

## CHAPTER II

### THEORY

#### Solvent Extraction.

Solvent extraction is one of the favored separation techniques because of its ease, simplicity, speed and wide scope, requiring several minutes at the most to perform and applicable to trace and macro levels of metals. The utilizing apparatus in addition is no more complicated than a separatory funnel. Batch extraction is one of the three basic types of solvent extraction and it is the simplest type among the three of them. The other two types are the continuous and discontinuous countercurrent distribution extraction. Chelate extraction system, which is one of the two systems of batch extraction, is a system that some of or all of the water molecules coordinated to the metal ions must be removed by replacing them with chelating agents to form neutral chelate compounds, this process is called the chelate extraction system, that can dissolve into an organic solvent. Such a chelate compound may be formed by metal-containing ions through coordination, involving chemical rather than physical bond.

#### 1. Fundamental Extraction Parameters.

1.1 Distribution Law. This law states that a solute will distribute between two essentially immiscible solvents in such a manner that, at equilibrium, the ratio of the concentration of the

solute in the two phases at a particular temperature will be a constant, provided that the solute has the same molecular weight in each phase. For the distribution of species M between solvent 1, aqueous phase, and solvent 2, organic phase.

$$\begin{aligned} K_D &= \{ M \}_2 / \{ M \}_1 \\ &= \gamma_2 [M]_2 / \gamma_1 [M]_1 \end{aligned} \quad (2.1)$$

where  $K_D$  is the distribution coefficient or partition coefficient which is a thermodynamic function.

$\gamma$  is the activity coefficient.

Brace is the activity and square bracket is concentration.

$K_D$  can be seen to result from variations in the activity coefficients in each of the phase. Often, activity coefficients are neither known nor easily measured. In practice, the distribution law, eq. 2.1, is normally useful only for simple systems at low analyte concentrations when the activity coefficient approach unity. Thus, the value of  $K_D$  becomes constant.

1.2 Distribution Ratio. Of much greater significance, because their effect on the distribution are the chemical interactions of the distribution species with the other components in each phase, since these interactions can profoundly affect the concentration of the distributing species, which are the form or forms of the analyte species in the aqueous and organic phase. The distribution ratio or extraction coefficient, which is the stoichiometric ratio including all species of the same component in the respective phase, is a tool for describing the extraction and is more useful than the partition coefficient.

Distribution ratio,  $D$ , is defined by the following expression :

$$D = \frac{\text{Total analyte concentration in the organic phase}}{\text{Total analyte concentration in the aqueous phase}} \quad (2.2)$$

1.3 Percentage Extraction. If the distribution ratio is known, it is relatively simple matter to calculate the fraction of the analyte species in both of the solvent phases. The fraction of the analyte species extracted from an aqueous to an organic phase is known as the degree of extraction, or recovery. Recovery is sometimes expressed as a percentage, although in this instance it is best known as the percentage extraction.

If the masses and analyte species in the aqueous and organic phases are  $M_A$  and  $M_O$ , respectively, and the volumes of two phases are  $V_A$  and  $V_O$ , respectively, then the percentage extraction,  $E$ , and distribution ratio,  $D$ , are given by the expressions

$$E = 100 M_O / (M_O + M_A) \quad (2.3)$$

$$D = \frac{M_O / V_O}{M_A / V_A} = \frac{M_O V_A}{M_A V_O} \quad (2.4)$$

Equation 2.4 may be rearranged to give an expression for  $M_O$  in terms of  $M_A$ ,  $V_O$ ,  $V_A$  and  $D$ . Substitution of this expression for  $M_O$  in eq. 2.3 and subsequent rearrangement leads to the equation

$$E = \frac{100 D}{D + (V_A/V_O)} \quad (2.5)$$

At any given distribution ratio value, the percentage extraction depends upon the extraction ratio,  $V_A/V_O$ . Fig. 2.1 shows the variation in percentage extraction with the distribution ratio for

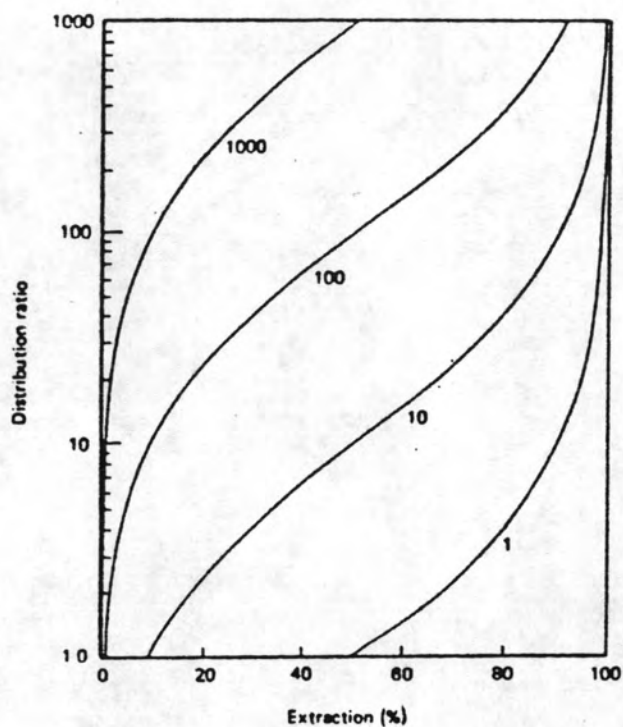


Fig 2.1 Relationship between percent extraction and distribution ratio.

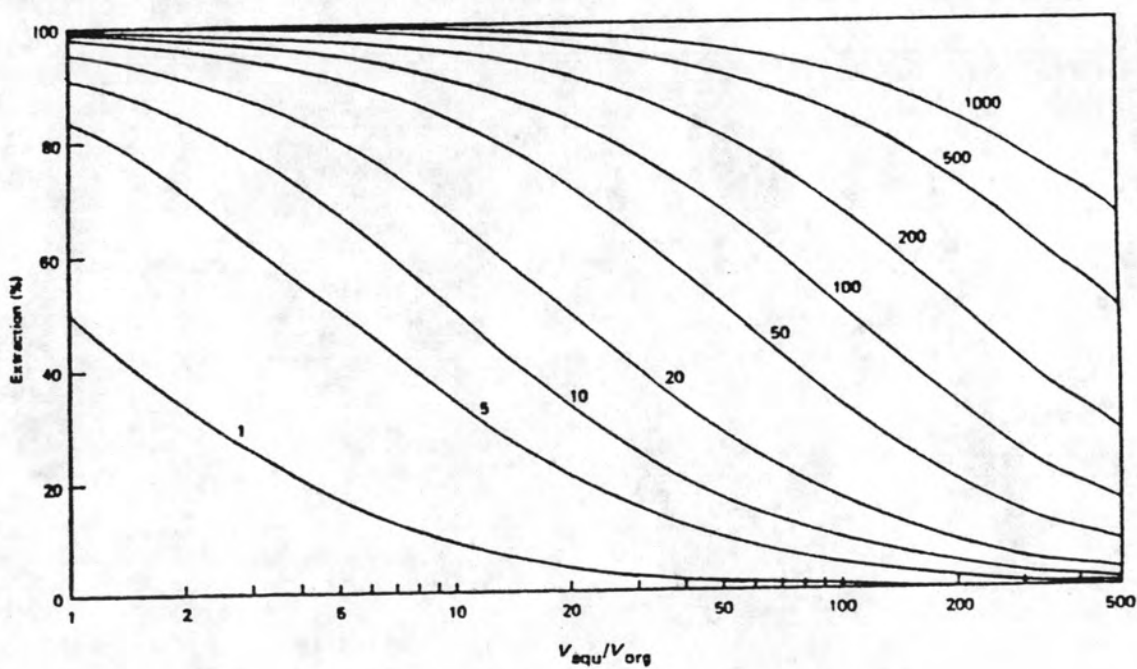


Fig 2.2 Relationship between percent extraction and extraction ratio.

various value of extraction ratio or in the other meaning it graphically portrays the interconversion of distribution ratio and percentage extraction, %E, at a unit volume ratio. When the extraction efficiency approaches 100%, the distribution ratio approaches infinity as a limit. Thus, for differences in extraction in the range 99 to 100%, the distribution ratio will vary from 99 to infinity.

The variation in percentage extraction with extraction ratio for various values of distribution ratio is showed in Fig. 2.2. These figures demonstrate the merit of studying percentage extraction rather than the distribution ratio in solvent extraction. It is important to note that extraction ratio must always be given as well if percentage extraction is to be used as a criterion for assessing the suitability of an extraction system. Whereas distribution ratio remains relatively constant, percentage extraction shows marked variation with extraction ratio.

## 2. Extraction Process.

Although detail of the specific nature of the interactions obviously must differ from one metal extraction system to another, a helpful organizational pattern may be adopted, based on three steps, common to every metal extraction process. The three steps are then expressed as

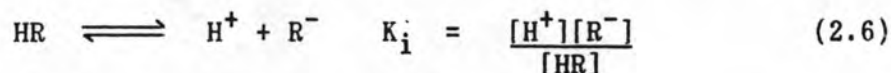
(1) The interaction of the compound in the aqueous phase. This step involves reaction of the metal in the aqueous phase, with chelating agent, leading to the formation of an extractable species, metal chelates.

(2) The distribution of the compound. This step is the distribution of the extractable species between the two liquid phase, the aqueous and the organic phase, follows the distribution law.

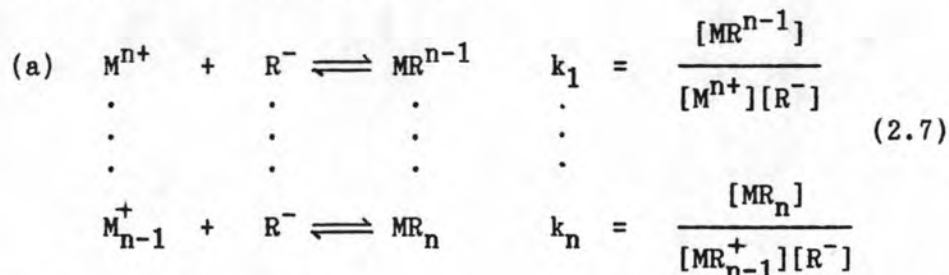
(3) The interaction in the organic phase. This step involves the reaction of the extractable complex in the organic phase, e.g., polymerization or dissociation of the complex, interaction with other components, such as the reagent, in the organic phase, are included in this stage. Since extractable metal chelates are essentially covalent compounds, their solutions in neutral organic solvents are relatively free from chemical interaction.

2.1 Chelate Extraction System. Among the more commonly encounter metal extractions is that involving a chelating agent, which is a weakly acidic chelating agent such as APDC or dithizone, dissolved in aqueous phase for APDC or dissolved in organic solvent for dithizone. Writing the formula for the chelating agent as HR, we can describe the reaction involved by the following equations.

(1) Ionization of the reagent to give the active chelating anion.



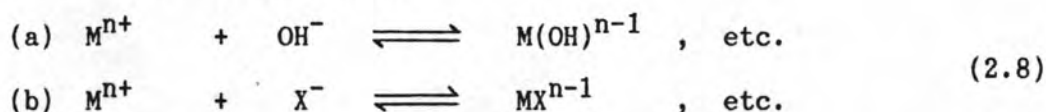
(2) Formation of the metal chelate.



The overall formation constant,  $K_f$ , may readily be seen to be

$$K_f = k_1 \cdot k_2 \cdot \dots \cdot k_n$$

(3) Competing reaction for the metal ion are those of hydrolysis and metal anion coordination.



where  $X^-$  represents the anion present, e.g.  $Cl^-$ ,  $NO_3^-$ , or  $SO_4^{2-}$

Finally, we must consider the distribution of the chelating agent as well as the chelate between the two phase. Thus

(4) Distribution of the reagent.

$$K_{D_R} = \frac{[HR]_o}{[HR]} \quad (2.9)$$

where subscript o refers to organic phase.

(5) Distribution of the metal chelate.

$$K_{D_x} = \frac{[MR_n]_o}{[MR_n]} \quad (2.10)$$

These equilibrium expressions may be used to derive an expression for the ratio of stoichiometric metal concentrations in the two phases, D. If it is assumed that the only metal-bearing species in the organic phase is the fully formed metal chelate,  $MR_n$ , then

$$\begin{aligned} D &= \frac{|M|_o}{|M|} \\ &= \frac{[MR_n]_o}{[M^{n+}] + [MR^{n-1}] + \dots + [MR_{n-1}^+] + \sum_i [M(OH)_i^{n-i}] + \sum_j [MX_j^{n-j}]} \end{aligned} \quad (2.11)$$

Dividing both numerator and denominator by  $[MR_n]$  and substituting appropriate values from eqs. 2.7 and 2.10 for the ratio obtained, we find

$$D = \frac{K_f K_{D_x} [R^-]^n}{1 + k_1 [R^-] + k_1 k_2 [R^-]^2 + \dots + K_f [R^-]^{n(1+x)}} \quad (2.12)$$

where  $x = \frac{\{\sum_i [M(OH)_i^{n-i}] + \sum_j [MX_j^{n-j}]\}}{[MR_n]}$

Further substitutions of eqs. 2.6 and 2.9 give

$$D = \frac{K_f K_{Dx} K_i^n}{K_{DR}^n} \left[ \left\{ \frac{[H^+]}{[HR]_o} \right\}^n + \frac{k_1 K_i}{K_{DR}} \left\{ \frac{[H^+]}{[HR]_o} \right\}^{n-1} + \dots \right. \\ \left. \dots \frac{k_1 \dots k_{n-1} K_i^{n-1}}{K_{DR}^{n-1}} \frac{[H^+]}{[HR]_o} + \frac{K_f K_i^n}{K_{DR}^n} (1+x) \right]^{-1} \quad (2.13)$$

A useful approximation for D may be obtained from eq. 2.13 by making the following assumptions :

- a) That the metal ion forms no appreciable amount of hydrolysis or anion coordination complexes,  $x = 0$ .
- (b) That the chelate concentration in the aqueous phase is negligible.

$$[MR_n] \longrightarrow 0 \quad \text{or} \quad \frac{[H^+]^n}{[HR]_o} \gg \frac{K_f K_i^n}{K_{DR}^n}$$

- (c) That the concentrations of the intermediate metal chelate species are negligible. In this manner, eq. 2.13 simplifies to

$$D = \frac{K_f K_{Dx} K_i^n}{K_{DR}^n} \left\{ \frac{[HR]_o}{[H^+]} \right\}^n = K^* \left[ \frac{(HR)_o}{(H^+)} \right]^n \quad (2.14)$$

The behaviour of many chelate extraction systems may be characterized by eq. 2.13, which correctly predicts that the extractability of a metal depends equally heavily on the hydrogen ion concentration in the aqueous phase and on the reagent concentration, although it is independent of metal concentration.

Equation 2.14 demonstrates the importance of chelate stability ( $K_f$ ) and relative solubility of the chelate in the organic phase ( $K_{Dx}$ ) to metal extractability. An acidic chelating agent (high  $K_a$ )



that is relative more soluble in water (low  $K_{DR}$ ) is also desirable for optimal extraction.

It can be seen with the aid of eq. 2.14 that, provided the reagent concentration is maintained constant, the distribution of the metal in a given system is a function of a pH alone. Equation 2.14 may be written as

$$D = K^* \frac{[HR]_O^n}{[H^+]^n} = K^{*'} [HR^+]^{-n} \quad (2.15)$$

Now, since D and the percentage extraction (%E) are related, then

$$E = \frac{100 D}{(D + 1)}$$

$$D = \frac{E}{100 - E} = K^{*'} [H^+]^{-n} \quad (2.16)$$

$$\text{or } \log E - \log(100 - E) = \log K^{*'} + n \text{ pH} \quad (2.17)$$

Equation 2.17 represents a family of symmetrical sigmoid curves, with the position of each along the pH axis depending only on the magnitude of  $K^{*'}$ .