CHAPTER 2

THEORY

Liquid-liquid extraction is one of the several mass-transfer techniques which generally rely upon the unequal equilibrium distribution of substance to be separated between two immiscible phases. One phase is usually an aqueous phase and the other is an added organic phase.

There are two approaches to the study of phase equilibria. These are the phase rule and the law of distribution.

## 2.1 PHASE RULE (46)

For all phase distribution, the classical phase rule of Gibbs

$$F = C-P+2 \tag{1}$$

where C is the number of components, or the

lowest number of independently variable constituents required to express the composition of each phase.

P   is the number of phases. A phase is defined as any homogeneous part of a system, bounded by surface and capable of mechanical separation from the rest of the system.

F   is the varience or the degrees of freedom or the number of intensive variables which can be altered independently arbitrarily within certain limits (e.g., temperature, pressure and concentration) without bringing about the disappearance of a phase or the formation of a new phase. It must be fixed to defined completely a system at equilibrium.

In the particular solvent extraction system which contains two immiscible solvents and one solute distributed between them so that P = 2 and C = 3. The rule predicts a

variance of unity at constant temperature and pressure. If the concentration of solute in one phase is chosen, the solute concentration in the other phase is fixed. The distribution law is a quantitatively description for the definite relation between the solute concentration in each of the solvent phases.

## 2.2 DISTRIBUTION LAW (47-48)

Nernst distribution law states that at equilibrium, the ratio of concentration of the solute in two phases at a particular temperature will be a constant.

$$K_d = \frac{C_O}{C_W} \qquad (2)$$

where $C_O$ is the concentration of solute in the organic phase.

$C_W$ is the concentration of solute in the aqueous phase.

$K_d$ is the distribution coefficient which independent of total solute concentration.

This approximate expression of the distribution law has two serious shortcomings. The first arises because the law as stated is not thermodynamically rigorous and the second is encountered when the distributing species is involved in chemical reactions such as dissociation or association in either phase.

The thermodynamic explanation of the distribution law will be expressed in term of the free energy (G) of the phase.

For any infinitestimal reversible change of state of the phase,

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

$$+ \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2,n_3,\ldots} dn_1 + \ldots + \left(\frac{\partial G}{\partial n_c}\right)_{P,T,n_1,\ldots} dn_c \quad (3)$$

G is a function of T, P, and $n_1, n_2, \ldots n_c$, of the C independent components.

the partial molal free energies, $\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,\ldots,n_c}$

is defined as the chemical potential, $\mu_1$.

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

$$+ \mu_1 n_1 + \mu_2 n_2 \qquad (4)$$

equilibrium is attained at constant temperature and pressure, thus

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \qquad (5)$$

if there is no change in the total amount of material involved in the partitioning phenomenon, the system is thermodynamically closed,

$$dG = 0 \qquad (6)$$

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

or $\mu dn = 0$ \qquad (8)

at equilibrium, closed system

if a small quantity of component 1 is moved within the system from phase I (aqueous phase) to phase II (organic phase),

$$-\mu_{1,I} dn_1 + \mu_{1,II} dn_2 = 0 \qquad (9)$$

$$\mu_{1,I} = \mu_{1,II} \qquad (10)$$

that is the chemical potential of the solute in each phase is equal.

next, substituting suitable expression for $\mu$

$$\mu = \mu^\circ + RT \ln a \qquad (11)$$

where $\mu^\circ$ is the chemical potential of solute in a hypothetical 1 molal solution, a constant independent of the composition but dependent on the temperature and pressure of the system.

a is the activity of the solute ,

$$a = m\gamma$$

where m is the solute concentration in molality.

$\gamma$ is the molal activity coefficient.

then $\mu_{1,I} = \mu^\circ_{1,I} + RT \ln a_{1,I} \qquad (12)$

$\mu_{1,II} = \mu^\circ_{1,II} + RT \ln a_{1,II} \qquad (13)$

substituting (12),(13) into (10)

$$\frac{a_{1,I}}{a_{1,II}} = \exp{-(\mu^o_{1,I} - \mu^o_{1,II})}$$

$$= P, \text{ partition coefficient} \quad (14)$$

in this equation the $\mu^o$ represent constants provided the presence of the solute does not significant affect the mutual solubilities of the two solvents.

For very dilute solution $\dfrac{a_{1,I}}{a_{1,II}}$ becomes $\dfrac{m_{1,I}}{m_{1,I}}$ or $\dfrac{C_o}{C_w}$

that is

$$K_d = \frac{C_o}{C_w}$$

## 2.3 DISTRIBUTION RATIO (49)

$$D = \frac{\text{Total concentration in organic phase}}{\text{Total concentration in aqueous phase}} \quad (15)$$

There are many chemical interactions of the

distributing species with the other components in each phase such as dissociation or association, since a stoichiometric distribution ratio (D) including all species of the same component in the respective phases is introduced. In ideal condition,i.e.,no reaction of the species in either phase, D would reduce to $K_d$.

## 2.4 PERCENTAGE EXTRACTION (48-49)

The calculation of the percent recovery (% E) for describing the extraction efficiency can be derived from the distribution law.

$$K_d = \frac{C_o}{C_w}$$

The total amount of solute in a water-solvent system is the sum of the amount solute in each phase of the system, as expressed by the equation :

$$C_s = C_o V_o + C_w V_w \qquad (16)$$

where    $C_s$    is the total amount of solute.

$V_o$    is the volume of organic

solvent.

$C_O$     is the concentration of solute in organic solvent.

$V_W$     is the volume of water, and

$C_W$     is the concentration of solute in water.

since     $C_O \;=\; K_d C_W$

then     $C_S \;=\; K_d C_W V_O + C_W V_W$          (17)

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

$$\% \; E \;=\; \frac{100 K_d C_W V_O}{K_d C_W V_O + C_W V_W} \tag{18}$$

which can be simplified to

$$\% \; E \;=\; \frac{100 K_d}{K_d + \dfrac{V_W}{V_O}} \tag{19}$$
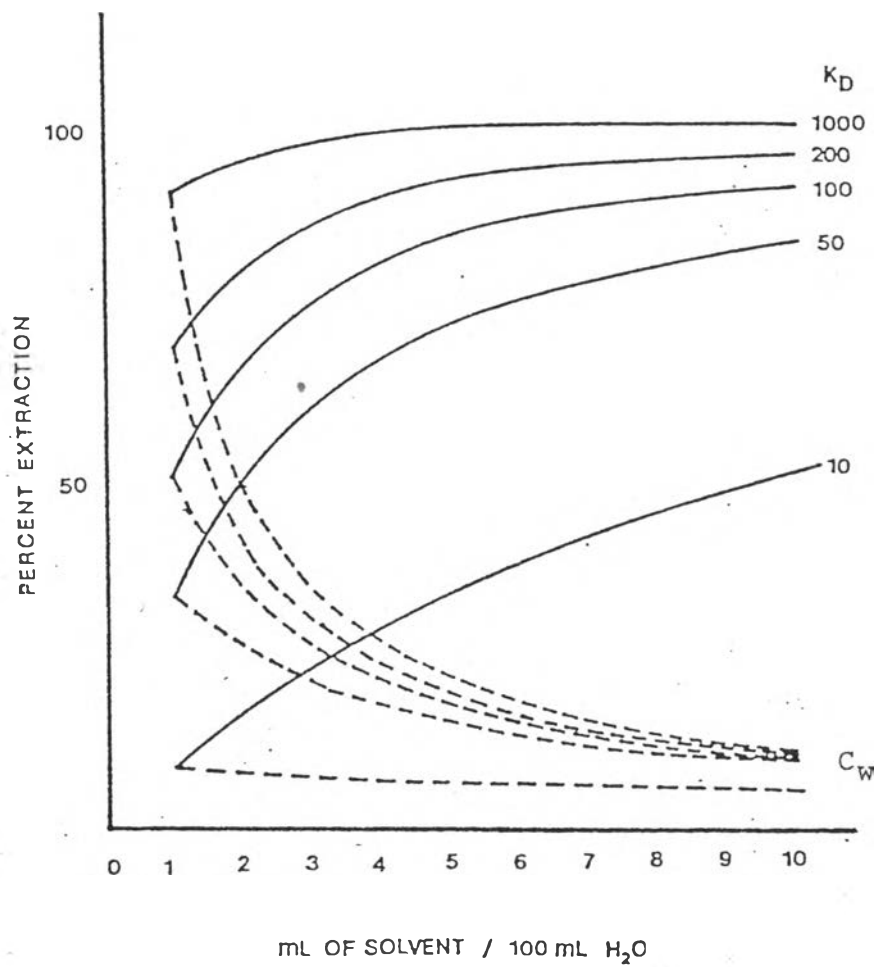
Figure 2.1   The effect of the solvent to water ratio
             on both the % recovery and the relative
             concentration of analytes with different
             distribution coefficients ($K_d$)

## 2.5 <u>SALTING OUT</u>  (47,50)

In general, the addition of a soluble inorganic salts (e.g.sodium sulfate, sodium chloride etc.) to an aqueous solution of an organic compound, which is called salting out, decreases the solubility of that compound in water according to the Setchenow's equation. (50)

$$\log S = \log S_O - kM \tag{20}$$

where　$S_O$　is the solubility of the organic compound in pure water.

$S$　is the solubility in a solution of salt.

$M$　is the molarlity of the salt, and

$k$　is the salting out constant, whose values depends on the organic compound and on the nature of the salts. It is independent on temperature and pH.

This equation is equivalent to that of Debye and McAuley.

$$\ln f \quad = \quad kM \tag{21}$$

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

## 2.6  CHOICE OF SOLVENT  (48-49)

In choosing a solvent for a liquid extraction process, there are frequently conflicting and certainly no single substance would ordinarily posses every desirable characteristics. Compromises must be made, and the following factors should be considered.

### Selectivity

This is the first property studied in deciding the applicability of a solvent. The most desirable solvent would dissolve a maximum of one component and a minimum of the other. The phase diagrams and distribution coefficient can be used to determine the selectivity of the solvent.

## Miscibility of the solvent

The concept of " like dissolves like " would be applied for choosing the solvent. The polar solute would be extracted with the polar solvent and the nonpolar solvent should be chosen for the extraction of the nonpolar solute.

## Capacity

The desirable solvent would have the capacity to dissolve relatively large quantities of the preferentially extracted solute, in addition to having a high selectivity.

## Density

Satisfactory density differences for the two phases should hold, so that the rate of separation of the immiscible layers enhanced.

## Interfacial tension

The interfacial tension between immiscible phases that must be settled or disengaged should be high

for rapid coalescence. Too high and too low interfacial tension cause the requirement of large energy for dispersion of one liquid into another and the formation of stable emulsions respectively.

### Viscosity

The solvent of low viscosity is required for rapid extraction, rapid settling of dispersiond and high heat- and mass-transfer rates.

### Boiling point and vapor pressure

Solvents may have either a higher or a lower boiling temperature than the other constituents of the system, and which of these pertains has an important influence on the next step after the extraction step. The solvent of low boiling point will be used if the solute is concentrated by evaporation. However, ordinarily low vapor pressure is desired so that storage and extraction operation are possible at atmospheric pressure.

### Chemical reactivity and stability

The solvent should be stable, not react with

the component of the feed solution irreversibly. The high purity solvent may occasionally be required for the extraction.

### Corrosiveness, toxicity and flammability

Low flammability, low toxicity and no severe corrosion with common materials are desirable for reason of safety and economy.

### Economy

Low cost and readily availability in adequate quantities are desirable solvent attributes. However it is not significant for a single extraction.