



CHAPTER 2

THEORY

Liquid-liquid extraction is a partitioning process based on the selective distribution of a substance in two immisible phases. A third component, when added to a two-phase system will distribute itself in the two phases in a definite manner. Gibbs' phase rule helps to predict the behavior of a multiphase system and elucidates the equilibrium state obtained.

2.1 GIBBS' PHASE RULE (69-71)

In general, in liquid - liquid extractions the liquid phases are not in equilibrium with the surrounding atmosphere, the above system will be described as a ternary, two - phase system. Gibbs' phase rule provides a general and useful connection and states that :

$$F = C - P + 2 \quad (1)$$

where F is the number of independent variable or degree of freedom

C is the number of components

P is the number of phases

Therefore, three variables, temperature,

pressure and composition, must be specified in order to define the system. However, at constant temperature and pressure only one variable, composition, must be specified to define the system completely. This means that the concentration of the solute in one phase has a direct relationship to its concentration in the other phase. The distribution law states clearly what this relationship is.

2.2 NERNST'S DISTRIBUTION LAW (4.71-72)

"A solute dissolved in one phase in equilibrium with another immiscible phase will distribute itself between the two phases so a ratio of the concentration in the two phases is constant at a given temperature". That is

$$\frac{(S)_{1,1}}{(S)_{1,2}} = K_d \quad (2)$$

Where K_d is the distribution constant or distribution coefficient.

$(S)_{1,1}$ is the concentration of the solute in phase 1 or organic phase.

$(S)_{1,2}$ is the concentration of the solute in phase 2 or water phase.

The above expression of the distribution law is valid only for ideal system as can be seen from a thermodynamic derivation of the law.

2.3 THERMODYNAMIC DERIVATION OF THE DISTRIBUTION LAW (69)

The change in free energy in a system, is expressed by the differential

$$\begin{aligned}
 dF &= \left(\frac{\partial F}{\partial T} \right)_{P, n_1, n_2, \dots} dT + \left(\frac{\partial F}{\partial P} \right)_{T, n_1, n_2, \dots} dP \\
 &+ \left(\frac{\partial F}{\partial n_1} \right)_{P, T, n_2, n_3, \dots} dn_1 + \left(\frac{\partial F}{\partial n_2} \right)_{P, T, n_1, n_3, \dots} dn_2 + \dots
 \end{aligned} \tag{3}$$

Since, by definition

$$\begin{aligned}
 \left(\frac{\partial F}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} &= \text{partial molar free energy} \\
 &= \mu_1 = \text{chemical potential} \tag{4}
 \end{aligned}$$

$$\begin{aligned}
 dF &= \left(\frac{\partial F}{\partial T} \right)_{P, n_1, n_2, \dots} dT + \left(\frac{\partial F}{\partial P} \right)_{T, n_1, n_2, \dots} dP \\
 &+ \mu_1 dn_1 + \mu_2 dn_2 + \dots
 \end{aligned} \tag{5}$$

At constant temperature and pressure

$$dF = \mu_1 dn_1 + \mu_2 dn_2 \tag{6}$$

Since there is no change in the total amount of material involved in the partition phenomenon, the system is thermodynamically closed. One of the conditions of equilibrium for a closed system is that $dF = 0$ at constant temperature and pressure. Therefore,

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

$$\text{or } \sum \mu dn = 0 \quad ; \text{ at equilibrium} \quad (8)$$

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

$$-\mu_{1,1} dn_1 + \mu_{1,2} dn_1 = 0 \quad (9)$$

$$\text{and } \mu_{1,1} = \mu_{1,2} \quad (10)$$

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 solution can be written as

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

Where a is the activity of the solute in solution

μ° is the chemical potential of the solute in a specific reference state. μ° is a constant independent of composition but 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

$$\mu_{1,1} = \mu_{1,1}^\circ + RT \ln a_{1,1} \quad (12)$$

$$\mu_{1,2} = \mu_{1,2}^\circ + RT \ln a_{1,2} \quad (13)$$

in phases 1 and 2 , respectively.

Since at equilibrium $\mu_{1,1} = \mu_{1,2}$ and μ°_1 is a constant, the expression reduces to

$$\frac{a_{1,1}}{a_{1,2}} = P = \text{partition coefficient} \quad (14)$$

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

$$\frac{(S)_{1,1}}{(S)_{1,2}} = \text{constant} = K_d \quad (15)$$

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

2.4 DISTRIBUTION RATIO (1.70-71)

Since the distribution constant , K_d , is valid only when the solute is the same species in both phases ,i.e., has the same molecular weight . If the solute has a different form in one of the phases, a better description of the equilibrium would be the distribution ratio , D.

$$D = \frac{\text{total concentration of solute(all form) in phase 1}}{\text{total concentration of solute(all form) in phase 2}} \quad (16)$$

The total concentration of all forms of the

solute is the analytical concentration, C_1 . The analytical concentration of a substance is equal to the sum of the equilibrium concentration, thus

$$(C_1)_1 = \sum_{i=1}^n (S_1)_1 \quad (17)$$

$$(C_1)_2 = \sum_{i=1}^n (S_1)_2 \quad (18)$$

$$D = \frac{(C_1)_1}{(C_1)_2} \quad (19)$$

The use of equation (19) only becomes important when one has ionic species, metal ion being removed by chelation or when dimerization or polymerization reactions are taking place.

2.5 EXTRACTION EFFICIENCY (4.70,71.)

The extraction efficiency (% E) is considered as the percent of solute extracted into organic solvent. The total amount of solute in the system can be expressed as the sum of the amounts of solute in each phase :

$$C_B = (S)_O V_O + (S)_W V_W \quad (25)$$

Where C_B is the total amount of solute.

$(S)_O$ is the concentration of solute in organic solvent.

$(S)_W$ is the concentration of solute in water.

V_O is the volume of organic solvent.

V_W is the volume of water.

$$\text{Since } (S)_O = K_d(S)_W \quad (26)$$

Substituting $(S)_O$ from equation (26) into equation (25) gives :

$$C_B = K_d(S)_W V_O + (S)_W V_W \quad (27)$$

The % E can be determined by deviding the amount of solute in the extracting organic solvent with the total amount of solute and multiplying by 100 as expressed in the following equation :

$$\%E = \frac{100 K_d(S)_W V_O}{K_d(S)_W V_O + (S)_W V_W} \quad (28)$$

which simplifies to

$$\% E = \frac{100 K_d}{K_d + V_W/V_O} \quad (29)$$

If the distribution constant is known, the percent of the solute extracted can be calculated from a given water-to-solvent ratio.

Figure 2.1 shows a series of curves relating % E to the ratio of solvent to water for a number of different K_d values. The relative concentration of the solute in the organic extract is also shown as a function of these same variables. It can be seen that for easily extracted compounds, which is the case for most priority pollutants under the extraction, increasing the volume of solvent results in small gains

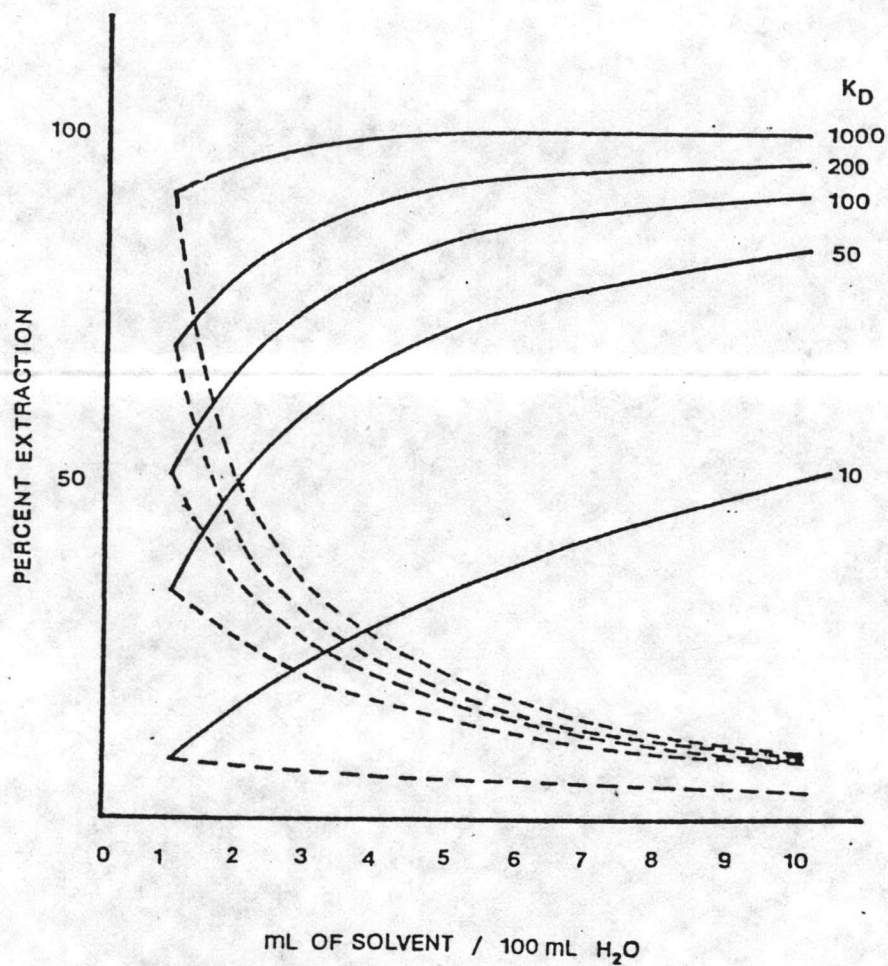


Figure 2.1 The effect of the solvent to water ratio on both the % recovery and the relative concentration of analytes with different distribution coefficients (K_D)

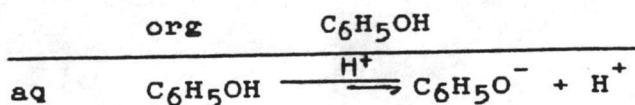
in the amount of analyte extracted and large decreases in its concentration. In contrast, the total amount of a poorly extracted compound increases in direct proportion to the volume of solvent used. Consequently, macroextraction for easily extracted compounds will provide little improvement in recovery of the analyte while increasing the recovery of potential interferences.

2.6 EFFECT OF pH (70)

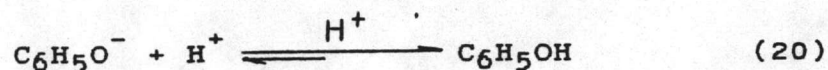
Ionic compounds will not be extracted into organic solvents from aqueous solution due to the large loss in electrostatic solvation energy which occurs. However, through addition or removal of a proton or a masking ion, an uncharged extractable species may be formed.

The most obvious way to make an ionic species extractable is to destroy its charge. This can be done by combining the solute ion of interest with an ion of opposite charge to a neutral molecular species. The larger, bulkier, and more hydrophobic the resulting molecule, the better will be its extraction.

An example is furnished by the anion of a phenol. By adjusting the pH of the aqueous phase,



the association of the phenolate ion with a hydrogen ion form the neutral phenol is controlled.



The chemical equilibria can be expressed by the association constant, K_{HA} ,

$$K_{\text{HA}} = \frac{(\text{C}_6\text{H}_5\text{OH})_{\text{aq}}}{(\text{C}_6\text{H}_5\text{O}^-)_{\text{aq}} (\text{H}^+)} \quad (21)$$

which is recognized as the reciprocal of the acidic dissociation constant. Only the neutral molecular species partitions between the contacting phases; the partition coefficient is given by

$$K_d = \frac{(\text{C}_6\text{H}_5\text{OH})_{\text{org}}}{(\text{C}_6\text{H}_5\text{OH})_{\text{aq}}} \quad (22)$$

The overall distribution ratio is expressed by

$$D = \frac{(\text{C}_6\text{H}_5\text{OH})_{\text{org}}}{(\text{C}_6\text{H}_5\text{OH})_{\text{aq}} + (\text{C}_6\text{H}_5\text{O}^-)_{\text{aq}}} \quad (23)$$

which is substituted by equation (21) and (22), becomes

$$D = \frac{K_d}{1 + 1 / K_{\text{HA}} (\text{H}^+)} \quad (24)$$

The equation (24) shows that the neutral molecular species is the dominant species in both phases at the higher concentration of hydrogen ion or

lower pH which can enhance the percent extraction.

2.7 SALTING OUT EFFECT (70.72-74)

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

$$\log S = \log S_0 - kM \quad (30)$$

Where S_0 is the solubility of the organic compound in the pure water.

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

M is the molarity of the salt.

k is a salting out constant whose value depends on the organic compound and on the nature of the salt. This equation is equivalent to

$$\log f = kM \quad (31)$$

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

When considering a system consisting of a small amount of an organic compound, varying concentrations of the salt in water, and organic solvent, the organic compound will be distributed between the water and the organic solvent. It assumes 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 condition, it can be proved that

$$D = fD_0 \quad (32)$$

Where D_0 is the distribution ratio in the absence of salt.

Combining equation (31) with equation (32) yields

$$\log D = \log D_0 + kM \quad (33)$$

Salting out effect can enhance the percent recovery of an organic compounds by increasing the ionic strength of the aqueous phase and increasing generally the distribution ratio.

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

Three major considerations influence the choice of salt are :

1. The salt must not interfere in the extraction of water samples.
2. The salt must have large salting out power.
3. The salt must have a high solubility.

2.8 CHOICE OF SOLVENT (69, 75-76)

The following factors and solvent properties can be used to consider the choice of extracting organic solvent for particular purposes in extraction in order to eradicate the major problems.

1. The solvent must be selective in its action. This refers to its ability to extract one component in a solution in preference to another. The interaction of solute and solvent will have a bearing on the selectivity of the solvent. If the solute is readily solvated by a given solvent, then it will be soluble in that solvent, hydrogen-bond formation between solute and solvent influences solubility and selectivity.

2. The solubility of the solute in a particular solvent is important, it should mutually soluble with the solute to be extracted in order to have a high value of distribution constant or distribution ratio so the solute will be readily extracted from water.

3. The ease of recovery of the solute from the solvent is also significant for subsequent analytical processing. Thus, the boiling point of the solvent should be high so that evaporation of solvent is not a problem or ease of stripping by chemical reagents enter into selection of a solvent when the

possibility of a choice exists.

4. The solvent must have a great density difference from water. The greater the difference in the solvent densities, the faster will be the rate at which the immiscible layers separate. Emulsions are more easily produced when the densities of the two solvents are similar.

5. The solvent must have a high interfacial tension for rapid separation of phases.

6. The solvent must be as immiscible with water as possible. One way of arriving at an excellent idea about the degree of immiscibility is through a comparison of the dipole moment of the liquid with that of water ($\mu = 1.84$ debyes). Solvent such as benzene, hexane, and carbon tetrachloride, etc., with dipole moments of zero have low water solubilities (less than 0.1 g/100 g), whereas solvents such as diethyl ether ($\mu = 1.2$ debyes), ethyl acetate ($\mu = 1.8$ debyes), or n-butyl alcohol ($\mu = 1.7$ debyes), etc., have relatively high aqueous solubilities (6.90, 7.94, and 7.80 g/100 g, respectively). This generalization has its exceptions, of course, chlorobenzene with a dipole moment of 1.6 debyes has an aqueous solubility less than that of benzene.

7. The viscosity of the solvent must be low to permit good contact between the two phases while

shaking and to rapid setting out of the two liquids after shaking.

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

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

11. The solvent should not be hazardous to the health. It should neither be toxic nor flammable.

12. The solvent should be inexpensive.

Sometimes it is possible to achieve many of the desired characteristics of a solvent by employing a mixed solvent system such as acetone/hexane which are mixed in the ratio of 1:1 for trace determinations of phenolic compounds in water in order to enhance the polarity of hexane phase, thus improving extraction (20).