PART I

INTRODUCTION
LITOCRATES OR COMING REVOLUTION

CHAPTER 1
SOLVENT EXTRACTION

Problems of chemical analysis involve mainly two stages, separation of the desired constituent and determination of the amount of this constituent. Further the analytical chemist is called upon to solve the problems concerned with mixtures of increasing complexity because of the rapid growth of chemical technology. Elements which were thought to be laboratory curiosities have now become industrially important ingredients of many products. In spite of the availability of modern discriminating methods of measurement, separation processes have assumed a vital role in the analysis of industrial products. Solvent extraction enjoys a favoured position among such separation processes. This is because of its simplicity, ease, speed and wide scope. Besides the above advantages, simple equipment such as a separating funnel is sufficient to conduct the separation. In most cases the equilibration time is not more than 10 to 15 minutes. It is unique in the sense that the separation is cleaner as compared to the separation through precipitation. Contamination of precipitates by co-precipitation phenomena is decidedly a point against the precipitation technique as a separation process.
Liquid-liquid extraction, using an aqueous-organic solvent pair, has become very important since the analysis of the metals is primarily concerned with samples in aqueous solutions. It goes without saying that the solubility of the metal to be determined in organic solvent is an essential factor. Therefore in all metal extraction systems some or all the water molecules co-ordinated to the metal ions must be removed to obtain a species that can be extracted into an organic solvent. Further the formation of an uncharged species is a necessary pre-requisite for extraction into organic solvents which generally have low dielectric constants. It is therefore convenient to classify extraction systems on the basis of the nature of the extraction species. The main types are - chelate extraction systems and ion-association extraction systems. In chelate systems organic complexing reagents are employed. These reagents replace co-ordinated water from many metal ions to form neutral, essentially covalent chelate compounds which are soluble in organic solvents. In ion-association systems the extractable species is formed by the association of ions. There are three different types in this category. In the first type the metal is incorporated in a very large ion containing bulky organic groups. For example, Cu(I) reacts with neocuproine to form a large univalent cation which forms an ion-pair with a nitrate or a perchlorate anion. In the second type the extractable species is formed by the
combined action of anions and of oxygen containing organic solvents. For example extraction of iron(III) from hydrochloric acid solutions into ethyl ether involves the following ion-pair

\[ \left( \text{C}_2\text{H}_5\right)_2\text{O}^+\text{FeCl}_3 \left[ \text{C}_2\text{H}_5\right]_2\text{O}^- \]

In this example the oxygen atom of the solvent molecule co-ordinates with the metal ion. Hence the term OXONIUM extraction system is applied for such type. In the third type metal ions are incorporated into salts of high molecular weights which dissolve in organic solvents by forming colloidal aggregates or micelles. The extraction of uranium by high molecular weight amines dissolved in kerosene exemplifies the above type.

The basic principle underlying solvent extraction is the distribution of the solute species (the metal ion species) between two immiscible solvents namely the water and the organic extracting solvent. The chemical interactions of the distributing species with the other components in each phase are also of great significance because of their effect on the distribution. An analytical chemist is concerned in the overall or stoichiometric distribution of the component of
interest between the two phases. Hence a more practical quantity called the distribution ratio 'D' is used to describe the extraction. This is a stoichiometric ratio of all species of the same component in the respective phases.

\[
D = \frac{\text{Total concentration in organic phase}}{\text{Total concentration in aqueous phase}} \quad \ldots \quad \text{I.1.1}
\]

In describing extractions, the term per cent extracted, \(\%E\) is of greater practical importance than the distribution ratio.

\[
\%E = \frac{100 D}{D + (V_0/V)} \quad \ldots \quad \text{I.1.2}
\]

Where \(V_0\) and \(V\) represent the volumes of the organic and aqueous phases respectively. When the volumes are equal the denominator simplifies to \(D + 1\).

**EXTRACTION EQUILIBRIA**

The subject was extensively treated by various authors such as Irving\(^1\), Williams\(^2\), Rydberg\(^3;4\), Morrison and Preiser\(^5\), Stary\(^6\), Tuck\(^7\), Ringbom\(^8\), Marcus\(^9\), etc.

The overall stoichiometric equilibrium constants are
defined by

\[ \beta_{\text{hmlws}} = \frac{[\text{H}^+ \text{M} \text{L} \text{(H}_2\text{O}) \text{w} \text{s}]}{[\text{H}^+ \text{M}^m \text{L}^l \text{(H}_2\text{O})^w \text{[S]}^6]} \quad \ldots \ I.1.3 \]

For the formation of a complex species of general formula \( \text{H}_n \text{M}_m \text{L}_l \text{(H}_2\text{O})_w \text{s} \) form an aqueous solution of constant ionic strength containing metal ions \( \text{M} \), hydrogen ions and ligand anions \( \text{L} \), and saturated with an organic solvent \( \text{I} \).

The stoichiometric partition coefficients are given by

\[ P_{\text{hmlws}} = \frac{[\text{H}_n \text{M}_m \text{L}_l \text{(H}_2\text{O})_w \text{s} \text{I}]}{[\text{H}_n \text{M}_m \text{L}_l \text{(H}_2\text{O})_w \text{s} \text{I} \text{aq}]} \quad \ldots \ I.1.4 \]

The general equation for the extraction coefficient of the metal ion \( \text{M} \), between the organic and aqueous phases is

\[ R = \frac{\sum [\text{M}]_{\text{org}}}{\sum [\text{M}]_{\text{aq}}} \quad \ldots \ I.1.5 \]

\[ = \frac{\sum m [\text{H}_n \text{M}_m \text{L}_l \text{(H}_2\text{O})_w \text{s} \text{I} \text{org}]}{\sum m [\text{H}_n \text{M}_m \text{L}_l \text{(H}_2\text{O})_w \text{s} \text{I} \text{aq}]} \quad \ldots \ I.1.6 \]

\[ \approx \frac{\sum P_{\text{hmlws}} \beta_{\text{hmlws}} m [\text{H}^+]^l [\text{M}]^m [\text{L}]^l [\text{H}_2\text{O})_w^w [\text{I}]^s]}{\sum \beta_{\text{hmlws}} m [\text{H}^+]^l [\text{M}]^m [\text{L}]^l [\text{H}_2\text{O})_w^w [\text{I}]^s]} \quad I.1.7 \]
Assuming that the concentrations of all other species except the metal ion are constant, the following logarithmic relation can be obtained

\[
\frac{\partial \log E}{\partial \log [H]} \cdot [H] [L] [H_2O] [S] = m_{\text{org}} - m_{\text{aq}} \quad \ldots \text{I.1.8}
\]

Similar expressions for hydrogen ions and ligand anions can be written when the species other than the one under consideration are at constant concentration.

\[
\frac{\partial \log E}{\partial \log [H^+]} [M] [L] [H_2O] [S] = m_{\text{org}}^{\text{horg}} - m_{\text{aq}}^{\text{h}\text{aq}} \quad \ldots \text{I.1.9}
\]

\[
\frac{\partial \log E}{\partial \log [L]} [M] [H] [H_2O] [S] = m_{\text{org}}^{\text{lorg}} - m_{\text{aq}}^{\text{l}\text{aq}} \quad \ldots \text{I.1.10}
\]

From the expression (I.1.8) it is obvious that the slope of the plot of log E against log [H] is positive if an acid species is extracted which contains more hydrogen atoms per molecule than does the metal species in the aqueous phase. If the slope is unity for a wide range of concentrations of mineral acid, it indicates the extraction of a acid complex with a single hydrogen atom per molecule of extracted complex.

**EXTRACTION OF CHLORATES**

In practice the organic reagent is added in large excess
in the metal extractions. This normally ensures complete complex formation and ML_n will be normally the only metal species extracted. Mixed ligand species that are extractable are unlikely to occur. However, if extractable mixed ligand species occur, their practical effect is to enhance the extraction coefficient and increase the physical separation of the metal. Formation of other metal species which remain in the aqueous phase is also of primary importance since it will diminish the degree of extraction. Competing side reactions such as protonation of the ligand, complex formation between the metal and other ligands present and stepwise formation of successive complexes ML, ML_2 etc. play an important role in extraction procedures. Any side reaction leading to mixed complexes soluble in organic phase will enhance the extraction while that leading to hydrophilic complex species will diminish it. From the above considerations it can be stated that the following factors influence the extraction of metal chelates.

1. Acidity
2. Concentration of the organic reagent
3. Masking agents
4. Organic solvent
5. The stability of the metal chelate
6. Salting out agents and
7. Synergistic agents.
1. **Influence of acidity**: Extraction of metal chelate can be viewed in general as follows: An uncharged metal chelate $ML_n$ is formed through the reaction of the metal ion $M^{n+}$ with the organic reagent $HL$ and is distributed between the aqueous and the organic phase according to the equation

$$M^{n+} + n(ML)_{org} = (ML)_n^{org} + nH^+ \quad \ldots \text{I.1.11}$$

The extraction constant $K$, i.e., the equilibrium constant of the above reaction is:

$$K = \frac{[ML]_n^{org} [H]^n}{[M^{n+}] [HL]_n^{org}} \quad \ldots \text{I.1.12}$$

This can be written as

$$K = D \frac{[H]^n/[HL]_n^{org}} \quad \ldots \text{I.1.13}$$

From the above equation it is clear that the distribution of the metal is a function of $pH$ if the reagent concentration is kept constant. It is therefore possible to calculate the value of $D$ at constant concentration of the organic reagent for every $pH$ value, from the known value of the extraction constant $K$. It is already pointed out earlier that from the
analytical point of view percentage of the metal extracted
F is more important than D. Hence the above equation is
modified and written in the logarithmic form as

$$\log F = \log K \cdot n \pi H + n \log [H]_{org}$$

$$= \log F \left( \frac{V_{aq}}{V_{org}} \right) - \log (100 - F) \quad \cdots \text{I.1.14}$$

The pH corresponding to the fifty per cent of the
extraction \((F = 50 \text{ or } D = 1)\) at 1.0 \text{ M} equilibrium concentration
of the reagent in the organic phase provided \(V_{aq} = V_{org}\)
is equal to \(\frac{\log K}{n}\). This pH value is called \((\text{pH}_{1.0})\).

2. **Influence of the concentration of the organic reagent:**

It is clear from the equation (I.1.14) that the extractability
of a metal with the given reagent into the given organic
solvent depends upon the concentration of the reagent. The
higher is the concentration of the reagent, the greater will
be the distribution ratio. The extraction curve is then
shifted to acid side permitting extraction from more acidic
solutions. Hence use of high reagent concentration is helpful
in the extraction of metals which are easily hydrolysed.
However, the solubility of the reagent in the organic solvent
controls the upper limit of the reagent concentration. The
lower limit is fixed by the formation of non-extractable
hydroxy complex.
3. **Influence of the masking agent** - The distribution of a metal between the organic phase containing the reagent ML and the aqueous phase containing masking agent \( n \text{B} \) that forms non-extractable metal complexes diminishes according to the equation:

\[
P = \frac{K[ML]^n_{\text{org}}}{[n]^n(1 + \beta_1[n] + \beta_2[n]^2 + \ldots)}
\]

where \( \beta_1 \) is the stability constant of the metal complex \( n \text{B} \).

4. **Influence of the organic solvent** - Organic solvent also influences the distribution of both reagent and metal chelate. The partition coefficient of both the reagent and the chelates will be higher if the solubility of these are higher in the organic solvent. However it is evident from the equation relating the value of \( K \) or \( pH_2 \) and percentage extraction \( E \), that the latter should not depend strongly on the nature of the solvent. The relative magnitudes of the co-ordination number and the charge of the central metal ion also play an important role in respect of the solvent influence. If the co-ordination number is more than twice the charge of the metal ion the chelate may contain free co-ordination positions. These will normally be occupied by water molecules. The hydrated chelates are normally poorly extracted. In order
to make the extraction more effective, it is necessary to
displace the water molecules. This can be achieved with the
help of the excess organic reagent (additive complexes,
MLₜ(HL)ₓ) or the organic solvent with the formation of complexes
of type MLₜₓ. Oxygen containing solvents are capable of
readily displacing the water molecules and therefore they
extract better than the solvents devoid of oxygen.

5. **Influence of the stability of the metal chelates:** The
extraction constant K is greater for the metal chelates of
higher stability. The extraction in such cases can be carried
out from more acidic solutions. The free energy of the
formation of a complex between a metal ion and the organic
reagent is expressed as

\[-\Delta G = \text{Const.} \frac{n}{r}\]

... I.1.16

where 'n' is the charge and r is the crystal radius of the
metal ion. This relationship was used by Dyrsen, to explain
the values of log K or pMₜ for acetyl acetonates of different
metal ions.

6. **Influence of salting out agents:** The electrolytes whose
addition to the aqueous phase greatly increases the
extractability of complex are called salting out agents.
These salts play an important role in oxonium extractions. Grunwald observed that addition of ammonium nitrate to the aqueous phase increased greatly the extraction of uranium into ether. Furman and others found that multivalent metal nitrates with pronounced hydration tendencies proved most effective as salting out agents. Salting out agent would supply not only the required anion in sufficient concentration but also influences the activity coefficients of the ions participating in the formation of complex. The decrease in dielectric constant of aqueous phase with addition of salt solution is also partly responsible for the enhanced extraction, since lower dielectric constant favours ion association complex. Besides the above effect, a salt added in high concentrations to the aqueous phase helps in obtaining a quicker equilibration and a better separation of the organic and aqueous phases. Thus addition of indifferent salts of multivalent cations would help in preventing the emulsion formation between the two phases. The phenomenon of salting out thus becomes an important one in solvent extractions involving especially the high molecular weight amines and other compounds as extracting agents.

7. Synergistic agents:— Synergism is a term first coined by Blake et al. in their report on the solvent extractions
employing a mixture of dialkyl hydrogen phosphate and neutral organophosphorus reagents. It was stated that this phenomenon greatly enhanced the extraction. That is, the extractions with the mixture are greater compared to the extractions involving individual components. The most intensively studied synergic system involved a chelating agent and a solvating solvent system. It was pointed out by Irving and Edgington \(^\text{14}\) that the following conditions are essential for synergic extractions.

a) One of the reagents should neutralize the charge on the metal ion by forming a chelate

b) The solvent should replace any residual co-ordinated water from the complex, rendering it less hydrophilic

c) The solvent should not itself be hydrophilic and co-ordinated less strongly than the chelating agent and

d) The maximum co-ordination number of the metal and the geometry of the ligands should be favourable.

The brief introduction presented above gives an account of the various factors that must be borne in mind for designing a successful procedure for the solvent extraction of a desired metal ion. In view of the possibility of varying different parameters to our advantage, solvent extraction has
occupied a covetable place in industrial chemical analysis. The utility of solvent extraction in chemical analysis has been enhanced to a very great extent with the advent of coupling this technique with polarography. Thus extraction polarography is not only helpful for the analysis but also found to be helpful in the investigation of fundamental aspects of extraction such as the nature of the extracted species and the oxidation state of the metal ion.
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