steric factors can also result in non-extractability of metals. Thus if the extractant molecule is so spatially oriented that the metal ion cannot fit sufficient molecules around it to form a neutral extractable complex, it probably will not be extracted. A good example here is that of a 8-hydroxyquinoline (oxine) and 2-methyl-8-hydroxyquinoline (quinaldine):



oxine



quinaldine

The former will complex with aluminum, and can be extracted by chloroform. The latter, however, will not complex with aluminum because the small size of the aluminum atom will not allow three molecules of quinaldine to fit around it to form a neutral complex, and hence aluminum is not extracted by quinaldine in chloroform. The methyl group on the 2-position sterically hinders the formation of aluminum quinaldinate.

It is factors like these, and a knowledge of the special requirements of a metal atom, which can be used in designing metal-specific extractants. We know that nickel can form square planar complexes, whereas cobalt rarely does. Thus if we design a molecule which can form such a complex with nickel and not with cobalt, we have the basis for a nickel -specific extractant.

But we seem to be straying from the subject. What this all boils down to is that unless the conditions in the aqueous phase are suitable for complex formation with an extractant, metal extraction will not occur, and this is the primary condition for solvent extraction. One should realise that no extractant is entirely specific for a particular metal ion; specificity is usually imparted by conditions existing in the aqueous phase.

By combining solvent extraction theory with the chemistry of metals in aqueous solutions and with organo-metal complexes we can go a long way towards an understanding of the reactions involved in metal extractions. Such things as the order of metal extraction, metal loading, effects of pH, and stripping of metals from loaded solvents can be predicted with a good degree of certainty.

We can also use data obtained on similar systems in order to predict metal extractions, and in understanding the extraction process. There is a considerable amount of data available in the literature on metal complexes, especially for those of the transition metals (and there are more transition metals in the periodic system than non-transition metals). For example, considerable data are available in the literature on 8-hydroxyquinoline (oxine) and metal-oxine complexes. Now we know that Kelex 100 is a (commercially available) substituted oxine, thus one can assume, with some confidence, that metal-Kelex complexes will resemble metal-oxine complexes. By comparison, then, one should be able to use these data to predict many of the metal extraction properties of Kelex 100.

Let us take this example a little further. Oxine has been shown to form adduct complexes with cobalt and zinc of the type $Co(Ox)_2 \cdot 2HOx$ and $Zn(Ox)_2 \cdot HOx$; both copper and nickel form regular complexes of the type $Cu(Ox)_2$ and $Ni(Ox)_2$. Now we discussed the formation and extraction of adducts on p. 41, and showed that the distribution curves for adducts would differ from those for non-adduct complexes. If we plot the $pH_{1/2}$ values for $Co(Ox)_2 \cdot 2HOx$ and $Ni(Ox)_2$ extraction versus log [oxine] in chloroform (obtained from ref. 16) we find that the curves cross at about 0.5 M oxine, that is, they have different slopes. Thus at oxine concentrations lower than about 0.5 M cobalt extracts preferentially to nickel, and above this concentration the reverse holds.

If we apply this reasoning to the extraction of cobalt and nickel by Kelex, then the same situation is predicted on the basis of the similarity between oxine and Kelex. Experiments have shown that this prediction holds, and at Kelex concentrations below about 0.5 M, cobalt is extracted preferentially to nickel. The reverse holds above about 0.5 M Kelex.

This result holds interesting possibilities for the separation of cobalt and nickel by variation of extractant concentration at a given pH.

We have not considered effects on metal extraction resulting from the properties of diluents and modifiers. There have been several attempts to determine the causes of diluent effects, but which have so far failed. Thus this area remains phenomenological in nature and we still cannot predict with any degree of certainty what the effects will be on the extraction of a metal by changing, for example, from an essentially aliphatic diluent to one essentially aromatic in nature. In some extraction systems the effect is minimal, while in others, dramatic effects are given. Perhaps the best example of the latter case is in the extraction of rare earths from acidic solution using D2EHPA as the extractant(42).

In conclusion, the usefulness of theory, knowledge of metal complexes, reagents, and comparative data has been demonstrated, and it is hoped that those engaged in studies of solvent extraction processes can find this dissertation to be of help in understanding and predicting the course of metal extractions. For those who wish to go further into the subject, a bibliography of useful texts is appended.

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APPENDIX I

The Nomenclature of Solvent Extraction

Antagonism: Antonym of synergism

A/O Ratio: Volume phase ratio of aqueous to organic phases; may also be expressed as O/A

Aqueous Feed: The aqueous solution feed to the extraction stage which contains the metal or metals to be extracted

Back Mixing: Deviation from an ideal (plug) flow pattern in a contactor

Contactor: A device for dispersing and disengaging immiscible solution mixtures; it may be single or multi-stage

Continuous Phase: The coherent phase in a contactor

Crud: The material resulting from agitation of an organic phase, an aqueous phase, and fine solid particles that form a stable mixture. Crud usually collects at the interface between aqueous and organic phases.

Countercurrent Extraction: Extraction in which the aqueous and organic phases flow in opposite directions

Diluent: The organic liquid in which an extractant and modifier are dissolved to form a solvent

Dispersed Phase: The phase, in a contactor, which is discontinuous. Generally the dispersed phase is in the form of droplets

Distribution: The apportionment of a metal (solute) between two phases

Distribution Coefficient: See Extraction Coefficient

Distribution Isotherm: See Extraction Isotherm

Equilibrium: The position when the chemical potentials of both aqueous and organic phases are equal

Equilibration: Treatment of the solvent prior to its entering the extraction stage

Extract: Used as a verb to describe the transfer of a metal from one phase to another

Extractant: The active organic component of the solvent primarily responsible for the extraction of a metal

Extraction: The operation of transfering a metal from an aqueous to an organic phase

Extraction Coefficient, E: The ratio of total concentrations of metal (in whatever form) after contacting an aqueous and an organic phase under specified conditions:

$$E = \frac{\text{concentration of metal in organic phase}}{\text{concentration of metal in aqueous phase}}$$

Extraction Isotherm: The graphical presentation of isothermal equilibrium concentrations of a metal in the aqueous and organic phases over an ordered range of conditions in extraction

Extraction Raffinate: The aqueous phase from which a metal (or metals) has been removed by contacting with an organic phase

Equilibrium Constant: The equilibrium constant of a specified distribution reaction expressed in terms of thermodynamic activities

Flooding: The discharge of mixed phases from one or both exit ports of a contactor

Load: To transfer a metal from an aqueous to an organic phase

Loaded Solvent: The organic solvent containing the maximum concentration of a metal for the conditions under which extraction occurred

Loading Capacity: Refers to the saturation limit of a solvent for a metal or metals

Maximum Loading: see Loading Capacity

Mixed Solvent: A solution of more than one extractant in an organic diluent

Modifier: A substance added to a solvent to increase the solubility of the extractant, salts of the extractant, or of the extracted metal species, during extraction or stripping. Also added to suppress emulsion formation

Partition Coefficient: The ratio of the concentration of a solute in a single definite form in the organic phase to that of the same form in the aqueous phase at equilibrium

Partition Constant: The value of the partition coefficient at infinite dilution, that is, the ratio of the thermodynamic activity of a solute in a single definite form in the organic phase to that of the same form in the aqueous phase at equilibrium

$pH_{1/2}$: That pH value at which the extraction coefficient is unity

Phase Ratio: See A/O ratio

Phase Inversion: The change in a solvent extraction system when the dispersed phase becomes the continuous phase, or vice versa

Raffinate: The aqueous phase from which the metal has been removed by extraction; generally a waste stream from a solvent extraction circuit

Scrubbing: The selective removal of a metal or impurities from a loaded solvent prior to stripping. Also removal of solvent degradation products and non-strippable complexes from the solvent usually after stripping

Scrubbed Solvent: The organic phase after removal of contaminents by scrubbing

Scrub Solution: The aqueous solution used to contact the loaded solvent for the removal of contaminents

Scrub Raffinate: The aqueous phase after contacting the loaded solvent

Separation Factor: The ratio of the extraction coefficients of two metals being compared

Settling: Separation of dispersed immiscible phases by coalescence or sedimentation

Solvent Extraction, (SX): Separation of one or more solutes from a mixture by mass transfer between immiscible phases in which at least one phase is an organic liquid.

Solvent: A mixture of an extractant, diluent, and in some cases a modifier. The organic phase which preferentially dissolves the extractable metal species from an aqueous solution

Solvent Inventory: The total quantity of solvent in the process

Stage: A single contact (dispersion and disengagement). Also refers to a theoretical stage which is a contact that attains equilibrium conditions in a particular system

Steady State: The state of a process operating in such a way that the concentration of solutes in exit streams remain constant with respect to time for constant feed concentrations, even though the two phases are not necessarily in thermodynamic equilibrium in any part of the process

Stripping: The removal of extracted metal from the loaded solvent. Selective stripping refers to separate removal of specific metals from a solvent containing more than one metal

Stripping Coefficient, S: The reciprocal of the extraction coefficient

Strip Solution: The aqueous solution used to contact the loaded (or scrubbed) solvent to recover the extracted metal

Strip Isotherm: Similar to extraction isotherm but for stripping

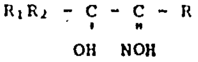
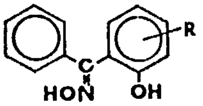
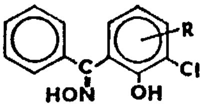
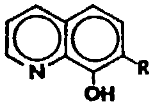
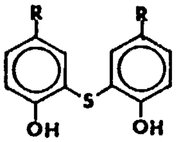
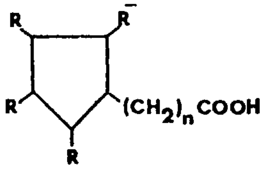
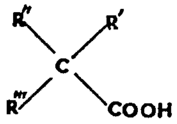
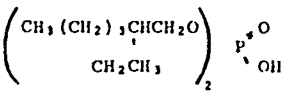
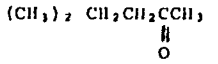
Strip Liquor: The aqueous solution containing the metal recovered from a loaded solvent by stripping

Stripped Solvent: The solvent after removal of extracted metal by stripping

Synergism: The cooperative and beneficial effect of two or more extractants or reagents that exceeds the sum of the individual effects

APPENDIX II

COMMERCIALLY AVAILABLE EXTRACTANTS

EXTRACTANT	TYPE	STRUCTURE	SUPPLIER
LIX - 63	CHELATING	 $R_1R_2-\underset{OH}{\underset{\mid}{C}}-\underset{NOH}{\underset{\|}{C}}-R$	General Mills Inc.
LIX - 64			General Mills Inc.
LIX - 64N			General Mills Inc.
LIX - 64N			
LIX -70			General Mills Inc.
LIX - 71			
LIX - 73			
KELEX 100 and 120			Ashland Chemicals
MEDIA I and II			Ashland Chemicals
Naphthenic Acids	ACIDIC		Shell Chemicals Imperial Oil
Versatic Acids			Shell Chemicals
Di(2-ethylhexyl)-phosphoric acid		 $\left(CH_3(CH_2)_3\underset{CH_2CH_3}{\underset{\mid}{C}}HCH_2O\right)_2P\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}$	Union Carbide
Primary Amines	ION ASSOCIATION	RNH_2 $(R{=}C_{12}{-}C_{14})$	Rohm and Haas
Secondary Amines		R_2NH (N-laurgl trialkyl methyl amine)	Rohm and Haas
Tertiary Amines		R_3N $(R{=}C_8{-}C_{10})$	General Mills Inc.
Quat. Ammonium Halides		$(R_3N^+CH_3)Cl^-$ $(R{=}C_8{-}C_{10})$	Ashland Chemicals
Tri-n-butyl Phosphate	SOLVATING	$(CH_3(CH_2)_3O)_3P{=}O$	Ashland Chemicals
Methyl isobutyl Ketone		 $(CH_3)_2CH_2CH_2\underset{O}{\underset{\|}{C}}CH_3$	Ashland Chemicals

APPENDIX III

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