

**CHAPTER – 2**  
**SOLVENT EXTRACTION**

## 2. SOLVENT EXTRACTION

Although solvent extraction as a method of separation has long been known to the chemists, only in recent years it has achieved recognition among analysts as a powerful separation technique. Liquid-liquid extraction, mostly used in analysis, is a technique in which a solution is brought into contact with a second solvent, essentially immiscible with the first, in order to bring the transfer of one or more solutes into the second solvent. The separations that can be achieved by this method are simple, convenient and rapid to perform; they are clean as much as the small interfacial area certainly precludes any phenomena analogous to the undesirable co-precipitation encountered in precipitation separations.

Solvent extraction is one of the most extensively studied and most widely used techniques for the separation and pre-concentration of elements [67-69]. The technique has become more useful in recent years due to the development of selective chelating agents [70-73] for trace metal determination. With proper choice of extracting agents, this technique can achieve group separation or selective separation of trace elements with high efficiencies. In analytical applications solvent extraction may serve the following three purposes:

- i) Preconcentration of trace elements
- ii) Elimination of matrix interference
- iii) Differentiation of chemical species.

The procedure is applicable to both, trace and macro levels. A further advantage of solvent extraction method lies in the convenience of subsequent analysis of the extracted species. If the extracted species are coloured, as is the case with many chelates, spectrophotometric methods can be employed. Alternatively, the solution may be

aspirated for atomic absorption or ICP-emission spectrometric analysis. If radiotracers are used, radioactive counting techniques can be employed.

Before going in detailed discussion of fundamental principles of extraction, the three mostly used terms for expressing the effectiveness of extraction processes are being defined below. These terms are basic for understanding of theoretical as well as practical considerations of the subject.

### **Distribution Ratio (D)**

The distribution of a solute between two immiscible solvents can be described by the distribution ratio “D”.

$$D = \frac{[A]_1}{[A]_2} \quad (2.1)$$

Where [A] represents the stoichiometric or formal concentration of a substance A and the subscripts 1 and 2 refer to the two phases. Since in most cases, two-phase system is of analytical interest, an organic solvent and aqueous are involved, *D* will be understood to be;

$$D = \frac{[A]_{Org}}{[A]_{Aq}} \quad (2.2)$$

The subscripts *org* and *Aq* refer to the organic and aqueous phases respectively.

### **Percent Extraction (E)**

The more commonly used term for expressing the extraction efficiency by analytical chemist is the percent extraction “*E*”, which is related to “*D*” as

$$\% \text{ Extraction}(E) = \frac{100[A]_{Org} V_{Org}}{[A]_{Org} V_{Org} + [A]_{Aq} V_{Aq}} = \frac{100D}{D + V_{Aq}/V_{Org}} \quad (2.3)$$

Where  $V$  represent solvent volume and the other quantities remain as previously defined. The percent extraction may be seen to vary with the volume ratio of the two phases as well as with  $D$ .

It may also be seen from equation (2.3) that at extreme values of “ $D$ ”, “ $E$ ” becomes less sensitive to changes in “ $D$ ”. For example, at a phase volume ratio of unity, for any value of  $D$  below 0.001, the solute may be considered quantitatively retained in the aqueous phase whereas for  $D$  values from 500 to 1000, the value of “ $E$ ” changes only from 99.5 to 99.9%.

### **Separation Factor ( $\gamma$ )**

Since solvent extraction is used for the separation of different elements and species from each other, it becomes necessary to introduce a term to describe the effectiveness of separation of two solutes. The separation factor  $\gamma$  is related to the individual distribution ratios as follows:

$$\gamma = \frac{[A]_{Org}/[B]_{Org}}{[A]_{Aq}/[B]_{Aq}} = \frac{[A]_{Org}/[A]_{Aq}}{[B]_{Org}/[B]_{Aq}} = \frac{D_A}{D_B} \quad (2.4)$$

where A and B represent the respective solutes.

In those systems where one of the distribution ratios is very small and the other relatively large, complete separations can be quickly and easily achieved. If the separation factor is large but the smaller distribution ratio is sufficiently large then less separation of both components occurs. It is then necessary to apply various techniques to suppress the extraction of the undesired component.

## **2.1 Distribution Law**

In the simplest extraction case, the distribution ratio is constant in accordance with the classical Nernst distribution law, a solute will distribute itself between two essentially

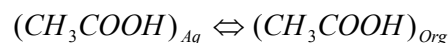
immiscible solvents so that at equilibrium the ratio of the concentrations of the solute in the two phases at a particular temperature will be constant, provided the solute is not involved in chemical interactions in either phase [74]. For such a solute, then

$$K_d = \frac{[A]_{Org}}{[A]_{Aq}} = D \quad (2.5)$$

where “ $K_d$ ” is termed as the distribution coefficient.

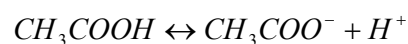
Deviations from the distribution law arise from two sources: (a) neglect of activity corrections and (b) participations of the distributing solute in chemical interactions in either or both of the two solvent phases. Although the distribution law, as described in equation (2.5) is not thermodynamically rigorous, variation in  $K_d$  due to variation in activity coefficients is likely to be under one order of magnitude for most extraction systems of interest to analysts. Far more important are the changes in extraction characteristics of solute because of chemical changes, which occur. Such changes do not represent failure of the law. Rather, they add complexity to the distribution expressions, which can be properly accounted for by using appropriate equilibrium expressions.

The distribution of acetic acid between benzene and water may serve as an illustration of the effects of chemical interactions of the solute. The distribution of acetic acid itself may be described as follows:



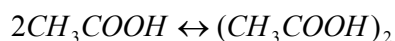
$$K_D = \frac{[CH_3COOH]_{Org}}{[CH_3COOH]_{Aq}} \quad (2.6)$$

However, acetic acid dissociates in aqueous phase



$$K_A = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]_w} \quad (2.7)$$

and forms a dimer in benzene



$$K_p = \frac{[(CH_3COOH)_2]_o}{[CH_3COOH]_o^2} \quad (2.8)$$

The overall distribution of acetic acid is described by “*D*”, which is

$$D = \frac{[CH_3COOH]_o}{[CH_3COOH]_w} = \frac{[CH_3COOH]_o + [(CH_3COOH)_2]_o}{[CH_3COOH]_w + [CH_3COO^-]} \quad (2.9)$$

Upon incorporation of the equilibrium expression in Eq. (2.6), (2.7) and (2.8) in Eq. (2.9) there results

$$D = \frac{K_D[1 + 2K_p[CH_3COOH]_o]}{1 + K_A/[H^+]} \quad (2.10)$$

This shows how the distribution of acetic acid varies as a function of pH and acetic acid concentration.

## 2.2 Process of Extraction

From the above equations, it is clear that three essential aspects are involved in the extraction of acetic acid:

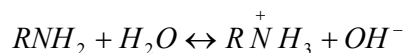
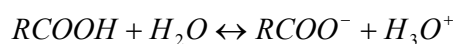
- A:** Chemical interaction in the aqueous phase.
- B:** Distribution of extractable species.
- C:** Chemical interactions in the organic phase.

These three aspects are shared by almost all extraction systems and serve as the basis of a useful organizational pattern.

### 2.2.1 Chemical interactions in the aqueous phase

A major point of differentiation between extraction of organic and inorganic materials is the extent to which the formation of an uncharged extractable species depends on chemical interactions in the aqueous phase. Most organic compounds are

already uncharged and extractable. Such aqueous phase reactions if do occur might well transform these to charged non-extractable species, e.g.



In contrast, most of the inorganic compounds are dissociated, so that in order to extract a species of interest into an organic solvent, reactions in the aqueous phase leading to the formation of an uncharged, extractable complex must be utilized. For example, in order to extract aluminum-III from an aqueous solution of aluminum nitrate, one must bring about the reaction of the aluminum-III cation with a reagent such as 8-quinolinol to form aluminum-8-quinolate, which may be extracted into a variety of organic solvents such as chloroform or benzene [75].

Therefore, the formation of an uncharged complex is very important in the extraction of metals and other inorganic species that makes it convenient to classify such extractions according to the nature of the complexes.

## 2.2.2 Distribution of extractable species

Although the ratio of solubilities of a solute in each of two solvents may not be critically equated to the distribution coefficient of the solute between the two solvents [76], the underlying factors affecting relative solubility and distribution are undoubtedly similar. It is, therefore, useful to discuss solubility characteristics of various types of substances and to note structural effects in both solvent and solute on the solubility.

In solutions where specific chemical forces are not active, the classical principle of “like dissolves like” is of great help in predicting solubility. This principle may be expressed in modern terms as Hildebrand’s theory of regular solutions from which, the solubility is seen to increase as values of the solubility parameter “ $\delta$ ” of solute and

solvent approach each other [76]. The solubility parameter, defined as the square root of the heat of vaporization per milliliter, is a measure of cohesive energy density. Comparison of solubility parameters should be of maximum assistance of dealing with those organic extraction systems in which specific chemical or associative forces are inoperative. Burrell has successfully used solubility parameters to rationalize the solubility behavior of various polymers [77].

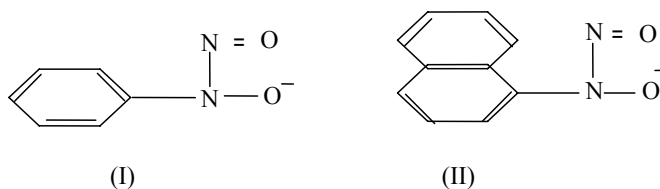
In systems, where hydrogen bonding may be present, particularly those involving an aqueous phase, the solubility parameter is inadequate in predicting solubility. This might be expected in as much as this concept is, strictly speaking, applicable only in regular solutions. Collander has been able to observe regularities in distribution characteristics in systems involving hydrogen bonding. On the basis of the determination of  $K_d$  values for two hundred organic compounds in the ethyl ether-water system, he noted that low  $K_d$  values were obtained for compounds having groups capable of hydrogen bonding, such as alcohol, amines, carboxylic acids, and acid amides [78]. Increasing the molecular weight of the organic portion of the molecule would increase the  $K_d$  value about two to four times for each additional methylene group in the homologous series. The effect to the oxygen in the molecule seemed to be about the same for alcohols, ketones, aldehydes and carboxylic acids. Increase in  $K_d$  resulting in replacing alcoholic or carboxylic hydrogen with methyl group seemed to be little more than would be expected upon the increase in molecular weight. Increase in  $K_d$  were observed with the introduction of a halogen atom.

Pasquinelli has been able to correlate the mutual solubilities of a pair of liquids with the electric and magnetic properties of the pure components [79]. The relation, that has been used to predict solubilities with probable absolute error of about  $\pm 3\%$  for 100 pairs of liquids, involves the dipole moments, dielectric constant, specific magnetic



susceptibility and molar volume. In as much as the prediction may be made for systems involving hydrogen bonding, the relation may be more generally applicable than the comparison of solubility parameters.

Solubility of metal salts in aqueous media can be explained on the basis of two special properties of water. First, its high dielectric constant permits dissociation of ionic species relatively easily. Even more important, the high basic character of water results in the solvation of cations (and anions), which gives these ions a solvent sheath serving to reduce electrostatic interaction and to make the ions more “solvent-like”. The role of the complex forming extraction agent is largely to replace the coordinated water from around the metal ion to give a species that is more likely to be soluble in organic solvents. The solubility characteristics of metal chelates in organic solvents in general terms are not at all unlike those of conventional organic compounds. For example, hydrocarbon substituents will increase the solubility of chelates in organic solvents. Although the neodymium chelate of cupferron-(I) is not soluble in chloroform where as the corresponding neocupferron (II) is soluble in chloroform.



Polar substituents will of course reduce solubility in organic solvents. The chelates of 8-quinolinol-5-sulphonic acid are not at all soluble in organic solvents but are quite soluble in water.

Among the ion association complexes, the oxonium type is noteworthy, since in most cases the solvent participates directly in complex formation. The ability of the oxonium solvent to replace water from the coordination sphere of the metal would depend upon the basicity of solvent, which in turn would reflect the electron density and steric availability of the electron pair in the oxygen of the solvent molecule. Many ion association extractions are aided by the use of salting-out agents, electrolytes used in high concentrations to;

- (a) Produce a mass action effect by adding a common ion,
- (b) Reduce water activity greatly,
- (c) Lower the dielectric constant so as to favor ion-pair formation.

The use of salting-out agents in organic extractions is also well known.

### **2.2.3 Chemical interactions in organic phase**

Chemical interactions of the extracted species in the organic phase would naturally lower its concentration in this phase and hence, improve extractability. If, in the case of a carboxylic acid extraction, the organic solvent is one in which the acid dimerizes, this would result in a higher  $D$  value than if the reaction does not occur. Ion association complexes, being dipoles, tend to form higher aggregates in organic solvents at higher concentrations. Where there is a polymerization reaction of any type, the value of  $D$  will be found to vary with the concentration of the extracted material.

## **2.3 Extraction Systems**

### **2.3.1 Types of inorganic extractable complexes**

Most salts are strong electrolytes whose solubility in water can be attributed to the high dielectric constant of water which greatly reduced the work of dissociation and

solvating tendency of water since hydrated ions experience less inter ionic attraction and resemble more closely the medium in which they are dispersed. In fact, for a metal to form an extractable complex, it is necessary to remove some or all of the water molecules associated with the metal ion.

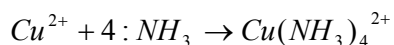
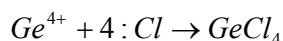
Complexing of metal ions leading to the formation of uncharged species falls into two main categories, one involving coordination and the other ion association.

### **2.3.1.1 Coordination complexes**

A coordination complex, as the term implies, is formed by coordinate bonds in which a previously unshared pair of electrons on donor atom or ion is now shared with an acceptor atom or ion [80]. Three types of coordination complexes are of interest here:

#### **2.3.1.1.1 Simple or monodentate complexes**

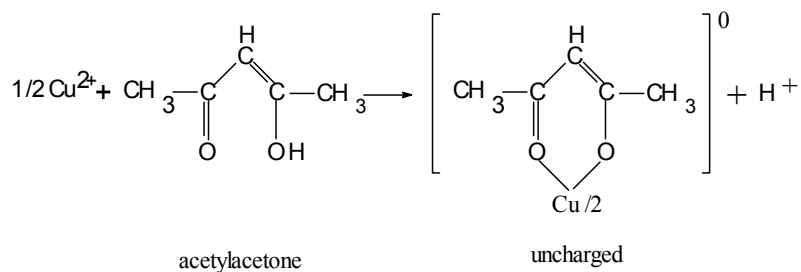
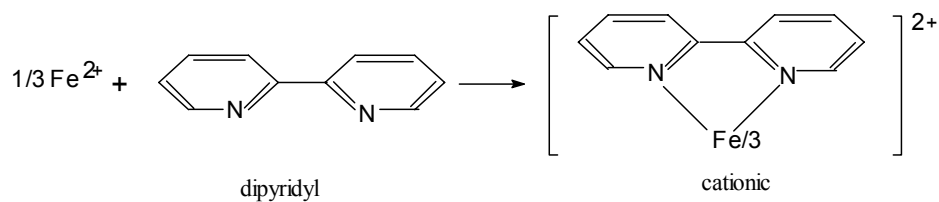
In simple or monodentate complexes, central metal ion acting as acceptor having a coordination number “n”, accepts ‘n’ pairs of electrons from ‘n’ individual donor groups, e.g.



From the above examples, only the first one give the neutral, extractable complex.

#### **2.3.1.1.2 Chelate or polydentate complexes**

Chelate or polydentate complexes [81] with the central metal atom or ion having coordination number n, combines with no more than n/2 molecules of a specie having at least two donor atoms per molecule; these being so located as to permit the formation of a relatively strain-free (i.e. , 5-6 membered) ring, e.g.



Chelates have relatively large stability constants, so their formation greatly lowers the concentration of hydrated metal ion. Those chelating agents such as acetylacetonate, cupferron, dithizone, and 8-quinolinol form uncharged, essentially covalent compounds, which are readily soluble in organic solvents. Chelating agents such as dipyrldyl or ethylene diamine tetra acid (EDTA) which form charged chelates are useful as metal masking agents.

Table-2.1 Metal Extraction Systems

**Chelate Systems**

**A. 4-Membered ring systems**

	<i>Reactive Grouping</i>
1. Dialkyl dithiocarbamates	(-) —N—C—S—
2. Xanthates	(-) —S=C—S—

**B. 5-Membered ring systems**

1. Benzoylphenylhydroxylamine	(-) —O=C—N—O—
2. Cupferron	(-) —O=N—N—O—
3. <i>o</i> -Dioximes	(-) —N=C—C=N—
4. Dithizone	(-) —N—N=C—S—
5. 8-Quinolinols	(-) —N=C—C—O—
6. Toluene-3:4-dithiol	(-)                      (-) —S—C=C—S—
7. Catechol	(-)                      (-) —O—C=C—O—

**C. 6-Membered ring systems**

1. $\beta$ -Diketones and Hydroxycarbonyls	(-) —O=C—C=C—O—
a) Acetylacetone	
b) Thenoyltrifluoroacetone	
c) Morin	
d) Quinalizarine	
2. Nitrosonaphthols	(-) —O=N—C=C—O—
3. Salicylaldoxime	(-) —N=C—C=C—O—
1. Pyridyl-azo-naphthol (PAN)	(-) —N=C—N=N—C=C—O—

### 2.3.1.2 Ion association complexes

Ion association complexes are uncharged species formed by the association of ions because of purely electrostatic attraction. The extent of such association increases sharply as the dielectric constant of the solvent decreases below 40 to 50 [82]. This condition not only exists in all of the commonly used organic solvents but also in highly concentrated aqueous solutions of strong electrolytes [83]. Ion-pairs, which preferentially dissolve in the organic phase, are those, which resemble the solvent. Ion association complexes are capable of forming clusters larger than just pairs with increasing concentration, particularly in organic solvents. In some cases, aggregates large enough to be described as micelles are encountered.

Two categories of ion association complexes may be recognized. The first includes those ion-pair formed from a reagent having large organic ion such as tetraphenylarsonium ion, tribenzylammonium ion or perfluorobutyrate ion. These reagents combine with a suitable metal-containing ion to give a large organic solvent-like ion-pair. The second type of ion-pair is essentially like that of the first with the exception that solvent molecules are directly involved in its formation. Thus in the extraction of uranyl nitrate with isobutyl alcohol, the extractable complex is probably  $\text{UO}_2(\text{BuOH})_6(\text{NO}_3)_2$  in which the coordinated solvent molecules contribute both to the size of cation and the resemblance of the complex to the solvent [84]. Most of the solvents which participate directly in the formation of ion association complexes are containing oxygen. The term oxonium complex is used here to describe such a complex, since the solvent molecules form coordinate linkages to the metal atoms through their oxygen atoms.

## Table-2.2 Ion Association Systems

- A. Metals contained in cationic number of ion-pair
  - 1. Alkylphosphoric Acids
  - 2. Carboxylic Acids
  - 3. Cationic chelates
    - a. Phenanthrolines
    - b. Polypyridyls
  - 4. Nitrate
  - 5. Trialkylphosphine oxide
- B. Metal contained in anionic number of ion-pair
  - 1. Halides ( $\text{GaCl}_4^-$ )
  - 2. Thiocyanate [ $\text{Co}(\text{CNS})_4^{2-}$ ]
  - 3. Oxyanions ( $\text{MnO}_4^-$ )
  - 4. Anionic Chelates [ $\text{Co}(\text{Nitroso R salt})_3^3$ ]

In view of the important role played by complex formation in inorganic extraction systems, it is appropriate to classify these systems in terms of the type of complex formed [85]. Two broad categories are utilized in Table 2.1 and 2.2.

Chelate extraction systems include only those involving neutral chelates, since charged chelates must pair with oppositely charged ions to form extractable species. It will be noted that the chelate systems are ordered with respect to the size of the chelate ring.

Differentiation of ion association extraction systems is based on the sign of the charge of the metal-containing ion. In those systems in which the metal is part of the

anion, a further classification on the basis of the nature of the cation is helpful. These cations are usually varieties of “onium” ions such as oxonium, ammonium, arsonium, etc., as mentioned in the Table 2.1.

Organic extractions may be classified in a manner similar to that utilized for metal extractions that is on the basis of chemical interactions. However, aside from conventional acid-base reactions which permit control of the extraction via pH, the utilization of chemical reactions in organic extractions are not frequently encountered. In view of the vast number of organic compounds and biological material that extract, a simple method of classification of organic extractions based on the class of compounds to which a particular solute belongs is often used [86, 87] and any general organic text may be consulted for these classes.

## **2.4 Extraction Equilibria**

A consideration of the extraction equilibria from a quantitative standpoint is helpful in pointing out which experimental parameters play an important role in the completeness as well as the selectivity of the extraction.

Apart from the utility in predicting the course of extractions, such a quantitative treatment opens the way for understanding the applicability of extractable substance. Treatment of the extraction equilibria is illustrated below. Although a chelate extraction was chosen to represent the inorganic type, the same general approach may be used for ion association extractions [88].

### **2.4.1 Extraction of metal chelates**

The equation describing the extraction of metal chelates may be derived by considering the reactions occurring when an aqueous phase containing a metal ion is contacted with an organic phase containing a chelate extractant. The steps leading to the



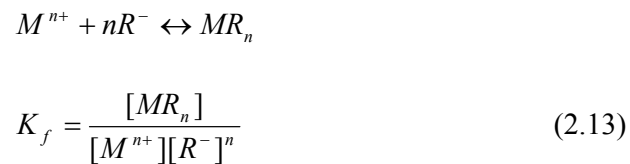
extraction may be conveniently visualized as follows. The chelating agent distributes between the two phases. Since the majority of chelating extractants exhibit an acid dissociation, the symbol  $HR$  will serve as a general formula for the reagent.



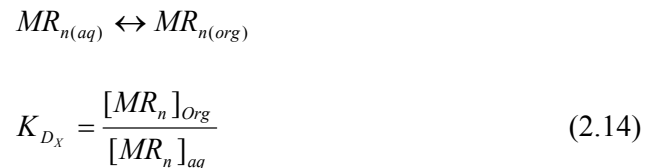
The reagent will dissociate in the aqueous phase



To give a chelating anion  $R^-$ , which reacts with the metal ion and forms the extractable chelate



Which, in turn distributes between the phases



The distribution ratio “ $D$ ” can be evaluated from these equilibrium expressions if the metal chelate  $MR_n$ , may be assumed to be the only metal-containing species in the organic

phase and the metal ion,  $M^+$ , essentially the only metal-containing species in the aqueous phase. Thus

$$D \equiv \frac{[M]_{Org}}{[M]_{Aq}} = \frac{[MR_n]_{Org}}{[M^{n+}]_{Aq}} = \frac{K_f K_a^n K_{D_x}}{K_{D_r}^n} \frac{[HR]_{Org}^n}{[H^+]_{Aq}^n} \quad (2.15)$$

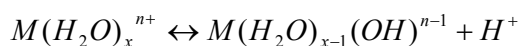
The validity of this equation was first verified by Kolthoff and Sandell [89] for dithizone extractions and later by Furman *et al.* for cupferron extraction [90], extends to many chelate extraction systems.

### 2.4.1.1 Effect of the reagent

Eq. (2.15) clearly indicates the importance of chelate stability ( $K_f$ ) and the relative solubility of the chelate in the organic phase ( $K_{D_x}$ ). It is also seen, that an acidic reagent having high  $K_a$  and relatively good solubility in water favours good extraction. Since chelate stability increases as reagent acidity decreases, these effects must be considered together [91]. Thus, if  $K_a$  values of a family of reagents increase faster than do the corresponding  $K_f$  values, the  $K_f K_a$  value would be larger for the reagent forming less stable chelates. This seems to be the case in the  $\beta$ -diketones, with TTA possessing this type of advantage over acetylacetone.

### 2.4.1.2 Effect of reagent concentration and pH

It may be noted from equation (2.15) that the extractability of a metal with a given reagent and organic solvent depends equally upon the organic phase concentration of the reagent and upon the hydrogen ion concentration in the aqueous phase. A tenfold increase in the reagent concentration will increase  $D$  as much as would a rise of one unit in pH. In case, where metal hydrolysis is significant, i.e., where the reaction



is important, the assumption made in the derivation of equation (2.15) that the only metal-containing species in the aqueous phase is  $M^{n+}$  must be modified to include the hydrolysis products. This results in an expression for  $D$  in which the average value of the exponent, and hence the importance of the hydrogen ion concentration decreases, while the reagent concentration factor remains unchanged [92].

In early extraction work, the reagent concentrations employed were little more than needed to form the metal chelate [93]. An increase in the pH range of good extraction was achieved by using somewhat higher reagent concentrations [94], with employment of very high reagent concentrations a substantial reduction in the pH of extraction can be achieved, permitting extraction from highly acidic solutions [95]. An advantage in using high reagent concentrations that is not evident from Eq. (2.15) arises when the metal involved commonly forms a hydrated, non-extractable chelate, which with high reagent concentrations is transformed to one in which the coordinated water molecules are replaced by those of the reagent [96].

### **2.4.1.3 Effect of metal ion concentration**

As indicated by the absence of any metal ion concentration term in Eq.(2.15), the distribution ratio is independent of initial metal concentration. Thus, both tracer and macro amounts of metal may be expected to extract to the same extent under similar equilibrium conditions, provided that the solubility of the chelate in the organic phase is not exceeded.

### **2.4.1.4 Effect of the organic solvent**

Quite a variety of organic solvents have been employed in metal chelate extractions and by and large, the nature of the solvent has not been too critical factor in determining the success of an extraction. The choice of benzene or chloroform for example, seems to be dictated more by the desire to have the organic extract lighter or

heavier than the aqueous phase than by the relative extraction efficiency of the solvents. However, a closer examination reveals differences, which, may be put to practical use. As may be seen from Eq. (2.15), the solvent affects two quantities, the distribution coefficients of the reagent and of the chelate. A change in solvent would bring about the following relative change in the value of  $D$ :

$$\frac{D^*}{D} = \frac{K_{D_X} \cdot K_{D_R}^{*n}}{K_{D_X}^* \cdot K_{D_R}^n} \quad (2.16)$$

If it is assumed that the change in  $K_d$  value for a reagent and chelate are about the same, then Eq. (2.16) predicts that a change to a solvent in which the reagent is more soluble will result in lower “ $D$ ” values for polyvalent metals ( $n > 1$ ). An interesting confirmation of this may be found in the comparison of the use of carbon tetrachloride and chloroform for dithizone extractions. Dithizone and its chelates are more soluble in chloroform than in carbon tetrachloride and extractions with the former solvent require a higher pH region than when the latter is used [97].

### 2.4.1.5 Selectivity in chelate extractions

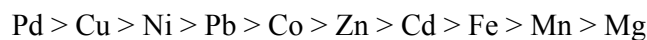
The separation of two metals with a particular reagent-solvent system may be evaluated with Eq. (2.15). The separation factor “ $\gamma$ ” defined as the ratio of  $D$  values of the metals in question, is seen to be

$$\gamma = \frac{D_1}{D_2} = \frac{K_{f_1} \cdot K_{D_{X_1}}}{K_{f_2} \cdot K_{D_{X_2}}} \quad (17)$$

The ease of separation of two metals is seen to be depending not only on the difference in the stability of their chelates but also on the relative solubility of these chelates in the organic solvent. A sufficiently great difference in solubility may result in an extraction sequence that differs from the stability sequence. For instance, although

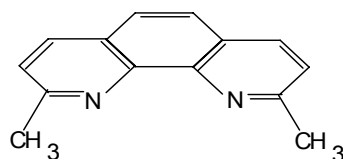
nickel-II and cobalt-II form more stable acetylacetonates than does zinc II [98], the latter is extractable whereas the former two are not [95].

With regard to chelate stability, the order of stability of a number of metal ions has been shown to be fairly independent of the nature of the chelating reagent employed. Mellor and Maley [99] list the following stability sequence for bivalent metal ions:



Despite the adherence of the behavior of many reagents to the “natural stability sequence for metals” a number of interesting exceptions are noteworthy. One such example involves the exceptionally high stability of the tris-phenanthroline-iron-II complex [100,101]. The fact that, this complex is more stable than of the corresponding nickel or cobalt chelats has been attributed to resonance stabilization.

Steric hindrance in a chelating agent can result increased selectivity. For example, 2,9-dimethylphenanthroline (neocuproine) (1)



(1)

no longer gives the typical phenanthroline like complex with iron-II since the methyl groups greatly hinder the attachment of three reagent molecules around the iron-II ion. This hindrance is minimum in the tetrahedral geometry of two reagent molecules about a univalent tetracoordinated ion such as copper. Steric hindrance of the 2-methyl groups to chelate formation is the reason for the non-reactivity of 2-methyl-8-quinolinol with the small aluminium ion [102]. This reagent offers a distinct advantage over 8-quinolinol in the determination of many metals in the presence of aluminium [103]. It is also possible

that reagents containing the mercapto functionality may exhibit a different metal stability sequence than do those containing oxygen [104].

A more generally applicable approach to increasing selectivity in chelate extractions than that of depending on “unusual” reagents may be based on the use of competing complexing agents, called masking agents. These masking agents, illustrated by cyanide ion or EDTA, form water-soluble complexes with some metals and thus alter the extraction characteristics of these metals. The use of two competing reagents will tend, in favorable cases, to exaggerate even small differences in the stability order to the point where dramatic changes may be observed. For example, copper-II gives more stable chelates with both 8-quinolinol and EDTA than does uranyl ion and hence in the presence of EDTA only uranyl ion may be extracted with 8-quinolinol [105].

## **2.5 Kinetic Factors in Extraction**

The previous discussion has been based on the assumption that the system had achieved equilibrium. Although, in most cases, optimum extraction is obtained under equilibrium conditions, occasionally the slow extraction rate of one or more components may serve to improve selectivity. The rate of extraction depends on factors affecting (a) the rate of formation of the extraction species and (b) the rate of transfer of the extractable species.

As expected the rate of formation of ion association complexes which involve essentially electrostatic forces is very rapid. Formation of metal chelates on the other hand may sometimes take place at measurable rates. Slow extraction has been observed with some of the chelates of dithizone [106] and thenoyltrifluoroacetone (HTTA) [107]. The presence of EDTA has been found to reduce the rate of extraction in a number of instances [105,108]. In cases where the formation of metal chelate is the rate-determining step, the extraction may be speeded by increasing the concentration of the reagent [109].

The rate of transfer of the extractable species from one phase to the other is relatively rapid when reasonable agitation is employed. Barry *et al.* have shown that simple repeated inversion of the two phases is sufficient to give equilibrium in a relatively short time even if the species concerned possessed a relatively high molecular weight [110]. Unless the liquids are viscous, it may be expected that transfer rates are sufficiently high to permit equilibration with a shaking time of several minutes.

## **2.6 Methods of Extraction**

Three basic methods of liquid-liquid extraction are generally utilized in the analytical laboratory. Batch extraction, the simplest and mostly used method, consists of extracting the solute from one immiscible layer by shaking the two layers until equilibrium is attained, after which the layers are allowed to settle before sampling. The second type, continuous extraction, makes use of a continuous flow of immiscible solvent through the solution or a continuous countercurrent flow of both phases. In the former case the spent solvent may be stripped and recycled by distillation or fresh solvent may be added continuously from a reservoir. Extraction by discontinuous countercurrent distribution is the third general type and is used primarily for fractionation purposes. A series of separatory funnels or contacting vessels are employed to achieve many individual extractions rapidly and in sequence. The choice of method to be employed will depend primarily upon the value of the distribution ratio of the solute of interest, as well as on the separation factors of the interfering materials.

The basic principles in designing an extraction for laboratory use are relatively simple and just a few basic types of apparatus are more than adequate for most needs. An infinite number of modifications of these basic designs, however, have resulted from the chemist's desire to improve a particular apparatus for the specific problem.

## 2.6.1 Batch extraction

The simplest extraction procedure possible and the technique most employed in the laboratory for analytical separations involves the bringing of a given volume of solution into contact with a given volume of solvent until equilibrium has been attained, followed by separation of the liquid layers. If necessary, the procedure may be repeated after the addition of fresh solvent. This batch extraction process provides rapid, simple, and clean separations, and is more beneficial when the distribution ratio of the solute of interest is large. In such instances, a few extractions will effect quantitative separation. Various methods for increasing the distribution ratio as well as the selectivity of an extraction are discussed later.

The most commonly employed apparatus for performing a batch extraction is a separatory funnel, since it is a relatively simple matter to add and withdraw the respective liquid phases. When extracting from a heavier liquid to a lighter solvent, it is necessary to remove the lower phase from the funnel after each extraction before removing the extracting solvent as in the case of ethyl ether extractions from aqueous solutions.

When performing a batch extraction, it is important to follow a few simple steps to separate the phases for sampling for subsequent processing or estimation. Most batch extractors are separatory funnels taper off into a narrow bottom with a sealed stopcock. Thus, it is a relatively easy task to separate the two phases on withdrawal for further processing. It is, of course, essential to wait until the phases have completely settled after agitation. Usually this will occur in a matter of minutes.

If only aliquots of the phases are to be used, it is necessary to notice any volume changes of the phases due to mutual solubility of the solvents. The extraction and sampling must be performed at a constant temperature, since both the distribution ratio and the volumes of the solvents are influenced by temperature changes. A useful method



of withdrawing the phases for sampling involves the use of three graduates. Most of the heavier phase is withdrawn into the first graduate and then the remainder of the heavier phase and a little of the lighter phase are withdrawn into the second graduate. The remaining portion of the lighter phase is run into the third graduate, and the volumes of the three are noted. The second graduate can now be discarded and aliquots of the other two taken without danger of contamination of one by the other.

If droplets of aqueous phase are entrained in the organic extract, it is possible to remove them by filtering the extract through a dry filter paper. The aqueous droplets will be absorbed by the paper, which should be washed several times with fresh organic solvent. Another method commonly used in extractions is the addition of a drying agent, such as sodium sulphate, to the organic extract. Perhaps, the simplest technique for removal of slight traces of the aqueous phase which may contain certain impurities is the use of the backwash technique, described later.

## **2.6.2 Continuous extraction**

Continuous extractions are particularly applicable when the distribution ratio is relatively small, so that a large number of batch extractions would normally be necessary for quantitative separation. Most continuous extraction devices operate on the same general principle, which consists of distilling the extracting solvent from a boiler flask and condensing it and passing it continuously through the solution being extracted. The extracting liquid separates out and flows back into the receiving flask, where it is again evaporated and recycled while the extracted solute remains in the receiving flask. When the solvent cannot easily be distilled, a continuous supply of fresh solvent may be added from a reservoir.

High efficiency in continuous extraction depends on the viscosity of the phases and other factors affecting the rate of attaining equilibrium, the value of the distribution

ratio and the relative volumes of the two phases and other factors. One practical method of improving the efficiency is to ensure as high an area of contact as possible between the two liquids. As the extracting solvent passes through the solution, fritted-glass discs, small orifices, baffles and stirrers may be used to bring the two immiscible layers in closer contact.

### **2.6.3 Countercurrent extractions**

The separation through continuous countercurrent method is achieved by virtue of the density difference between the fluids in contact. In vertical columns, the more dense phase enters at the top and flows downwards while the less dense phase enters at the bottom and flows upwards. Only one of the phases can be pumped through the column at any desired flow rate, the maximum rate of the second will be limited by that of the former and the physical properties of both. The method has the advantage for separating materials for purification purposes and is extensively used in engineering problems.

## **2.7 Factors Influencing the Extraction Efficiency**

Primary requirement of solvent extraction for separation /removal purposes is a high distribution ratio of the solute of interest between the two liquid phases. Though, continuous and countercurrent distribution techniques may be used for the cases where low distribution ratios are present, it is generally desirable to attain as high a value as possible for the development of simple analytical procedures. It is useful to employ a number of different techniques for enhancing the distribution ratio. These depend on the nature of the species being extracted and extraction system.

The attainment of selectivity in an extraction procedure is also very important. Some of the factors, which affect the distribution of solute of interest are given below.

### **2.7.1 Choice of solvent**

Use of a suitable solvent for effective separation is very important. Metal chelates and many organic molecules, being essentially covalent compounds do not impose many restrictions on the solvent and the general rules of solubility are of great use. In ion association systems and particularly in oxonium type ions, the role of solvents is very important. This is due to involvement of solvent in the formation of extractable species.

In addition to the consideration of the distribution of the solute in a particular solvent system, the ease of recovery of the solute from the solvent is important for subsequent analytical processing. Thus, the boiling point of the solvent or the ease of stripping by chemical reagents is considered in the selection of a solvent where the choice exists. Similarly, the degree of miscibility of the two phases, the relative specific gravities, viscosity and tendency to form emulsions should be considered. With regard to safety, the toxicity and flammability of the organic solvents must be considered.

Some times it is possible to achieve the desired characteristics of a solvent by employing a mixed-solvent system. An example of this is the use of mixtures of alcohols and ethers for the extraction of the thiocyanate complexes of metals. Another method of varying the properties of the extracting solvent is to use organic diluents. Various organic compounds such as kerosene and other hydrocarbons are employed to dilute tributyl phosphate for extraction purposes.

### **2.7.2 Acidity of the aqueous phase**

The extractability of metal complexes is greatly influenced by the acidity of the aqueous phase, so it is necessary to assure optimum concentration of  $H^+$  ions for maximum extraction.

In case of chelate extraction, it can be seen from Eq.(2.15) that provided the chelating reagent concentration is maintained constant, the distribution of the metal in a

given system is a function of pH. For this reason, curves of extractability versus pH at constant reagent concentration are of great analytical significance.

Acidity greatly affects many of the oxonium type of extraction systems, particularly when the metal is extracted as a complex acid. In many of the extractions involving metal halide complexes, e.g., the distribution increases within certain limits with increasing acid concentration. Thus, maximum extraction of iron as the chloride is observed at 6M hydrochloric acid using ethyl ether as the solvent [111]. A decrease in extraction at higher acid concentrations has been attributed to the high solubility of ethyl ether in highly concentrated hydrochloric acid and extraction does not occur until there is a much higher acid concentration with the less soluble isopropyl ether. No decrease is observed even at 12 M hydrochloric acid when  $\beta$ :  $\beta'$  - dichloroethyl ether is used [112]. The addition of high concentrations of acid also enhances the distribution of metal complexes as a result of the common ion effect resulting from the anion of the acid.

As the removal of the acidic or basic solute will tend to change the pH value, even more important in multiple extractions (countercurrent distribution), the use of buffer mixture in the aqueous phase aids in the attainment of reproducible constant distribution ratios. Buffers should be chosen which do not interfere in the subsequent analysis [113].

### **2.7.3 Salting-out agents**

A technique that has resulted in marked enhancement of extraction of metals, particularly in the oxonium type of extraction systems, is the use of salting-out agents. The addition of high concentrations of inorganic salts to the aqueous phase greatly increases the distribution ratio of many metal complexes to the organic phase. This salting-out effect may be explained in part by the pronounced effect of the added salt on the activity of the distributing species, the common ion effect, as well as the strong ability of these ions to bind water around them, thereby depleting the aqueous phase of water

molecules for use as a solvent. High concentrations of inorganic salts are usually required to produce the desired effect, the aqueous phase often being saturated with the added salt. It is essential that the added salt is not extracted to an appreciable extent with the desired species in order to maintain the optimum effect and to permit direct use of the organic extract without further separation. Sometimes the aqueous phase after extraction may be of interest so that the presence of large amounts of added cations prevent further use of this phase in the subsequent analytical steps unless the added salt can be easily removed or destroyed, like ammonium salts.

In addition to enhancement of the extraction of the metal of interest using salting-out agents, it is also possible to increase the extraction of impurities in the system. Thus, it is necessary to choose an agent that produces a favorable separation factor between the element of interest and the impurities. The magnitude of enhancement of extraction by the added salt depends on the charge as well as the ionic size of the added cation for a given anion. Thus, polyvalent cations provide better salting-out agents, and for a given charge, the smaller the cationic size, the greater the effect on extraction. However, it must be remembered that anomalies sometimes result from specific interaction effects. Aluminum or calcium salts are strong salting-out agents, whereas ammonium salts are much weaker but analytically more convenient.

Among the metal extraction systems that have benefitted through the use of salting-out agents are the nitrate, halide, and thiocyanate systems. Other oxonium extraction systems should be investigated so that useful analytical separations may result where now only limited extractability of a substance occurs.

#### **2.7.4 Oxidation state**

A useful method of increasing the selectivity of metal extractions involves modification of the oxidation states of the interfering ions present in solution, in order to

prevent the formation of their extractable metal complexes. For example, the extraction of iron from chloride solutions can be prevented by reduction to iron-II, which is not extractable. Similarly, antimony-V may be reduced to the trivalent state to suppress its extraction. Conversely, it is important in the preparation of a solution for extraction to adjust the proper valence state of metal ion required for formation of the complex in order to insure complete extraction of that element. Selectivity can also be achieved by variation of the oxidation state of the co-extracted interfering ions during the stripping operation.

### **2.7.5 pH**

The attainment of selectivity in metal chelate extractions is greatly dependent upon proper pH control. As has been mentioned earlier, the distribution of chelates in a given system is a function of pH alone, provided the reagent concentration is maintained constant. Increased selectivity can be achieved in the extraction of acidic or basic organic substances by the addition of buffer salts to the aqueous phase to control the pH [113].

### **2.7.6 Masking**

In the extraction procedures for metal pairs that are difficult to separate, masking or sequestering agents are introduced to improve the separation factor. The masking agent forms water-soluble complexes with the metals in competition with the extracting agent. Masking agents form sufficiently strong complexes with interfering metals to prevent their reactions with the extraction agents, either altogether or at least until the pH is much higher than the value needed for quantitative extraction of the metal of interest. Very often the metal of interest also forms a complex with masking agent, with the result that a somewhat higher pH range is needed for the extraction. The application of masking agents, which include cyanide, tartarate, citrate, fluoride, and EDTA, is restricted largely to metal chelate extraction systems, since in the highly acidic solutions encountered in

many inorganic extraction systems most masking agents, being weak bases, do not function effectively. Ethylenediaminetetraacetic acid, which is proving a most useful masking agent, has been applied to dithizone, 8-quinolinol, carboxylic acids, acetyl acetone, and diethyldithiocarbamate extractions.

### **2.7.7 Backwashing**

An auxiliary technique used with batch extractions to effect quantitative separations of elements is backwashing. The combined organic phases from several extractions of the original aqueous phase contain practically all the desired elements and possibly some of the impurities that have been extracted to a much smaller extent. This combined organic phase when shaken with one or more small portions of a fresh aqueous phase containing the optimum reagent /salting agent concentration, acidity, etc., will result in a redistribution of the impurities in favour of the aqueous phase since their distribution ratios are low. Under optimum conditions, most of the elements of interest will remain in the organic layer, since their distribution ratio is high. This technique is analogous in many respects to the re-precipitation step in a gravimetric precipitation procedure. With the proper conditions, most of the impurities can be removed by this backwashing operation, with negligible loss of the main component, thereby attaining a selective separation.

## **2.8 Synergic Extraction**

Synergism is defined as the combined action of two complexing reagents, which is greater than the sum of the actions of the individual reagents used alone. A typical example of the synergic extraction of Ce(III) with picrolonic acid (HPA) and benzo-15-crown-5 (B15C5) system [114] is shown in Fig. 1, which reveals that no extraction was

observed by the B15C5 while little extraction with HPA was observed but quantitative extraction exhibits with the mixture.

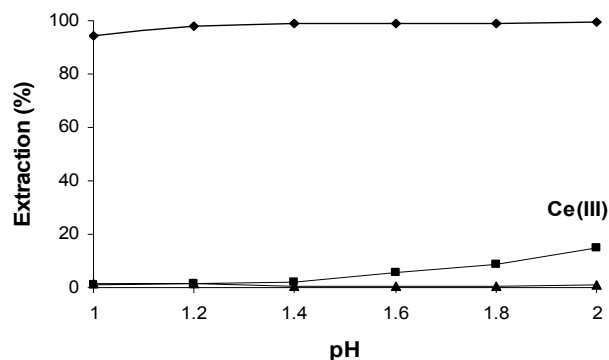


Fig. 1 Extraction of Ce(III) B15C5(▲), HPA (■) and HPA+B15C5(◆)

In general, the enhancement of the extraction may be attributed to either thermodynamical changes in the activities of the extractants or the composition of the metal-bearing species in the organic phase, which is not the same as in the cases of individual extractant systems. Synergic systems are usually mixture of cation exchange extractant and coordination extractant and the synergistic effect is thought to operate by an enhancement of the ease with which the coordination sphere of the metal ion can be satisfied.

Two methods of accomplishing this have been proposed. In the first, the synergist, “S” replaces coordinated water in an extracted metal complex, thus making the resulting complex more organophilic. In the second, the original extractable complex is coordinately unsaturated and the synergist “S” adds to the complex, thereby enhancing its stability.

Synergism was first reported in the literature for the extraction of uranium (VI) with various dialkylphosphoric acid and neutral phosphorus alkylesters [115]. Now the synergism appears to be a common phenomenon in many mixed extractant systems. In



addition to organophosphorus compounds, heterocyclic bases, sulfoxides, carboxylic acids, phenols and amines are also common synergists. The synergistic effect is extremely useful in solvent extraction practices and has been used for the extraction of various alkali and alkaline earth metals [116-119], transition metals [120-123] and rare earths [124-129] using different combinations of reagents.

### **2.8.1 Methods used for the study of synergistic extraction**

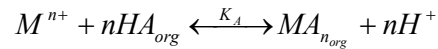
The study of the nature of species formed and the equilibrium constants involved with the synergistic extraction of metal ions have mostly been evaluated by the slope analysis method [52]. This method basically deals with the determination of distribution coefficient values ( $K_d$ ) of the metal ions by varying one of the parameters i.e., pH, concentration of one extractant (chelating agent) or the other (neutral donor), while keeping the other parameters constant. Sekine and Dyrssen [130] have used a curve fitting method for the calculation of synergistic equilibrium constants of different metal ions. Taketatsu *et. al.*, [131,132] have evaluated the equilibrium constant values of the rare earths using HTTA – TOPO system in the presence of different anions by a spectrophotometric method. Desreux *et.al.*, [133] have calculated the stability constants of the adduct formed between  $\text{Eu}(\text{TTA})_3$  and 4-methyl-2-pentanone, TPPO, or 2-methylpyridine from the analysis of the concentration dependence on the induced shift yields by a proton nuclear magnetic resonance study. Due to the simplicity of the “slope analysis method” it has been widely used to get a clear picture of the stoichiometry and extraction constant of adducts formed in the synergistic extraction of metal ion, while the other methods mentioned above have been used only rarely.

### 2.8.1.1 Slope analysis method

Slope analysis method is applied to determine the number of ligand molecules in simple extraction using single extractant as well as in synergistic extraction where a neutral donor is also added to the extraction system.

#### 2.8.1.1.1 Extraction with acidic ligand

As an example we can consider the equilibria of a metal ion,  $M^{n+}$  with chelating agent (e.g. HA), the extraction of  $M^{n+}$  by HA alone can be represented by the following reaction.



for which the equilibrium constant  $K_A$  is

$$K_A = \frac{[MA_n]_{org} [H^+]^n}{[M^{+n}] [HA]_{org}^n} \quad (2.18)$$

$$\frac{[MA_n]_{org}}{[M^{+n}]} = D_A$$

$$K_A = D_A \frac{[H^+]^n}{[HA]_{org}^n} \quad (2.19)$$

or

$$D_A = K_A \frac{[HA]_{org}^n}{[H^+]^n} \quad (2.20)$$

$$\log K_A = \log D_A + \log [H^+]^n - \log [HA]_{org}^n \quad (2.21)$$

$$= \log D_A + n \log [H^+] - n \log [HA]_{org}$$

$$pH = - \log [H^+]$$

$$= \log D_A - npH - n \log[HA]_{org} \quad (2.22)$$

$$\log D_A = \log K_A + npH + n \log[HA]_{org} \quad (2.23)$$

At constant concentration of HA, this equation represents the equation of a line. If  $\log D_A$  is plotted against  $pH$ , the plot will give a straight line of intercept of this line. At constant  $pH$ , the plot of  $\log D_A$  vs  $\log [HA]$  will give a straight line, having slope equal to total number of HA molecules participating in the complex formation.

### 2.8.1.1.2 Synergistic Extraction

As an example we can consider the equilibria of a metal ion,  $M^{n+}$  with chelating agent (e.g. HA) and a neutral oxo-donor, S (TBP, TOPO, TPPO and DOSO etc.).

Considering the synergistic extraction



Where  $m=1$  or  $2$  and  $K_{syn_n}$  is the mixed equilibrium constant.

It can be shown that

$$D_{syn_1} = K_{syn_1} \frac{[HA]_{org}^n [S]_{org}^2}{[H]_{aq}^n} \quad (2.25)$$

$$D_{syn_2} = K_{syn_2} \frac{[HA]_{org}^n [S]_{org}^2}{[H^+]_{aq}^n} \quad (2.26)$$

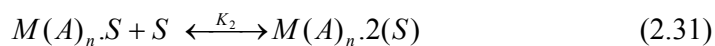
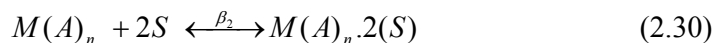
The equilibrium constants of such reactions refer only to concentration quotients whose calculations are based on the assumption that the activity coefficient of the species involved do not change significantly under the experimental conditions applied. If it is assumed that  $M(A)_n \cdot 2S$  are the only synergistic species present in the organic phase, the overall distribution coefficient  $D$  is given by

$$D = D_A + D_{syn_1} + D_{syn_2} \quad (2.27)$$

It can be shown by Eqs.2.20, 2.25, 2.26 and 2.27) that

$$\frac{D - D_A}{[S]_{org}} = K_{syn1} \frac{[HA]_{org}^n}{[H^+]_{aq}^n} + K_{syn2} \frac{[HA]_{org}^n}{[H^+]_{aq}^n} [S]_{org} \quad (2.28)$$

It is clear from Eq. (2.28) that if  $[HA]_{org}$  and  $[H^+]_{aq}$  are maintained constant, plot of  $(D - D_A)/[S]_{org}$  vs  $[S]_{org}$  would be straight line with intercept and slope equal to  $K_{syn1} \cdot ([HA]_{org}^n / [H^+]_{aq}^n)$  and  $K_{syn2} \cdot ([HA]_{org}^n / [H^+]_{aq}^n)$  respectively. The organic phase equilibrium constants  $\beta_1, \beta_2$  and  $K_2$  of the synergistic reactions



can be easily obtained from the slope and intercept mentioned above. Further details of these calculations can be seen from references [134] and [135].

In earlier publications [136,137,138,139,140] on the synergistic extraction of metal ions (trivalent lanthanides), several authors have reported the formation of only  $M(A)_3 \cdot (S)_2$  type species in the organic phase. The conclusions have been drawn from the observed second power dependence of the neutral donor ( $S$ ) in the plots of  $\log D$  vs  $\log [S]_{org}$  (keeping other parameters constant). With the knowledge of the stepwise formation of all the complex species, the above supposition would be highly misleading. However, in most of the publications of seventies and later, the formation of the stepwise first and second synergistic species have been reported.

### 2.8.1.2 Job's Method

Job's method or method of continuous variation is also applied to determine the composition of extracted species in synergistic extraction system [62]. In this method,

overall concentration of both the ligands used in the synergistic extraction is maintained constant (e.g.,  $0.01 \text{ mol dm}^{-3}$ ) while changing concentration of both the ligands.  $\log D$  is plotted vs. mol fraction of the ligands. Number of ligands of both the extractants is determined from the mol fraction of the ligands where maximum extraction is achieved.