

## CHAPTER II

### THEORY

#### 2.1 Liquid-Liquid Extraction

##### 2.1.1 Introduction

The liquid-liquid extraction process had been a powerful separation technique for a long time. Due to simple operation, this technique was used in wide separation industries. Demanding transfer of solute from one phase to the interface and thence into the other phase was the principle of this process (Bailes et al., 1976).

Bailes et al. also described that the rate of extraction was proportional to area and the derivation of the actual solute concentrations in the two phases from the equilibrium (not the simple difference in concentrations between the two phases).

Treybal (1980) defined the important words used in the liquid extraction, such as feed referred to the solution which was extracted, solvent referred to the liquid which was contacted to feed in this process. The solvent-rich product of the operation was called the "extract", and the residual liquid from which solute had been removed was the "raffinate". A simple schematic of liquid-liquid extraction was shown in figure 2.1.

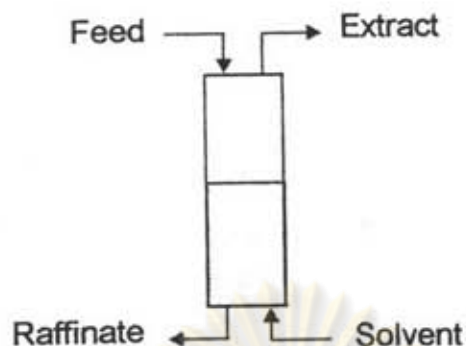


Figure 2.1. Single schematic of countercurrent liquid-liquid extraction

In a liquid-liquid extraction process, using solvent must be insoluble or at least soluble to only a limited extent in the extracted solution. In addition, the extracted solute should have a high affinity for the solvent (Hinos and Maddox, 1985).

For enhancing mass transfer performance of the system, mechanical agitation was used. The mechanical agitation increased the interfacial contact area of the two liquids and made one phase being in the form of drops dispersing through a continuum of the other phase. The drop phase was called the dispersed phase and the other was called the continuous phase (Bailes et al., 1976).

Considering the actual transport process, this might involve both molecular and eddy diffusion. The former arose from the general random movement of the molecules, which led to a net movement in the direction of a concentration gradient (thus tending to give a uniform overall concentration). Eddy diffusion arose from bulk movement of the fluid, usually resulting from some forms of turbulence. Molecular diffusion was a comparatively slow transport process. In a turbulent situation, eddy diffusion would be several orders of magnitude greater

than the molecular diffusion, thus it was normally desirable to promote it. If sufficient agitation was provided to create turbulent conditions, eddy diffusion was likely to predominate within the continuous phase, yielding a reasonably high mass transfer within that phase. However, agitation only affected the dispersed phase indirectly. When a drop was moving through a continuous phase, drag at the interphase tended to set up internal circulation of the drop contents. Large drops also oscillated in shape. Both phenomena promoted mixing of the contents of the drop, giving an effective eddy diffusion component and enhancing mass transfer in the dispersed phase. Whether this internal circulation occurred, mass transfer depended on the velocity of the drop relating to the continuous phase, the drop diameter, and the physical properties. The smaller the drop, the smaller the drag forces were relative to the force of inertia. As a result, small drops behaved as rigid spheres, and mass transfer within them was controlled by the slow process of molecular diffusion.

After a period of contact time of two liquids, coalescence of drop took place. Large and small occurred drops would have a tendency to aggregate at the interface between two liquids and introduce phase separation.

Laddha and Degalleson (1978) described that the interfacial effects at the drop-liquid boundary were two types of surface effect. The first was Marangoni effect. This effect was due to motion caused by local variations of interfacial tension which were caused in turn by differences in composition or temperature. The second was due to the departure from equilibrium tension that was produced by extension or contraction of an interface or dilational deformation. Surface instability which occurred Marangoni effect was usually associated with the transfer of a solute

and its direction of transfer. Interfacial tension was usually promoted by: (1) transferring of solute into the phase of lower viscosity or from the phase in which its diffusivity was lower; (2) large differences in kinematic viscosity and solute diffusivity between the liquid phases; (3) steep concentration gradients near the interface affecting the interfacial tension; and (4) diffusivities in both phases.

### 2.1.2 Extraction Equipment

The liquid-liquid extraction processes could be carried out by using many types of equipment. For a batch process, we could use a simple tank with an agitator in which two phases were mixed and then allowed to settle. In general industries, a lot of types of continuous multistage extractors were used.

Hinos and Maddox (1985) described a method to select extractor by using selection chart which had been developed by Hanson (1968) and Laddha and Degaleesan (1978). They said that the criteria considered when selecting a contactor were settling characteristic, number of stages required, space availability, volume throughput, and contact time. The selection chart given in figure 2.2 summarized the important factors to be considered in selecting the extractor.

The advantages and disadvantages of different extraction equipment were shown in table 2.1.

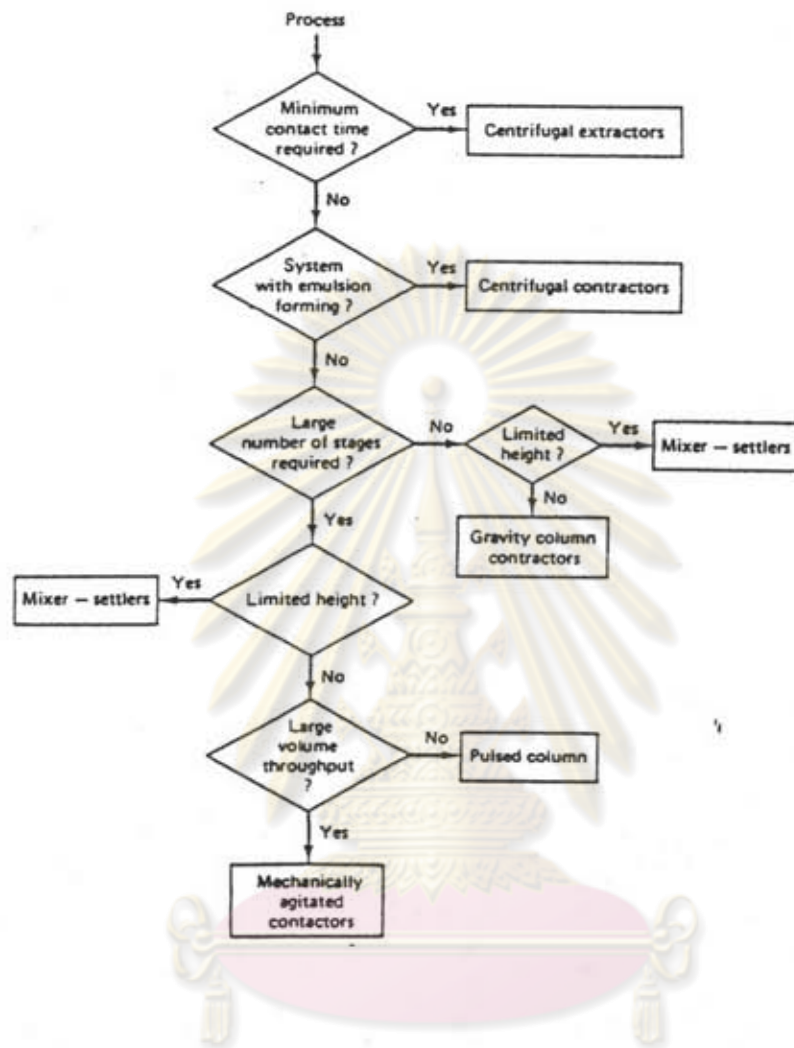


Figure 2.2 Select chart for liquid-liquid contactors

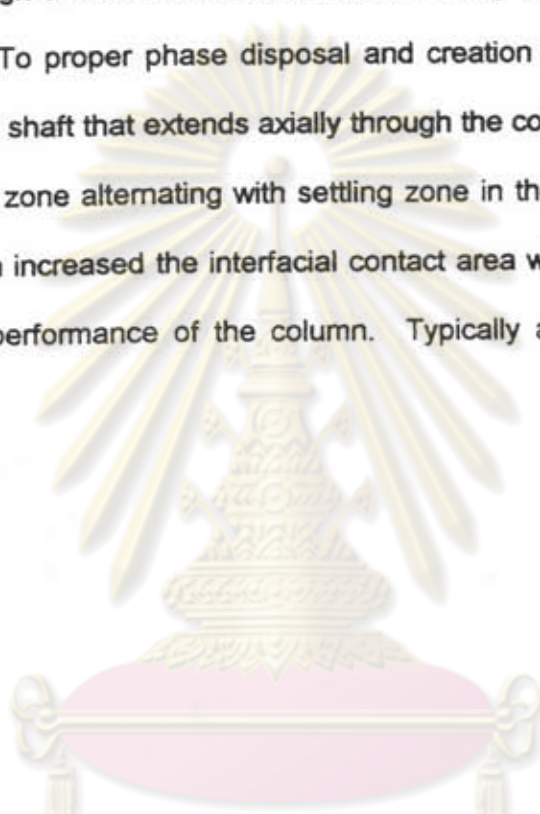
ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

Table 2.1 Advantages and disadvantages of different extraction equipment

Class of Equipment	Advantages	Disadvantages
Mixer-settler	<ul style="list-style-type: none"> <li>Good contacting</li> <li>Handles wide flow ratio</li> <li>Low headroom</li> <li>High efficiency</li> <li>Many stages available</li> <li>Reliable scale up</li> </ul>	<ul style="list-style-type: none"> <li>Large holdup</li> <li>High power costs</li> <li>High investment</li> <li>Large floor space</li> <li>Interstage pumping may be required</li> </ul>
Continuous counterflow contactors (no mechanical driven)	<ul style="list-style-type: none"> <li>Low initial cost</li> <li>Low operating cost</li> <li>Simplest construction</li> </ul>	<ul style="list-style-type: none"> <li>Limited throughput with small density difference</li> <li>Cannot handle high flow ratio</li> <li>High headroom</li> <li>Sometimes low efficiency</li> <li>Difficult scale-up</li> </ul>
Continuous counterflow (mechanical agitation)	<ul style="list-style-type: none"> <li>Good dispersion</li> <li>Reasonable cost</li> <li>Many stages possible</li> <li>Relatively easy scale up</li> </ul>	<ul style="list-style-type: none"> <li>Limited throughput with small density difference</li> <li>Cannot handle emulsifying systems</li> <li>Cannot handle high flow ratio</li> </ul>
Centrifugal extractors	<ul style="list-style-type: none"> <li>Handles low density difference between phases</li> <li>Low holdup volume</li> <li>Short holdup time</li> <li>Low space requirements</li> <li>Small inventory of solvent</li> </ul>	<ul style="list-style-type: none"> <li>High initial costs</li> <li>High operating costs</li> <li>High maintenance costs</li> <li>Limited number of stages in single unit</li> </ul>

### 2.1.3 Mechanically agitated column extractor (Henley and Seader, 1981)

Mechanically agitated column extractor could handle systems having problems such as high surface tension and/or low density differences between the two liquid phases. To proper phase disposal and creation of turbulence, rotating agitators driven by a shaft that extends axially through the column were arranged to create shear mixing zone alternating with settling zone in the column. In addition, mechanical agitation increased the interfacial contact area which greatly enhanced the mass transfer performance of the column. Typically agitated columns were shown in figure 2.3.



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

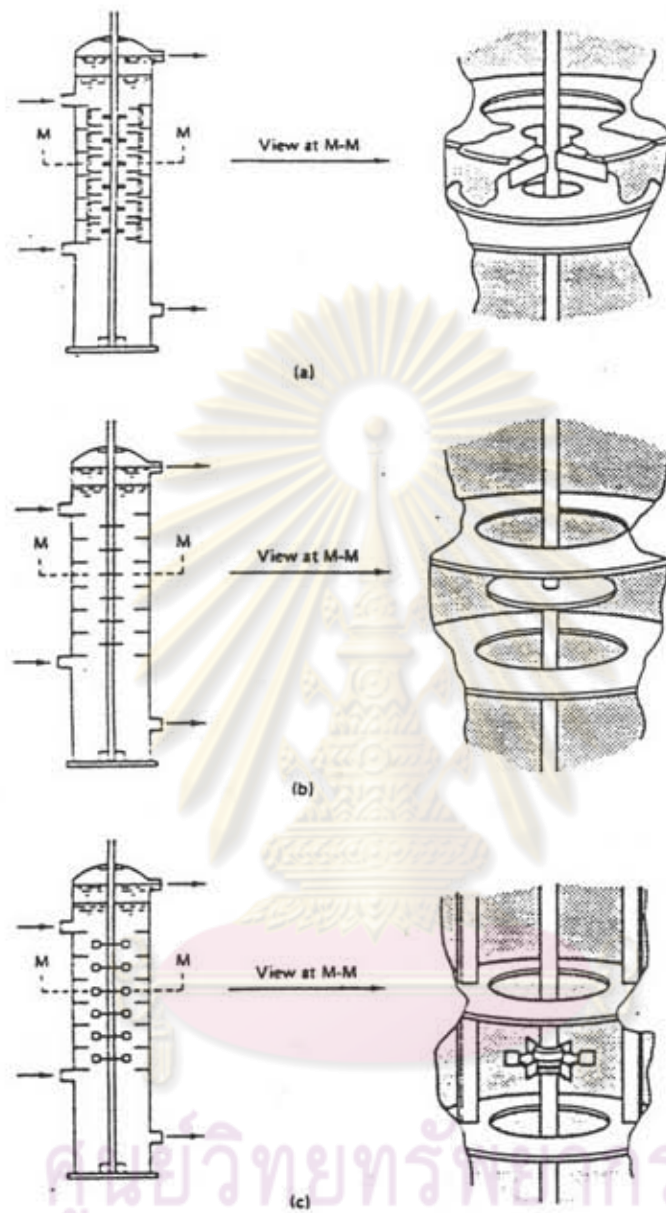


Figure 2.3 Typically agitated columns : (a) Scheibel column; (b) rotating disk column; (c) Oldshue- Rushton column.



For liquid phase equilibrium, the factor that determined the amount of solute in two liquid phases was distribution coefficient (or liquid-liquid equilibrium ratio).  $K$  was defined for each species by

$$K = X^I / X^{II}$$

Where superscript I meant the first phase and II meant the second phase. As assumption for this system, the feed and solvent were mutually insoluble. It was more convenient to define the distribution coefficient for solute in term of mass ratios,

$$X^I = (\text{mass of solute}) / (\text{mass of solvent})$$

and

$$X^{II} = (\text{mass of solute}) / (\text{mass of feed})$$

Hence

$$\begin{aligned} K &= (X^I / X^{II}) \\ &= (X^S / X^F) \end{aligned}$$

Since the solute was the only species transferring between the two phase. Let I = S for solvent phase and let II = F for the feed phase.

In a separation operation, we could use single equilibrium stage or multiple stages in order to get maximum percentage of extraction.

For a single stage, as shown in Fig 2.4 (a), a mass balance on solute gave

$$FX_0^F + SX_0^S = FX_1^F + SX_1^S \quad (2.1.4-1)$$

Where F and S were the mass flow rate of feed and solvent, respectively.

Assuming the exit streams were at equilibrium.

$$K = \frac{X_1^S}{X_1^F} \quad (2.1.4-2)$$

Combining equations (2.1.4-1) and (2.1.4-2) to eliminate  $X_1^S$  and solving for  $X_1^F$ , we found that the mass ratio of solute to feed in the exit raffinate phase was given by

$$X_1^F = \frac{X_0^F + (S/F)X_0^S}{1+E} \quad (2.1.4-3)$$

Where E was the extraction factor (SK/F). The percentage of extraction of solute was  $[100 \cdot (X_0^F - X_1^F)]/X_0^F$ .

In the countercurrent flow arrangement shown in figure 2.4(b), feed entered the first stage, while the entire solvent entered the final stage. Two liquids were passed from stage to stage counter to each other. For example, we had two stages counter current arrangement. Mass balance on each stage was given by

For the first stage,

$$FX_0^F + SX_2^S = FX_1^F + SX_1^S \quad (2.1.4-4)$$

For the second stage,

$$FX_1^F + SX_0^S = FX_2^F + SX_2^S \quad (2.1.4-5)$$

To calculate  $X_1^F$ , we required the value for  $X_2^S$ , but  $X_2^S$  was not initially known. This difficulty was circumvented by combining the following step equations to eliminate  $X_1^F$  and  $X_2^S$ .

$$X_1^F = \frac{X_0^F + (S/F)X_2^S}{1+E} \quad (2.1.4-6)$$

$$X_2^F = \frac{X_1^F + (S/F)X_0^S}{1+E} \quad (2.1.4-7)$$

$$X_2^S = X_2^F K \quad (2.1.4-8)$$

Solving for  $X_2^F$  gave the following relation for the two countercurrent equilibrium stages with  $X_0^S = 0$  :

$$X_2^F = \frac{X_0^F}{1+E+E^2} \quad (2.1.4-9)$$

In general, for N countercurrent equilibrium stages, similar combinations of stage equations with  $X_0^S = 0$  led to the equation.

$$X_N^F = \frac{X_0^F}{\sum_{n=0}^N E^n} \quad (2.1.4-10)$$

The limitation of above equation as N approaching to  $\infty$  depended on the value of E as following equations.

$$X_\infty^F = 0, \quad 1 \geq E \geq \infty \quad (2.1.4-11)$$

$$X_\infty^F = (1-E)X_0^F, \quad E \geq 1 \quad (2.1.4-12)$$

Therefore we should select solvents and solvent rate which gave extraction factor greater than 1.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

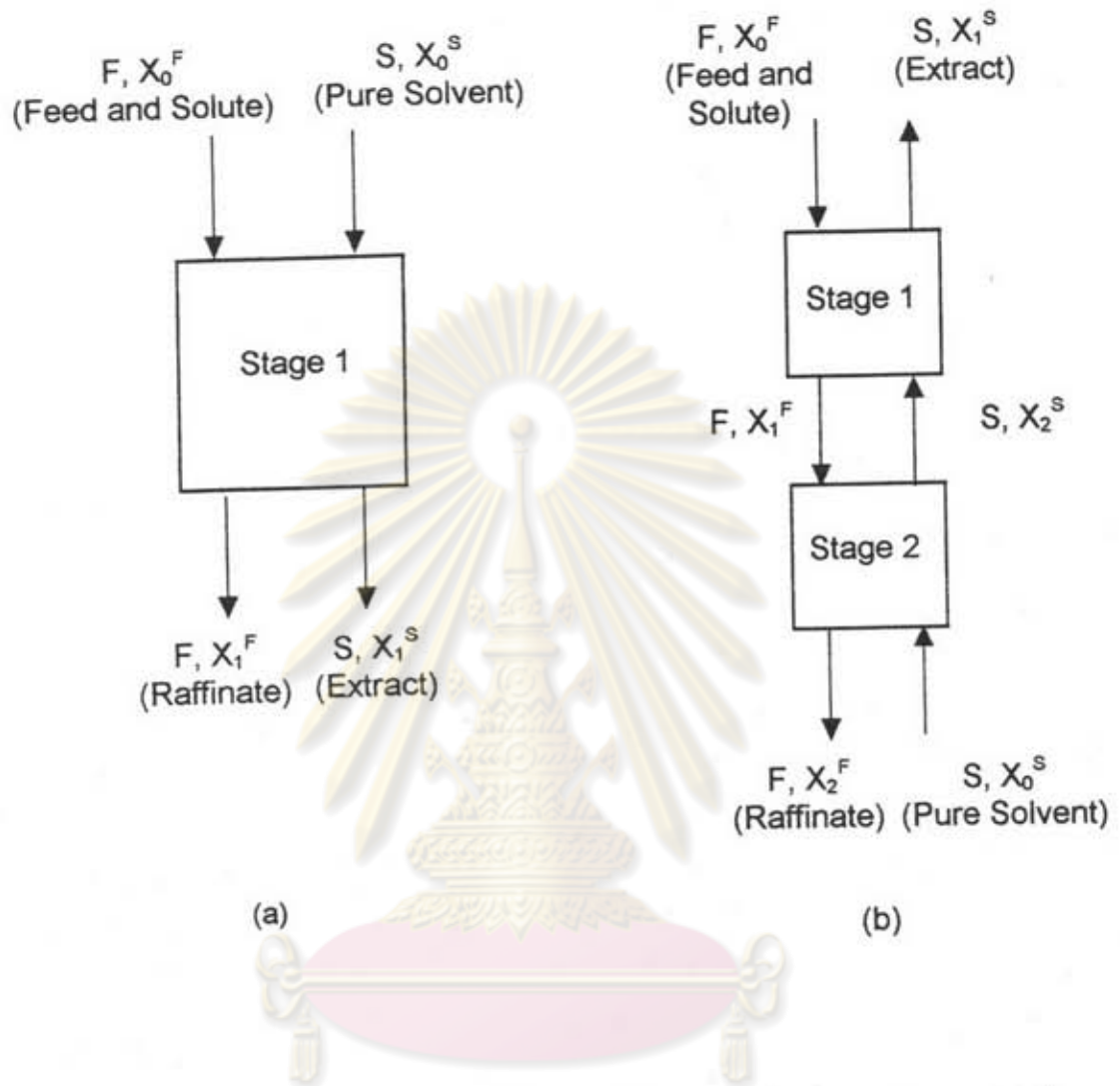


Figure 2.4 Single and multiple-stage arrangements (a) single stage arrangement.

(b) two-stage countercurrent arrangement.

ศูนย์วิทยาศาสตร์สุขภาพ  
จุฬาลงกรณ์มหาวิทยาลัย

## 2.2 Surfactant

### 2.2.1 Definition and Structure

Surfactants were one of the most unique and versatile classes of the chemical compounds. They were used in such diverse products as the motor oils we used in our automobiles, the detergents we used in cleaning our laundry and our homes, the drilling muds used in prospecting for petroleum, etc.

A surfactant (a contraction of the term surface-active agent) was substance that, when presented in low concentration in the system, had the property of adsorbing onto the interfaces of the system and of altering to a marked degree interfacial free energies of those surfaces (or interfaces). The term interface indicated a boundary between any two immiscible phases (Rosen,1988). In the circumstance that the phase boundary area of the system was so large relative to the volume of the system. A substantial fraction of the total mass of the system was presented at boundaries (e.g., in emulsions, foams, and dispersions of solids). The surfactants could always be expected to play a major role in the system.

Surface-active agents had a characteristic molecular structure consisting of a structural group that had very little attraction for the solvent, known as a lyophobic group, together with a group that had strong attraction for the solvent, called the lyophilic group. This structure was known as an amphipathic structure. When a surfactant was dissolved in a solvent, the presence of the lyophobic group in the interior of the solvent might cause distortion of the solvent

liquid structure, increasing the free energy of the system. If water acted as a solvent, the lyophobic could be called hydrophobic group and the lyophilic could be called hydrophilic group. The hydrophobic group was usually a long-chain hydrocarbon residue. The hydrophilic group was an ionic or highly polar group. The structural molecule of surfactant could be shown in figure 2.5.

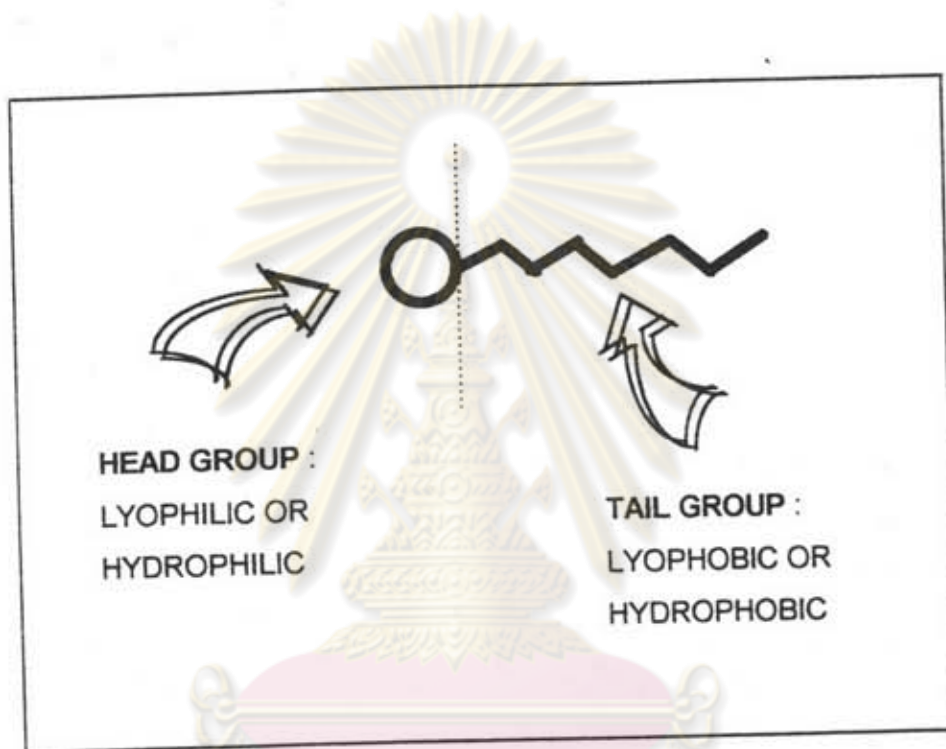


Figure 2.5 Structural molecule of surfactant.

ศูนย์วิทยาศาสตร์  
จุฬาลงกรณ์มหาวิทยาลัย

The presence of the surfactant decreased the work needed to create unit area of surface (the surface free energy per unit area, or surface tension). On the other hand, the presence of lyophilic group prevented the surfactant from being expelled completely from the solvent as a separate phase. The amphipathic structure of the surfactant caused not only concentration of the surfactant at the interface and reduction the surface tension of the water, but also orientation of the molecule at the interface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

In a highly polar solvent such as water, the lyophobic group might be a hydrocarbon or fluorocarbon, whereas in the less polar solvent only some of these might be suitable (e.g., fluorocarbon or siloxane chains in polypropylene glycol). In a polar solvent such as water, ionic or highly polar groups might act as lyophilic groups whereas in a nonpolar solvent they might act as lyophobic groups.

The surfactants were classified by depending on the nature of the hydrophilic group. That were :

- (1) Anionic. The surface-active portion of the molecule bore a negative charge.
- (2) Cationic. The surface-active portion of the molecule bore a positive charge, for example,  $\text{RNH}_3^+\text{Cl}^-$  (salt of a long-chain amine).
- (3) Zwitterionic. Both positive and negative charges might be present in the surface-active portion, for example,  $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$  (long-chain amino acid).



- (4) Nonionic. The surface-active portion bore no apparent ionic charge, for example,  $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$  (monoglyceride of long-chain fatty acid).

### 2.2.2 Micellization

At low concentration, surfactants dissolved in water were characterized of molecule. Hydrophobic portion of molecules distorted the structure of the solution and therefore increased the free energy of the system. At sufficiently high concentration in solution, surfactant molecules would nucleate to form aggregation called micelles (Scamahorn et al., 1993). The hydrophobic portions were directed toward the interior of the micelles while their hydrophilic portion were directed toward the aqueous solution. These reduced the free energy of the system (Rosen, 1988). Although micellization resulted in a decrease in the free energy of the system, the loss of the several translational degree of freedom of monomers in being confined to the micelles, and also the electrostatic repulsion in the case of ionic surfactant, between the hydrophilic head groups caused free energy increase, thus opposing micellization. Therefore micellization depended upon the balance between the factors promoting and opposing it (Warophat Kimchuwant, 1995). The concentration at which this occurred was characteristic of each surfactants and was called critical micelle concentration (CMC). Porter (1991) reported that the micelles behaved as large molecules and influenced two important properties that were solubility of organic hydrocarbons and oils in aqueous solution and viscosity of the solution. The picture of spherical micelle formation was shown in figure 2.6.

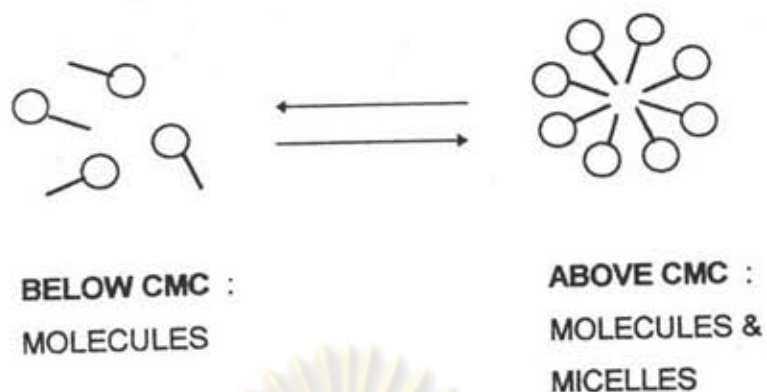


Figure 2.6 Spherical micelle formation

In surfactant-based separations, surfactant was known that it could improve separation of metal ions from waste water. The micelle of anionic surfactant could bind positive charges of metal ion by electrostatic attraction. The characteristic of binding metal ion by micellar phenomena was shown in figure 2.7.

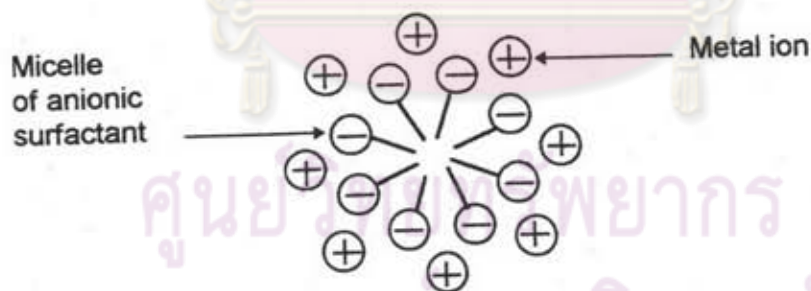


Figure 2.7 Characteristic of binding metal ion of anionic micelle

The majority of surfactants was the most stable thermodynamic state, being dependent upon the relative size of the hydrophobic and hydrophilic group. Spheres were the common shape of the micelle at concentrations just above the CMC which would be less than 1% concentration for most surfactants. As the concentration of the surfactant was over CMC value, then the solution properties showed strange behavior in solubility and viscosity. The reason for this behavior was suggested that the micelles changed shape as the available free space decreased. The first change was to lamellar micelles where they could form lamellar sheets or take the form of long cylinders.

The surfactant solution with spherical micelles behaved like Newtonian liquid, i.e. the viscosity was dependent upon shear rate and not very different from water. The transition from spherical to cylindrical or lamella micelles resulted in a large viscosity increase which changed to non-Newtonian, i.e. dependent upon shear rate. At a certain concentration, the solution were so viscous that a gel was formed. The cylindrical micelles were usually formed at medium concentration and usually represented the maximum viscosity. At higher concentrations of surfactant, the lamellar phase was formed with water trapped between the surfactant double layers. Thus, in aqueous solution, many surfactants would be soluble at low concentration (up to 25 to 35%), then give very viscous solutions or gel at concentrations in the range 60 to 80%, followed by viscous solution at 70 to 90% concentrations. The molecules in the micelles were not fixed but they were in dynamic equilibrium. In dilute solution, micelle formation and micelle disintegration could occur in fraction of a second in spherical micelles. In the case of the formation of lamellar of cylinder shaped micelles, the formation of micelles was much slower and could take hours or days.

If a water insoluble compound (e.g. a hydrocarbon oil) was added to an aqueous solution of a surfactant. There were the possibility of :

(a) *O/W* emulsion: this consisted of two liquid phases, the oil phase dispersed as globules in the continuous water phase. The appearance of such a system was opaque and white in color. The unstable systems were found and separated after settling. They showed high electrical conductivity.

(b) *W/O* emulsion: this consisted of two liquid phases, the water phase dispersed as globules in the continuous oil phase. The appearance of such a system was opaque and white in color. The unstable systems were found and separated after settling. They showed low electrical conductivity.

(c) Solubilization of the oil in the water/surfactant: the oil apparently dissolved in the aqueous solution. The appearance of the solution was the same as before the oil added. Such system were stable and did not separated on standing. They showed high electrical conductivity.

(d) The formation of microemulsion: the oil dissolved on disperses in the aqueous solution. The appearance was a transparent or translucent solution which often gave a colored solution (reddish orange to blue). Such system were stable and did not separated on standing. They showed high electrical conductivity.

### 2.2.3 Solubilization

Solubilization might be defined as the spontaneous dissolving of a substance by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution which reduced thermodynamic activity of the solubilized material.

If the solubility of a normally solvent-insoluble material was plotted against the concentration of the surfactant solution that was solubilizing it, we found that the solubility was very slight until a critical concentration was reached at which the solubility increased approximately linearly with the concentration of the surfactant. That critical concentration was the CMC of the surfactant in the presence of the solubilize. Plot amount of material solubilized as a function of concentration of the surfactant in the bulk phase was shown in figure 2.8. This indicated that solubilization was a micellar phenomenon.

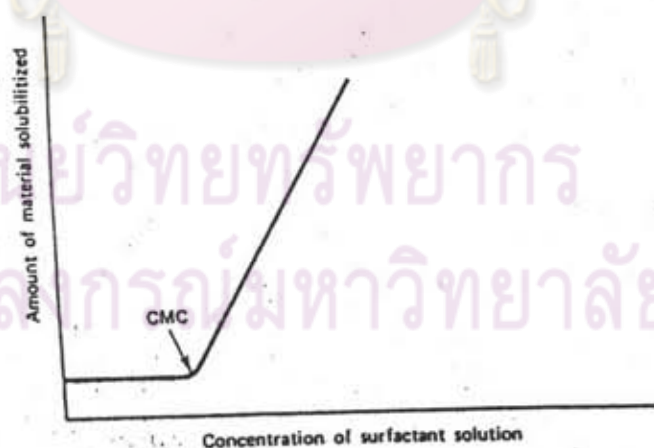


Figure 2.8 Plot amount of material solubilized as a function of concentration of the surfactant in the bulk phase.

It was well established that the location of a solubilized molecule in a micelle relative to the structural components of the surfactant would be determined primarily by the chemical structure of the additive. In aqueous solutions, nonpolar additives such as hydrocarbon were intimately associated with the core of the micelle (Myers, 1992). This phenomenon could be shown in figure 2.9.

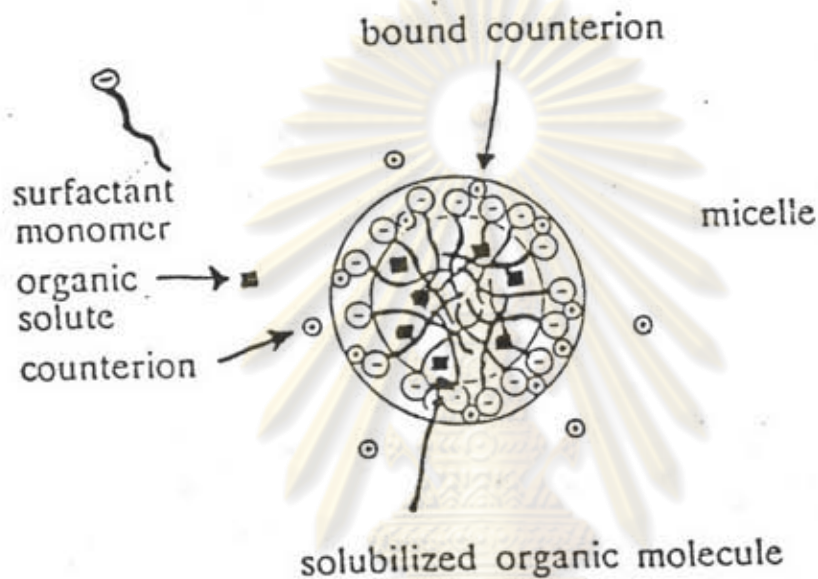


Figure 2.9 Solubilization phenomenon

#### 2.2.4 Emulsion

An o/w emulsion were produced by emulsifying agents that were more soluble in the water than in the oil phase while w/o emulsion were produced by emulsifying agents that were more soluble in the oil phase than in the water phase (Scamahorn et al., 1993). The most frequently method for selecting suitable surfactant for any system could be known in the Hydrophilic/Lipophilic Balance (HLB method).

This method could be roughly correlated with the dispersion behavior of the pure surfactant in water (See table 2.2).

Table 2.2 Relationship between HLB value and dispersion behavior.

HLB value	Dispersion behavior
1-4	No dispersibility
3-6	Poor dispersion
6-8	Milky dispersion after vigorous shaking
8-10	Stable milky dispersion upper and almost translucent
10-13	Form translucent to clear dispersion
>13	Form clear solution

The application of HLB method could be seen in table 2.3.

Table 2.3 HLB ranges and their general areas of application.

Range	Application
1-3	Reverse micelles
3-6	W/O emulsion
7-9	Wetting
8-13	OW emulsion
3-15	Detergency
15-18	Solubilization

From table 2.3, the surfactants having HLB value in the range of 8 to 18 were selected for making o/w emulsion and used for solubilization applications.

Emulsion droplets, for instance, could never be perfectly monodispersed; as a result, they were possible for smaller droplets to locate themselves in the space between closed-packed and larger droplets to increase the total potential packing density of the system. Large excursions spherical were, of course, generally unfavorable, since they entailed the formation of additional interfacial area for a given dispersed volume fraction. As mentions above, such an increase in interfacial area could strain the ability of adsorbed emulsifier film to the point of droplet coalescence.

As two emulsion droplets approached and contacted each other during the process of flocculation or coalescence, a thin lamellar film of the continuous phase liquid would form in the intervening space. If that film destroyed, coalescence of the drops would occur. If the film remained intact, but droplet adhesion occurred, flocculation was the result. If film destruction occurred, it usually took place at a specific spot in the film excessively thinned out by the mechanical cation of the approaching drops in stretching the film or of depletion of emulsifier as a result of deformation and increase in the interfacial area.

The presence of almost any surfactants would affect to an increase in the stability of most oil-water systems subjected to agitation. The action of many organic materials, even those not normally considered to be surfactants, in lowering the interfacial tension between the water and the oil phases affected both the eases



with which the interfacial area could be increased and the rate at which individual droplets would coalesce and lead to complete phase separation.

From figure 2.10, we could see two phenomena that occurred after primary emulsion. The definition of two important words concerning to this process could be described. Firstly, coalescence referred to the jointing of two (or more) drops to form a single drop of greater volume, but smaller interfacial area (See figure 2.10a). Such a process was obviously energetically favorable in almost all cases. The second was breaking of an emulsion (See figure 2.10b). It referred to a process in which a gross separation of the two phases occurred. This process was a macroscopically apparent consequence of the microscopic process of drop coalescence. In such an event, the identity of individual drops was lost, along with the physical and chemical properties of the emulsion. Such a process obviously represented a true loss in the stability the emulsion.



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

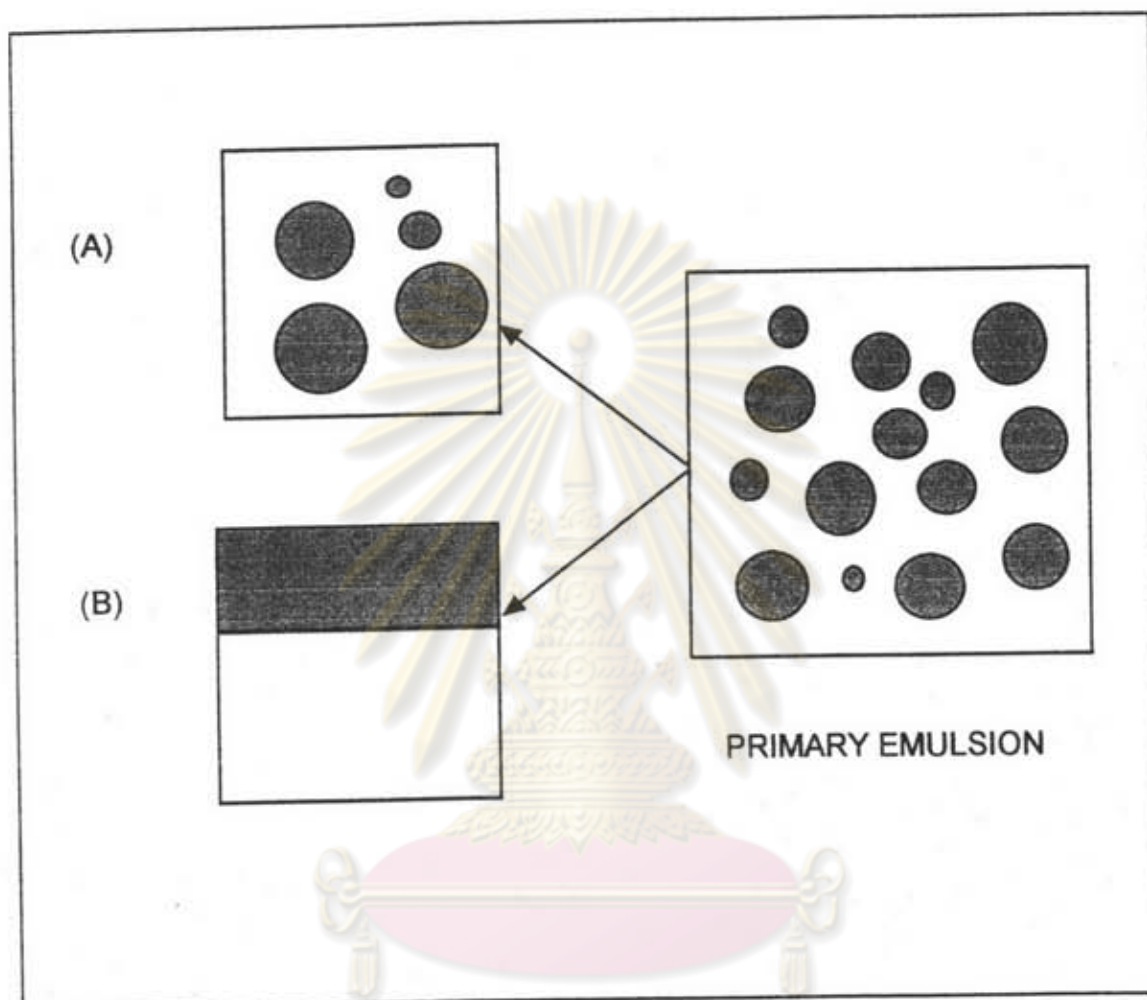


Figure 2.10 Ultimate fate of emulsions relates to colloidal stability :

(a) coalescence; (b) breaking.