CHAPTER 2

THEORY

2.1 GIBBS' PHASE RULE (41)

Solvent Extraction is a partitioning process based on the selective distribution of a substance in two immiscible phases. A third component, when added to a two-phase system, will distribute itself into two phase in a difinite manner to predict the behavior of a multiphase system and elucidates the equilibrium state obtained. Since, in generally in the liquid-liquid extractions, the liquid phases are not in equilibrium with the surrounding atmosphere. The above system would be described as a ternary, two phase system.

For all distributions, the classical phase rule of Gibbs'

$$P + F = C + 2 \qquad\qquad (1)$$

Where P is the number of phases

F is the variance or degree of freedom

and C is the number of components

When P = 2 and C = 3 then F = 3 therefore, three variables which are temperature, pressure and composition must be specified in order to define the system. At constant temperature and pressure only one variable, i.e., composition, must be specified in defining the system completely. This means that the solute

concentration in one phase has direct relationship to the solute concentration in the other phase.

2.2 NERNST DISTRIBUTION LAW (42,43)

A solute which dissolved in one phase in equilibrium with another immiscible phase will distribute itself between two phases so that a ratio of the concentrations in two phases is constant. The system may be defined by Nernst distribution law as the following equation :

$$\frac{[S]_{1,1}}{[S]_{1,2}} = K_d \qquad (2)$$

Where $[S]_{1,1}$ is the concentration of solute 1 in the phase 1.

$[S]_{1,2}$ is the concentration of solute 1 in the phase 2.

and K_d is the distribution coefficient.

Such an expression of the distribution law is valid only for ideal systems as can be seen from a thermodynamic derivation of the law. The change in free energy in a system, is expressed by the differential

$$dF = \left(\frac{\partial F}{\partial T}\right)_{P,n_1,n_2,\ldots} dT + \left(\frac{\partial F}{\partial P}\right)_{T,n_1,n_2,\ldots} dP$$

$$+ \left(\frac{\partial F}{\partial n_1}\right)_{P,T,n_2,n_3,\ldots} dn_1 + \left(\frac{\partial F}{\partial n_2}\right)_{P,T,n_1,n_3,\ldots} dn_2 + \ldots \qquad (3)$$

Since, by definition

$$\left(\frac{\partial F}{\partial n_1}\right)_{T,P,n_2,n_3,\ldots} = \text{partial molar free energy}$$

$$= \mu_1 = \text{chemical potential} \qquad (4)$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_{P,n_1,n_2,\ldots} dT + \left(\frac{\partial F}{\partial P}\right)_{T,n_1,n_2,\ldots} dP$$

$$+ \mu_1 dn_1 + \mu_2 dn_2 + \cdots \qquad (5)$$

At constant temperature and pressure,

$$dF = \mu_1 dn_1 + \mu_2 dn_2 \qquad (6)$$

Since there is no change in the total amount of material involved in the partitioning phenomenon, the system is thermo-dynamically closed. One of the conditions of equilibrium for a closed system is that dF is equal to 0 at constant temperature and pressure. Therefore,

$$\mu_1 dn_1 + \mu_2 dn_2 = 0 \qquad (7)$$

or

$$\Sigma \mu dn = 0 \quad \text{at equilibrium}$$

This condition applies to the entire closed system. If a small quantity of component 1 is moved within the system from phase 1 to phase 2, then at equilibrium

$$-\mu_{1,1} dn_1 + \mu_{1,2} dn_1 = 0 \qquad (8)$$

and

$$\mu_{1,1} = \mu_{1,2} \qquad (9)$$

That is the chemical potential of a component distributed between two phases that are in equilibrium is the same in both phases.

The chemical potential of any solute in the solution can be written as

$$\mu = \mu^O + RT \ln a \qquad (10)$$

Where a is the activity of the solute in solution

and μ^O is the chemical potential of the solute in a specific reference state. μ^O is a constant independent of composition but is dependent on the temperature and pressure of the system.

The chemical potential of a substance distributed between two phases in equilibrium can be expressed as

$$\mu_{1,1} = \mu^O_{1,1} + RT \ln a_{1,1} \qquad (11)$$

$$\mu_{1,2} = \mu^O_{1,2} + RT \ln a_{1,2} \qquad (12)$$

in phases 1 and 2, respectively.

Since at equilibrium $\mu_{1,1} = \mu_{1,2}$ and μ^O_1 is a constant, the expression reduced to

$$\frac{a_{1,1}}{a_{1,2}} = P \text{ (partition coefficient)} \qquad (13)$$

This is an exact expression of the distribution law and shows that the original form

$$\frac{[S]_{1,1}}{[S]_{1,2}} = \text{constant} \qquad (14)$$

is only an approximation that holds true for dilute solutions and ideal behavior. For many practical application the approximate form of the law is adequate.

2.3 DISTRIBUTION RATIO (44)

The distribution coefficient, K_d is valid only when solute is the same species in both phases. If the solute has a different form in one of the phases, a better description would be the distribution ratio, D

$$D = \frac{\text{total concentration of solute (all form) in phase 1}}{\text{total concentration of solute (all form) in phase 2}} \qquad (15)$$

The total concentration of the forms of solute is the analytical concentration, C. The analytical concentration of a substance is equal to the sum of the equilibrium concentration, thus

$$C_{1,1} = \Sigma_{i=1}[S_i]_{1,1} \qquad (16)$$

$$C_{1,2} = \Sigma_{i=1}[S_i]_{1,2} \qquad (17)$$

$$D = \frac{C_{1,1}}{C_{1,2}} \qquad (18)$$

2.4 EXTRACTION EFFICIENCY (43,44)

The extraction efficiency considers from the percent of solute extracted, %E. The total amount of solute in water-solvent system is the sum of the amount of solute in each phase of the system, as expressed by the equation :

$$C_S = [S]_O V_O + [S]_W V_W \qquad (19)$$

Where C_S is the analytical concentration of solute.

V_O is the volume of organic solvent.

$[S]_O$ is the concentration of solute in organic solvent.

V_W is the volume of water.

$[S]_W$ is the concentration of solute in water.

since

$$[S]_O = K_d [S]_W \qquad (20)$$

substitute equation (20) into equation (19) yields

$$C_S = K_d [S]_W V_O + [S]_W V_W \qquad (21)$$

If the distribution coefficient is known, the percent of the solute extracted into the organic solvent can be calculated :

$$\% E = \frac{100 K_d [S]_W V_O}{K_d [S]_W V_O + [S]_W V_W} \qquad (22)$$

which can be simplified to

$$\% E = \frac{100 K_d}{K_d + V_w/V_o} \tag{23}$$

Using equation (23), a series of the curves can be drawn relating % E to the ratio of solvent to water at different values of K_d as shown in figure 2.1. The dashed lines represent the change in the concentration of solute as a function of the solvent to water ratio. It can be seen that for easily extracted materials, e.g., most of the priority pollutants increasing the volume of solvent results in small gains in the amount of solute extracted and large decreases in its concentration. Alternately, the total amount of a poor extracted compound increases almost in direct proportion to the increase in extracting solvent volume.

2.5 SALTING OUT EFFECT (42,45)

The percent recovery can be improved by increasing ionic strength of the aqueous phase. This effect is sometimes called "salting out".

In general, the addition of a soluble salt to an aqueous solution of an organic compound decreases the solubility of that compound according to Setschenow's equation

$$\log S = \log S_o - kM \tag{24}$$

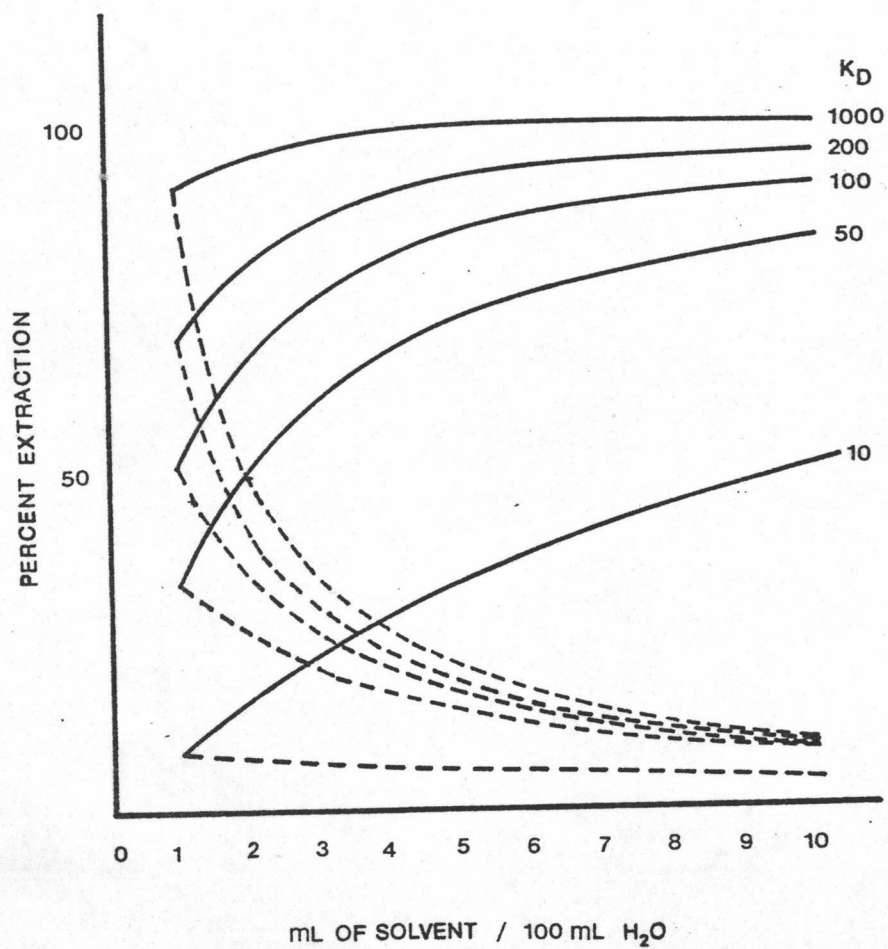Where S_o is the solubility of organic compound in pure water.

Figure 2.1 The effect of the solvent to water ratio on both the % recovery and the relative concentration of analytes with different distribution coefficients (K_d)

S is the solubility of organic compound in the salt solution.

M is the molarity of the salt

and k is a constant called a salting out constant

whose value depends on the organic compound and on the nature of the salt. This equation is equivalent to

$$\log f = kM \qquad (25)$$

Where f is the activity coefficient of organic compound in the aqueous solution.

When consider a system consisting of a small amount of an organic compound, varying concentrations of the salt in water, and organic solvent, the organic compound would be distributed between the water and the organic solvent. When assume that the organic phase is not changed by variation in the concentration of salt. Then the activity coefficient of organic compound inside the organic phase remains constant. Under these conditions, it can be proved that

$$\frac{D}{D_o} = f \qquad (26)$$

Where D_o is the distribution ratio in the absence of salt. Combining this equation with equation (25) yields

$$\log D = \log D_o + kM \qquad (27)$$

Adding salts such as ammonium chloride, sodium chloride, sodium sulfate, etc. into the water before extraction, the salts dissolve quickly and they can shift the distribution coefficient of solutes in favor of the organic phase.

2.6 CHOICE OF SOLVENT (43,44)

The choice of extracing solvent for a particular purposes in extraction is certainly one of the major problems. Not only one is confronted with almost limitless possibilities as far as different solvents are concerned but also the choice is always made, conciously or unconciously with many different factors :

1. The solutes should be very soluble in the solvent so as to have a high value of K_d or D, and thus require only one or two extractions.

2. The solvent should be as immiscible with water as possible. One way of arriving at an excellent idea about the degree of immiscibility is through the comparison of the dipole moment of the liquid with that of water (μ=1.84 debyes). Solvent such as benzene, hexane, and carbon tetrachloride with a dipole moments of zero have very low water solubilities, whereas solvent such as diethyl ether (μ=1.2 debyes), ethyl acetate (μ=1.8 debyes), or n-butyl alcohol (μ=1.7 debyes) have relatively high aqueous solubilities.

3. The solvent should have as great a density difference from water as possible. This permits a clean-cut phase boundary between the two phases and facilitates the physical separation of the two liquids after extraction.

4. The viscosity of the solvent should be low to permit good contact between the two phases while shaking and to rapid setting out of the two liquids after shaking.

5. The solvent should have a sufficiently high boiling point so that evaporation of the solvent is not a problem.

6. The solute should be able to be recovered readily from the solvent for subsequent operations.

7. The solvent should not form stable emulsions with water.

8. The solvent should be readily available in sufficient state of purity for convenient use.

9. The solvent should not be hazardous to the health.

10. The solvent should be inexpensive.

The first problem encountered in choosing a solvent for extraction is its selectivity. The distribution coefficient of the solute must be high if it is going to be readily extracted from one phase. If the solute is to be separated from other solutes, then the solvent must be selective in its action. That is the distribution coefficients of the various solutes must be distinctly different. The principal difficultly is simply that too few published distribution coefficients. The result is that the choice of solvent for an extraction procedure is based on either semiempirical or experience considerations. The choice of solvent needs not be completely empirical if something is known about the nonpolar or polar character of the solute to be extracted.