CHAPTER 3

PRINCIPLES OF SOLVENT EXTRACTION
Solvent extraction is perhaps the most versatile of all analytical techniques, in that it has a wide range of applications and involves most of the physico-chemical principles used generally in analytical chemistry. It enjoys a favourable position among the separation techniques because of its elegance, simplicity, speed and wide scope.\(^1-3\) The same technique can be applicable to both trace and macro amounts of metal ions. The important advantage of the extraction method over the widely used precipitation method for analytical separation lies in the fact that the former method offers a cleaner separation. The apparatus employed is a simple separatory funnel. The equilibration period is not more than 10 to 15 minutes. The basic principle involved in the method is that a solute distributes itself in a fixed ratio between two immiscible solvents, one of which is usually water and the other an organic solvent.

**CLASSIFICATION OF METAL EXTRACTION SYSTEMS**

The metal extraction systems are classified mainly into two types on the basis of the nature of the extractable species. These are neutral covalent chelate compounds and ion-pair association complexes. In neutral covalent
compound systems, complexing agents such as 8-quinolinol, dithizone or cupferron replace coordinated water from metal ions during complex formation. These complexes are usually soluble in organic solvents such as hydrocarbons and halo hydrocarbons.

The second type involving ion association extraction system, is further sub-divided into three classes. In the first type, a charged metal complex containing bulky organic groups associate with another ion of opposite sign. For example copper(I) reacts with 2,9-dimethyl phenanthroline to form a large univalent cation which associates with a nitrate or perchlorate anion, to form an ion-pair association species extractable into chloroform.

In the second type, organic solvent plays an important role. For example, the iron(III) complex extracted out of hydrochloric acid by ethyl ether probably has the formula \( \{(\text{C}_2\text{H}_5)_2\text{O}^+: \text{H}^+, \text{FeCl}_4[(\text{C}_2\text{H}_5)_2\text{O}]_2^- \} \).

The third type is characterised by the species formed by the incorporation of metal ion into salts of high molecular weight which dissolve in organic solvents in much the same fashion as does soap in water, forming colloidal aggregates or micelles.
Distribution or Extraction Coefficient ($E$):

For a given metal $M'$ present as various species $M_1, M_2, M_3, \ldots, M_i$ and partitioned between organic and aqueous phases, the extraction coefficient can be defined in the following way:

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

$$= \frac{[M]_{\text{org}}}{[M]_{\text{aq}}}$$

$$= \frac{[M_1]_{\text{org}} + [M_2]_{\text{org}} + [M_3]_{\text{org}} \ldots + [M_i]_{\text{org}}}{[M_1]_{\text{aq}} + [M_2]_{\text{aq}} + [M_3]_{\text{aq}} \ldots + [M_i]_{\text{aq}}}$$

If poly nuclear species are formed, their concentrations are multiplied by the appropriate stochiometric coefficients. The extraction co-efficient depends on the concentration of the solute and on the composition of the phases.

Degree of Extraction ($R$):

The fraction of total weight of the metal extracted into the organic phase is called the degree of extraction. This is also called the degree of variance or recovery, and is generally more useful than the extraction coefficient.
Partition coefficient (P):

The partition coefficient is a true constant and is independent of the total amount of partitioned solute in the two phases. For simple systems in which only one species is distributed and has the same form in both phases, the thermodynamic partition coefficient is expressed as

\[ P_M = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} = \frac{\gamma_{\text{org}} [M]_{\text{org}}}{\gamma_{\text{aq}} [M]_{\text{aq}}} \]

where braces indicate activities, square brackets indicate concentration and \( \gamma \) denotes the activity coefficient for the species. Phases are indicated by subscripts.

Extraction equilibria:

Irving and Williams,\(^2\) Dyrssen and Sillen,\(^5,6\) Rydberg,\(^7,8\) Morrison and Freiser,\(^9\) Stary,\(^10\) Diamond and Tuck,\(^11\) Ringbom,\(^12\) and Marcus,\(^13\) have provided excellent treatments of extraction equilibria of various systems.

The overall stoichiometric equilibrium constants are defined by
The stoichiometric partition coefficients are given by

$$
\beta_{h_{\text{mlws}}} = \frac{[H_h M_m L^l (H_2O)^w S_s]}{[H]^h [M]^m [L]^l [H_2O]^u [S]^s}
$$

The general equation for the extraction coefficient (E) of the metal 'M' between the organic and aqueous phases is

$$
E = \frac{\sum [M]_{\text{org}}}{\sum [M]_{\text{aq}}} = \frac{\sum m [H_h M_m L^l (H_2O)^w S_s]_{\text{org}}}{\sum m [H_h M_m L^l (H_2O)^w S_s]_{\text{aq}}} = \frac{\Sigma P_{h_{\text{mlws}}} \beta_{h_{\text{mlws}}} \cdot m [H]^h [M]^m [L]^l [H_2O]^u [S]^s}{\Sigma \beta_{h_{\text{mlws}}} \cdot m [H]^h [M]^m [L]^l [H_2O]^u [S]^s}
$$

Assuming that the concentrations of all the other species except the metal ion are constant, the following logarithmic relation can be obtained.
Similar expression for hydrogen ions and ligand anions can be written when the species other than one under consideration are at constant concentration.

\[
\left( \frac{\partial \log E}{\partial \log [\text{m}]} \right)_{[\text{M}] [\text{L}] [\text{H}_2\text{O}][\text{s}]} = \bar{m}_{\text{org}} - \bar{m}_{\text{aq}} \tag{1}
\]

\[
\left( \frac{\partial \log E}{\partial \log [\text{H}]} \right)_{[\text{M}] [\text{L}] [\text{H}_2\text{O}][\text{s}]} = \bar{m}_{\text{org}} \bar{h}_{\text{org}} - \bar{m}_{\text{aq}} \bar{h}_{\text{aq}} \tag{2}
\]

\[
\left( \frac{\partial \log E}{\partial \log [\text{L}]} \right)_{[\text{M}] [\text{H}] [\text{H}_2\text{O}][\text{s}]} = \bar{m}_{\text{org}} \bar{l}_{\text{org}} - \bar{m}_{\text{aq}} \bar{l}_{\text{aq}} \tag{3}
\]

From equation (2) it is obvious that the slope of the plot of log E against log [H⁺] is

\[
\bar{m}_{\text{org}} \bar{h}_{\text{org}} - \bar{m}_{\text{aq}} \bar{h}_{\text{aq}}
\]

A positive slope means that an acid species is extracted which contain more hydrogen atoms per molecule than does the metal species in the aqueous phase. If the slope is unity over an acidic range, it indicates the extraction of an acid complex with a single hydrogen atom per molecule of extracted complex.
Extraction of Chelates:

The general expression for the extraction of a metal ion $M^{n+}$ with an organic reagent $HL$ into a solvent 'S' at the optimum conditions is given as

$$E = \frac{\sum P_{hlw} \beta_{hlw} m [H]^n [M]^m [L]^l [H_2O]^w [S]^s}{\sum \beta_{hlw} m [H]^n [M]^m [L]^l [H_2O]^w [S]^s}$$

$ML_n$ is the only metal species that need usually be considered in the organic phase. If extractable mixed ligand species do occur, however, there practical effect is to enhance the extraction coefficient and physical separation of the metal. Other species, if there are remaining in the aqueous phase are much more important since any such metal species will diminish the degree of extraction. The extraction system may be disturbed by a set of competing side reaction such as protonation of the ligand or formation of other complexes between the metal ion and the other ligands present, and step wise formation of complexes $ML, ML_2$ etc. From the above considerations, it can be stated that the following factors influence the extraction equilibrium of metal ion with an organic reagent.

1. Acidity of the aqueous phase
2. Reagent concentration
3. Masking agents
1. **Effect of Acidity on the Extraction Chelates:**

   Some of the chelating agents are usually weak acids. So the acidity or pH of the aqueous phase has a great importance and must be specified.

   It is possible to calculate the 'E' value at different pH values if the equilibrium constant 'K' of the following reaction is known:

   \[ M^{n+}_{aq} + nHL_{org} \rightleftharpoons ML_{org} + nH^+_{aq} \]

2. **Effect of reagent concentration on the extraction of metal chelates:**

   The extraction of the metal with a given reagent in an organic solvent depends on the reagent concentration in the organic phase. The higher concentrations of reagent increases the 'E' value and extraction in such cases can be carried out easily in more acidic solutions. The only limiting factor is the solubility in the organic phase of the reagent and the product formed in the extraction system.
3. Effect of masking agents on extraction of metal chelates:

The influence of masking agents which form non-extractable complexes with the metal concerned will depend on the conditional stability constant of the complex formed. The pH and its effect on the reaction of the masking ligand with hydrogen ions, therefore play an important role. Masking agents are generally used to prevent interference by other ions, by preferential formation of complexes more stable than those formed with the reagent. It must not form too stable a complex with the ion of interest.

4. Effect of nature of the organic solvent on the extraction of metal chelates:

The choice of the solvent depends mainly on the high distribution ratio for the solute and low distribution ratio for undesirable impurities. The solvent should have low viscosity, low toxicity and inflammability. The relative magnitude of the coordination number and the charge of the central metal ion also play an important role in choosing the solvent for extraction. Generally the hydrated chelates are poorly extracted. To enhance the extraction it is necessary that the water molecules are to be replaced either by a reagent or a solvent. In particular oxygen containing solvents are capable of displacing water molecules.
more readily than other solvents because the high basicity of the oxygen. It is essential to mention the overall weight or the volume of the solvent employed for the extraction process.

5. Effect of the salting-out agents on the extraction of metal chelates:

It is found that extractability of complexes is enhanced by the addition of some electrolytes which are called salting-out agents. The function of the salting-out agent is probably to provide a high concentration of complexing anion to increase the concentration of the ion association complex and thus improves the extractability. Another important factor is the binding of water by the ions of the salting agent. The dielectric constant of the aqueous phase thus decreases with the increasing concentration of the salting-out agent and favours the formation of the ion association complexes. The enhancement of the extraction of metals by salting-out agents has been observed by number of workers. Munday\textsuperscript{14} and Hecht and Grunwald\textsuperscript{15} independently discovered that the addition of ammonium nitrate to the aqueous phase greatly enhanced the uranium extraction. Furman et al.\textsuperscript{14} found that multivalent metal nitrates with pronounced hydration tendencies proved to be most effective salting-out agents.
6. Effect of the stability of metal chelate on the extraction of metal:

The extraction coefficient 'S' is greater for those complexes where the stability constant of the metal complex is high in aqueous phase. The extraction in such cases can be carried out from more acidic solution. The free energy of the formation of a complex between a metal ion and the organic reagent is expressed as

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

where 'n' is the charge and 'r' is the crystal radius of the metal ion. This relationship was used by Dyrssen to explain the values of log \( K_{cr} (pH) \) for acetylacetanates of different metal ions.

7. Effect of synergic agents on the extraction of metal chelates:

The term synergism was first coined by Blake et al. in their report that when dialkyl hydrogen phosphate \((RO)_2POOH\) is used in conjunction with certain neutral organophosphorus reagents such as tertiary butylphosphate (TBP), the extracting power of the mixture exceeds the sum of the extracting power of its components. This phenomenon of greatly enhanced extraction or synergism due to a mixture of extractants has attracted considerable attention in recent years. Irving and Edington postulated that the
conditions required for synergic extraction are

(a) One of the active reagents (HX) should be able to neutralize the charge on the metal ion preferably by forming a chelate.

(b) The solvent (S) should displace any residual co-ordinated water from the neutral metal complex rendering it less hydrophilic.

(c) The solvent (S) should not itself be hydrophilic and be co-ordinated less strongly than HX.

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

Solvent extraction has thus occupied a covetable place in the chemical analysis in view of the great possibility of varying different parameters to our advantage.
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17. Irving, H. and Edington, D.N.
