

CHAPTER I  
INTRODUCTION



Solvent extraction techniques are widely applied in science and technology . The field of solvent extraction covers several aspects, such as studies of complex chemistry, separation and purification processes, the chemistry of solvents, extractants and diluents, the mechanism of distribution reactions , etc

Basis of the Solvent Extraction Method : The Distribution Law

In the separation by solvent extraction, advantage is taken of the fact that, if a substance is soluble in two solvents which are immiscible, it will distribute itself between the two phases . When the equilibrium is reached the ratio of the concentration of the substance in the two phases is called the " distribution ratio " or " partition coefficient ". This ratio is constant at a given temperature, and is independent of the concentration for system where the molecular weight of the substance involved is the same in both solvents. The concentration of the substance may be expressed as molecular fractions, molar concentrations, gram /unit-volume, or in other ways. The earliest experimental study of the distribution of a solute between two liquid phases is that of Berthelot and Jungfleishsch.<sup>1</sup> The problems were later examined, both theoretically and experimentally, by Nernst (1891).<sup>2</sup> The distribution law is usually written :

$$\frac{C_2}{C_1} = D$$

where  $C_1$  = the concentration of solute in the first solvent  
 $C_2$  = the concentration of solute in the second solvent  
 $D$  = distribution constant.

In simple systems,  $\frac{C_1}{C_2}$  is approximately equal to the ratio of the saturation concentrations of the solute in each of the two solvents. If the distribution or association of the solute in one solvent is different from that in the second solvent according to the relation,

$$nA(\text{solvent I}) = A_n (\text{solvent II})$$

then the distribution constant will have a concentration dependence, given by  $D = \frac{C_2(A_n)}{C_1^n(A)}$

Usually, in practice, the substance in question is dissolved in a particular solvent, generally water. A quantity of the immiscible extractant is added to this solution, the two are shaken together, and are then separated. This may need repetition, depending upon the completeness of extraction desired and the distribution constant. The amount of the desired substance remaining in the initial solution (solution I) can be calculated by assuming that there are M ml of solution I containing "g" gram of the substance to be extracted. The extraction will be carried out with "n" quantities of N ml of extractant. If, after a single extraction, there are "x<sub>1</sub>" gm of substance left in the solvent I, there will be (g-x<sub>1</sub>) gm in solvent II. Then

$$C_M = \frac{x_1}{M}$$

$$\text{and } C_N = \frac{(g-x_1)}{N}$$

$$\text{therefore } D = \frac{C_M}{C_N} = \frac{x_1/M}{(g-x_1)/N}$$

$$x_1 = \frac{DM}{N+DM} g$$

$$\text{For "n" extractions, } x_n = \left[ \frac{DM}{N+DM} \right]^n g$$

In practice, it is sometimes convenient to express the per cent extraction as a measure of the extractability for a given system. The per cent extracted and the distribution constant are related as follows :

$$\text{Per cent extracted} = \frac{100 D}{D + \frac{V_1}{V_2}}$$

for a single equilibration resulting in the equilibrium volumes  $V_1$  and  $V_2$ . The effect of volume ratio is most pronounced for small values of  $D$ .

The selectivity of a solvent extraction process can be expressed in term of a separation factor defined as

$$\alpha = \frac{D_A}{D_B}$$

in term of distribution ratios. The separation factor relates the extraction of one substance relative to a second substance in the mixture to be separated. A value of  $\alpha$  greater than unity means that component A is preferentially extracted, and the greater the value of  $\alpha$ , the purer the extract of A relative to B; a value of unity means no separation.

In many cases the distribution of a solute, between two phases, varies with the concentration of the solute, e.g. the formation of colloids during the process of extraction may affect the distribution of substance in question between two immiscible solvents, because the colloid may concentrate in the interface. Also, the formation of complexes, or dissociated species or the reactions such as hydrolysis etc., may take place on dilution, and any one of these will cause a difference in the distribution from what obtaining in a concentrated solution.

The types of compounds which undergo extraction into organic solvents may be classified broadly into four categories<sup>3</sup>:

1. neutral covalent compounds, such as the halogens, and mercury halides ;
2. inner complexes of metals with reagents such as acetyl-acetone, dithizone, and 8-hydroxyquinoline ;
3. the mineral acids, their salts, and metal acido-complexes.
4. certain salts or ion pairs which incorporate bulky anions or cations, e.g., tetraphenylarsonium per-rhenate.

The halo-metallic acid extraction involves anionic complexes of metal with ligands, mainly halide anions are interesting here. They are extracted as acids, the protons of which are solvated by solvating solvent, containing as donor atoms mainly oxygen, such as alcohols, ketones, ethers, esters, nitrocompounds. Usually it is not possible to assign a definite solvation for the proton.

The primary purpose of this work was in fact to study the extent of the formation of the higher chloro metallic complex occurred in the ferric chloride-hydrochloric acid-amyl acetate system and also in the ferric chloride-hydrochloric acid-butyl acetate system. The programme of the work consisted of the analysis of the organic and of the aqueous phases after the mixing of the appropriate components resulting in the separation into two phases, organic and aqueous phases. It is therefore essentially the solvent extraction to begin with. The subsequent analysis of the species present in each phase at various acid and metal concentrations was accomplished via the spectrophotometric and the radiometric methods.

According to Irving, Rossotti and Williams<sup>3</sup>, the systems under investigation were termed the "non-ideal" systems. The classification was based on the following criteria,

1. there are changes in the solvent properties of the two phases, and/or
2. there are changes in the extent of solvation (by organic solvent and/or water, of any species in either phase.

It was therefore the secondary purpose of this work to test the validity of this classification.