CHAPTER 3
THEORY

There are two types of liquid membrane, which can be classified by configulation of membrane phase as mentioned in Chapter 2. The first is known as a suppported liquid membrane (SLM) and the second is an emulsion liquid membrane (ELM).

3.1 Supported Liquid Membrane (SLM)

In supported liquid membrane technique [Figure 3.1], an organic liquid is immobilized in the pore of a microporous membrane interposed between two aqueous solutions. At the interface between the feed solution and the membrane, the solute is extracted into the liquid membrane where the strip aqueous flow. At the strip solution and membrane interface, the solute is back extracted into the strip solution. Often the solute obtained is in a highly concentrated form in the strip solution (Bloch, 1970 and Cussler, 1971).

SLMs have many advantages; a high separation factor in each stage, low capital operating and energy costs, very low inventory of extractants (or membrane liquid), no extractant loss due to poor coalescence as in solvent extraction, and fewer moving parts resulting in lower maintenance costs.

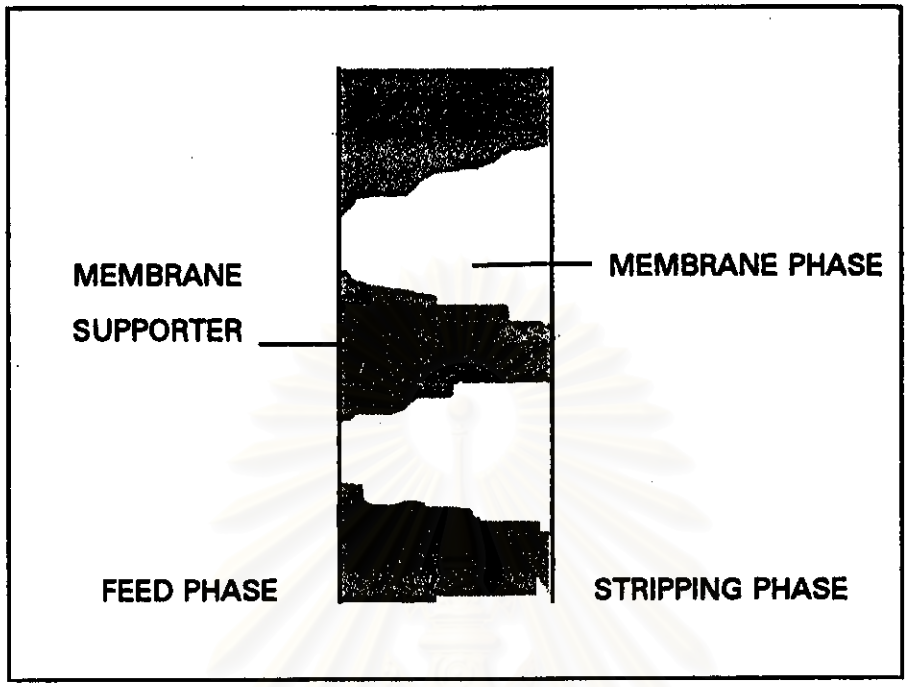

Figure 3.1 Schematic Diagram of a Supported Liquid Membrane

To obtain large interfacial areas for mass transfer, various types of supports have been used, i.e. ultrafiltration membrane cartridges, and semi-permeable membranes used in reversed osmosis. The most popular solid support used are generally microporous polymeric film made of polypropylene, polysulfone or hydrophobic materials. Generally dimensions are 25-50 μm in membrane thickness, 0.02-1.0 μm in pore sizes (Danesi, 1984-1985).

The application of SLM has mainly been considered under the following categories :

a. Wastewater treatment,

b. Metal extraction concentration, and

c. Fermentation product recovery.

3.2 Emulsion Liquid Membrane (ELM)

An emulsion liquid membrane consists of three phases as shown in Figure 3.2

a. The external (continuous) phase in which the emulsion globules are dipersed,

b. The membrane phase which forms emulsion with the internal phase, and

c. The internal (stripping) phase which is encapsulated by the membrane phase.

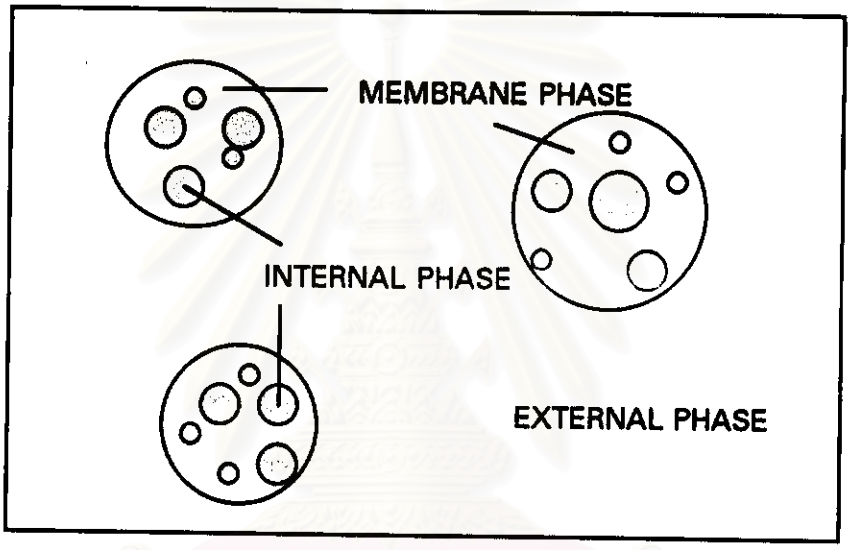

Figure 3.2 Schematic Representation of an Emulsion Liquid Membrane

In the emulsion liquid membrane process, the membrane is a liquid phase moving an emulsion configuration. Sometimes this is also called surfactant liquid membrane or liquid surfactant membrane. They are two types of ELM system, i.e. water/oil/water (w/o/w) and oil/water/oil (o/w/o) systems. In the case of w/o/w systems, the oil phase separating the two aqueous phases is the liquid membrane while for the o/w/o systems, the water phase is the liquid membrane, separating the two oil phases.

An emulsion liquid membrane is usually prepared by first forming an emulsion between two immiscible phases, and then dispersing the emulsion in the third phase

(continuous phase) by agitation for extraction. Many small globules of emulsion are formed. The size of the globules depends on concentration and characteristics of the surfactant in the emulsion, the viscosity of the emulsion and the mode and intensity of mixing (Ohtake, Hano, Takagi and Nakashio, 1987). The size of the globule is 100 to 2000 μm in diameter. Each emulsion globule contains many internal droplets of 1 to 3 μm in diameter. So the internal mass transfer area is about 10^6 m^2/m^3 (Rautenbach and Machhammer, 1988; Ho, 1986). It should be noted that the internal encapsulated phase and the external (continuous) phase are miscible. However, the membrane phase must not be miscible with either of these two phases in order to be stable. To maintain the integrity of the emulsion during the extraction process, the membrane phase generally contain some surfactant as a stabilizing agent, carrier as a facilitated agent and a base material that is solvent.

The solute partitions into the organic phase of the emulsion diffuses through this phase and they are stripped at the interface with the aqueous droplets (internal phase) inside the emulsion. A rapid mass transfer in emulsion liquid membrane process can occur from either the external phase to the internal phase.

The concentration of the solute occurs when the volume of the internal phase is made smaller than that of the feed phase. After the process has been contacted, the emulsion is allowed to settle out from the external phase and the internal phase (extracted solute) is recovered by breaking the emulsion.

Separation of mixtures can be achieved by selective diffusion of a component through the membrane phase into the internal (stripping) phase of lower equivalent concentration. Surfactant and carrier in the membrane phase can control the selectivity and permeability of the membrane. A component can be trapped and concentrated in the internal phase for later disposal or recovery. After separation, the external and emulsion phases are separated by settling in a separatory funnel until it

divides into two distinct phases. The extracted component can be recovered from the loaded internal phase of the emulsion by breaking the emulsion. It has many ways of breaking the emulsion such as heating, centrifugal, ultrasonic, solvent dissolution, high shear and electrostatic coalescer (Martin and Davies, 1977 and Yan and Wang, 1988).

As discussed above, a schematic of a continuous ELM process is shown in Figure 3.3. This process includes four steps:

1. Emulsification,
2. Dispersion of the emulsion in contact with the external phase for extraction,
3. Settling to separate the emulsion from the external phase which is the raffinate if the internal phase becomes the extract, and
4. Breaking the emulsion to recover the internal phase as the extract and the membrane phase for recycle.

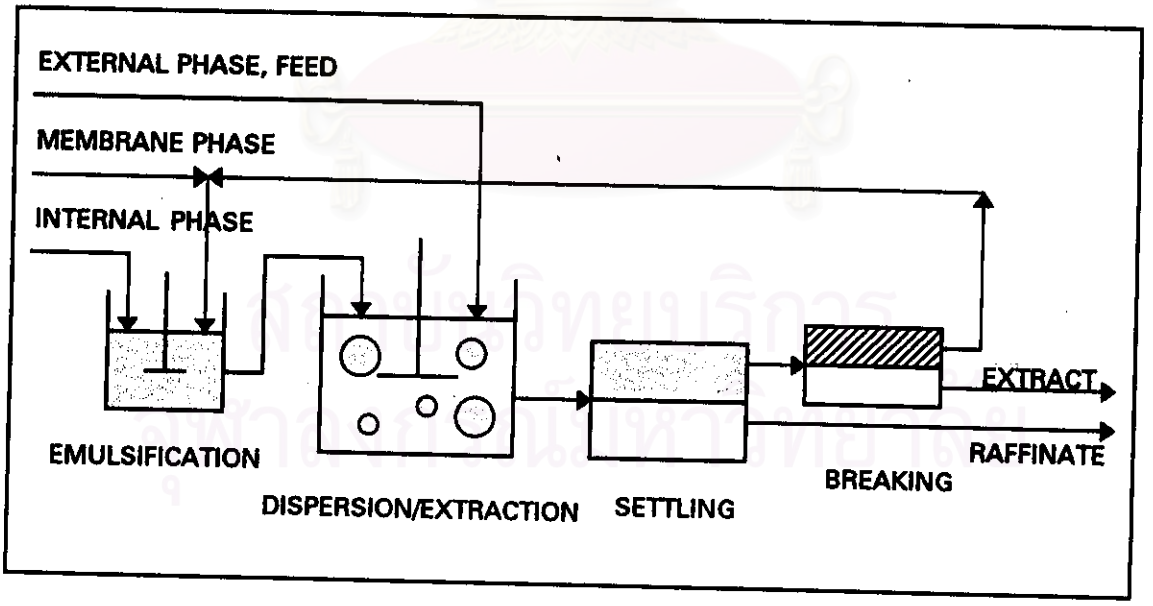

Figure 3.3 Schematic of a Continuous Emulsion Liquid Membrane Process

3.3 A Form of Solvent Extraction

Liquid-Liquid Extraction is a separation technology which has found wide application in the separation of biomolecules. This operation relies on the partitioning of the solute between an aqueous and organic phase. The equilibrium can be related by means of distribution (partition) coefficient, K_D

$$K_D = \frac{C_2}{C_1} \qquad ...(3.1)$$

where C_1 and C_2 are the concentration at equilibrium of the solute in the aqueous feed phase and the extracting solvent phase, respectively. After the solute has partitioned into the organic solvent, the solute is usually stripped or re-extracted back into an aqueous phase.

In emulsion liquid membrane extraction, the emulsion phase can be considered to be an extracting solvent phase. Extraction and stripping occur simultaneously on both sides of the membrane and under non-equilibrium conditions.

In solvent extraction, the distribution (partition) coefficient can be increased by other conditions such as pH, temperature and etc. or by the introduction of an extractant into the organic phase, to increase the solubility (Likidis and Schugerl, 1987). Therefore, solvent extraction can be applied to liquid membrane extraction to enhance extraction efficiency and improve selectivity.

Liquid membrane extraction has several advantages over solvent extraction. As the liquid film is very thin and high specific interfacial areas are available for mass transfer, separation is fast. As only one extraction stage is required with respect to solvent extraction, there is a reduction in equipment and solvent requirements. Two obvious disadvantages of emulsion liquid membranes are the formation of emulsion

and the requirement for an emulsion breakage operation to recover the extracted product.

3.4 Facilitated Mechanism and Driving Forces

There are two facilitated mechanisms of solute transport across the membrane phase (Matulevicius and Li, 1975). They are unfacilitated transport and facilitated transport.

3.4.1 Unfacilitated Transport

In this transport, the solute transports through the membrane phase in the absence of any carrier species by diffusion process. The reaction in the internal phase maintains a solute concentration of effectively zero. This is the minimization of the diffusing species in the internal phase. The reaction of the diffusing species with a chemical reagent in the internal phase forms a product incapable of diffusing back through the membrane. The driving force for transport is the chemical potential difference in the solute across the membrane phase.

The driving force can be managed by the inclusion in the internal phase of a chemical reagent which reacts with the solute. Now the solute is in a different form which, if insoluble in the organic solvent, it cannot back-diffuse or the concentration of the transportable species in the internal phase, is effectively zero and hence the concentration gradient is maximized, as mentioned above, thus enhancing mass transfer.

3.4.2 Facilitated Transport

In this type of transport which is also called carrier facilitated transport, the solute transports through the membrane phase in present of carrier species. The carrier compound carries the diffusing species and reactions take place both at the external interface between the external and membrane phases and the internal interface between the membrane and internal phases. This application is for membrane-insoluble materials, such as charge species, e.g. organic acids, switterions and metal ions. The solute is transported across the membrane by the reversible formation of the carrier-solute complex. There are two possible ways of carrier mechanism: counter-transport mechanism and co-transport mechanism.

3.4.2.1 Counter-Transport Mechanism

The solute is transported across the membrane by the formation of a complex and the driving force of the difference between the activities of the counter-ion in the internal and external phases (Lorbach and Marr, 1987) [Figure 3. 4] as follows:

a. At the interface between the external and membrane phases, the solute (A) reacts with the carrier complex (BC), to form the carrier-solute complex (AC) and liberates the part of carrier (B) in the external phase. The carrier-solute complex is insoluble in either aqueous phase but it is soluble in the membrane phase.

b. The carrier-solute complex diffuses across the membrane to the interface with the internal phase.

c. At the interface with the internal phase, the reverse reaction occurs brought about by a shift in the reaction equilibrium due to the higher concentration of the counter-ion (B), in the internal phase. Hence the solute is released into the internal phase reagent.

d. The carrier reacts with the counter-ion to form the carrier complex (BC), which diffuses back through the exterior interface where the counter-ion is released, hence completing the process.

3.4.2.2 Co-Transport Mechanism.

This mechanism is less common mode of facilitated transport than counter transport mechanism [Figure 3. 5]. The carrier (C) is reacting reversibly with the solute (A) and the other component (B), and transporting them in one direction across the membrane. The free carrier diffuses back across the membrane, therefore, two coupled fluxes exist across the membrane in the same direction (Cussler, 1984).

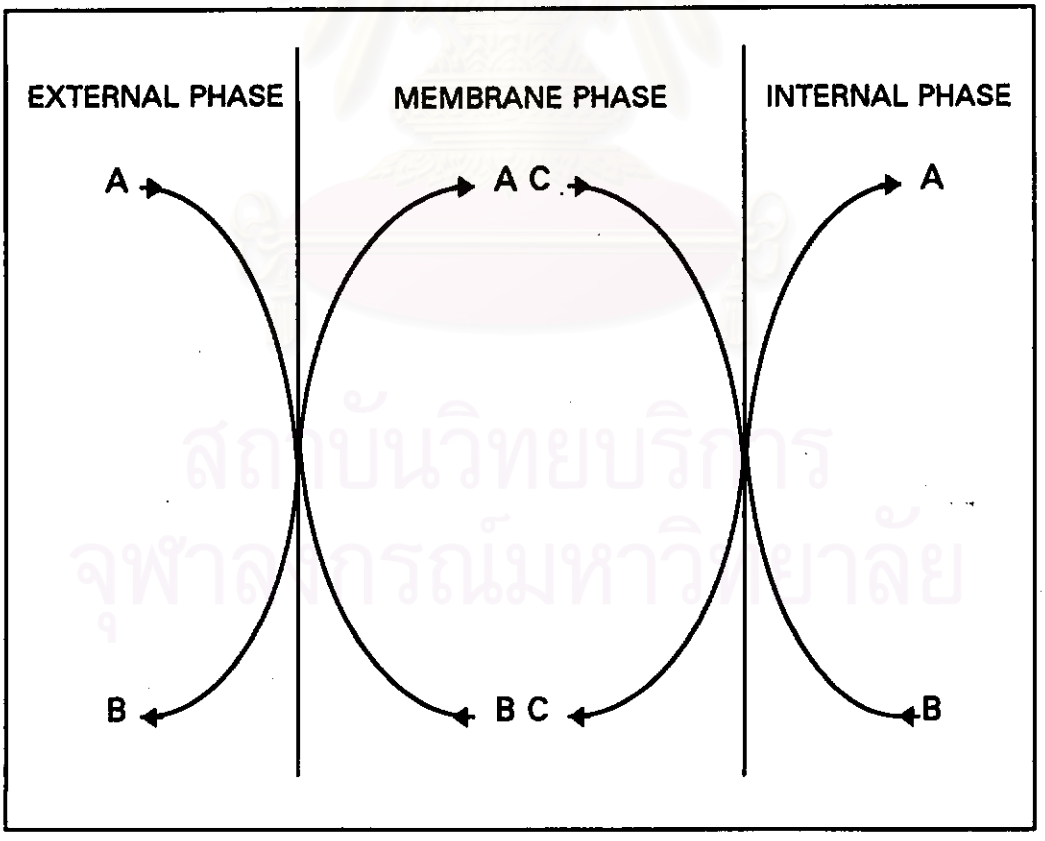

Figure 3. 4 Schematic of Counter Transport of Solute A by Carrier C

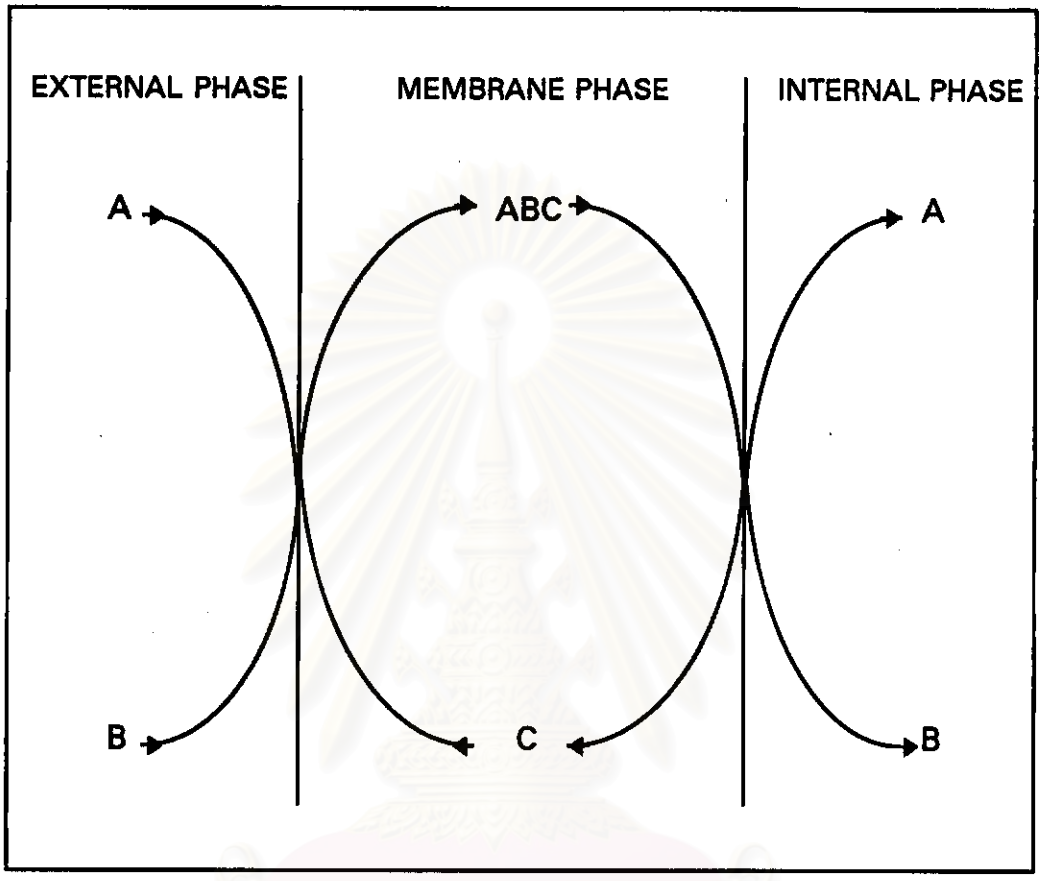

Figure 3. 5 Schematic of Co-Transport of Solute A and B by the Carrier C

3.5 Process Considerations

This part deals with practical considerations for emulsion liquid membrane extraction. This process includes three steps: emulsification, dispersion/extraction/ settling, and demulsification.

3.5.1 Emulsification

3.5.1.1 Choice of Membrane Phase Components

In ELM process, the function of the membrane is to allow the selective transport of the solute from external (continuous) phase into the internal (stripping) phase. The membrane must also prevent any physical contact between the external and internal phase. The membrane phase consists of three components: membrane solvent, surfactant, and solute-specific carrier species.

a. Membrane Solvent

Draxler and Marr (1986) state that aliphatic diluents are preferred as the membrane solvent because of their lower solubility in water, such as cyclohexane, kerosene, shellsol A (a paraffin containing xylene) and S100N (a high molecular weight isoparaffin), etc.

b. Surfactant

In ELM system, a surfactant is used in order to stabilize the w/o emulsion against coalescence. The surfactants are characterized mainly by hydrophilic/ lipophilic balance HLB of the molecule, expressd in HLB scale. On this scale, the high HLB values are mean, the species with high hydrophilic character and which molecules with low lipophilic character.

In order to select the surfactant to use as emulsifier, it should have the following properties:

1. It must alleviate osmotic swelling, so it carries no water during the operation.
2. It does not react with the extractant in the membrane phase.
3. It has a low interfacial resistance to mass transfer.
4. It does not inhibit demulsification.

5. It is soluble in the membrane phase but insoluble in the external (continuous) and internal (stripping) phases.
6. It is stable against acids and bases.
7. It is cheap and nontoxic for environmental and economic considerations.

In the study, the non-ionic surfactant Span-80 (sorbitan monooleate) was used, which has an HLB (Hydrophilic-Lipophilic) value of 4.3 . This is close to the optimum HLB value of 5.0 for w/o emulsifier. It is the most popular surfactant widely used in ELM systems (Li and Shrier, 1972 ; Abou-Nemch and Van Peteghem, 1989 ; and Boey et al., 1987).

Span-80 has a molecular weight of 428 (see chemical structure in Figure 3.6).

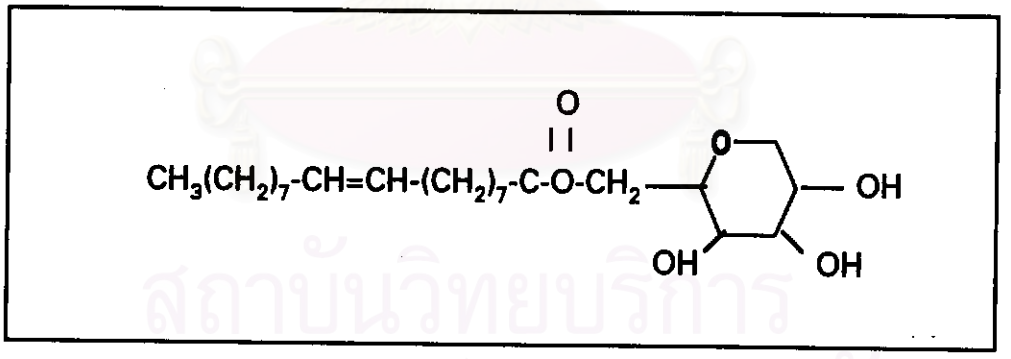

Figure 3.6 Chemical Structure of Span-80

During the ELM operations, the membrane incorporated with Span-80 shows less resistance to mass transfer than those with other surfactants (Draxler and Marr, 1986 ; Lee and Chan, 1990). Span-80 as an emulsifier lies in its poor chemical stability, especially when the NaOH is incorporated into the internal phase

(Zhang et al., 1988 ; Hirato et al., 1990). Van Peteghem (1990) proposed that the instability of Span-80 was caused by its decomposition due to hydrolysis and by macroemulsion formation due to the presence of water in Span-80 and other membrane components. The emulsion breakdown was serious when the solution containing NaOH was used as the internal phase (Hirato et al., 1990).

The concentration of surfactant used should be the minimum required to maintain stability for the duration of separation. Too much surfactant will increase the mass transfer resistance at the interface with the external and internal phases. It will also lead to a more stable emulsion which will be harder to break (Draxler and Marr, 1986).

c. Solute-Specific Carrier Species

As mentioned above, the carrier species are used only in facilitated transport to enhance solute solubility and selectivity. There are two types of carrier species, the first one is charged and the second one is uncharged. The common criteria for both are the carrier and formed complexes that must be insoluble in the external and internal phases, as any leakage from the membrane phase decreases the efficiency of the process. The other important criterion is the affinity of the solute for the carrier, if the solute-carrier complex is very strong, then a stable complex is formed and thus the solute cannot release to react with the chemical reagent in the internal phase (Cussler and Evans, 1974).

3.5.1.2 Internal Phase Reagent

In ELM process, the internal phase contains the chemical reagent which reacts with the solute to form a compound which is insoluble in the membrane phase. Usually the chemical reagent in the internal phase reagent is an

acid or base (Li et al., 1973). When choosing the chemical reagent for the internal phase, the chemical compatibility of the surfactant with the reagent must be considered. For example, if the reagent in the internal phase was sodium hydroxide, the surfactant Span-80 is an ester. So that results in an unstable emulsion (Boey et al., 1987).

Generally, the selection of the internal phase reagent is based on the thermodynamic and kinetic considerations. Thermodynamically, the selected internal phase reagent must be thus selected to partition the solute from the membrane phase to the internal phase.

A thermodynamic condition exists under which the liquid membrane process can be operated while solvent extraction cannot. A solvent extraction process needs a high distribution ratio for extraction so as to increase the extraction ability. The non-equilibrium feature of emulsion liquid membranes allows the selected extractant to have a lower distribution ratio for extraction than solvent extraction, which has a low distribution ratio for extraction and thus is unsuitable for a solvent extraction process

Kinetically the selected internal phase reagent should usually exhibit fast reactions for stripping.

3.5.1.3 Emulsion Formation

Emulsion liquid membranes are formed by subjecting the internal phase and the membrane phase components to high speed agitators to form a stable emulsion or a dispersion of internal phase droplets in the membrane phase. Emulsion are usually made by several methods such as commercially available emulsifiers Tekmar Homogenizer (Itoh et al., 1990), Waring Blender (O'Brrien and

Senske, 1989) with stirring rates up to 20,000 rpm, high speed stirrers, speeds greater than 600 rpm (Boey et al., 1987) and ultrasonic emulsifier (Shere and Cheung, 1988a, 1988b).

3.5.2 Dispersion/Extraction/Settling

Extraction of the solute is carried out by dispersing the emulsion into the external (continuous) phase. The contact between the emulsion and solute in the external phase is done by dispersing the emulsion in a stirred batch reactor (Boey et al., 1987; Ortiz Uribe et al., 1988; Terry et al., 1982) and then by stopping the agitation to allow settling, which displays the phase separation between the solute-containing emulsion from the droplet external phase due to their density difference. The size of emulsion globules is controlled in the range of 0.5 to 1.5 mm in diameter (Lorbach and Marr, 1987), although this depends very strongly on factors such as the viscosity of the solvent used, the stirring speed and the temperature. Each emulsion globules contains many tiny encapsulated droplets with a typical size of 1 to 3 μm in diameter. Such a large number of emulsion globules together with the numerous per encapsulated droplets provides large interfacial areas for both extraction and stripping.

Before dispersing the emulsion into the external phase, the pretreatment of the external phase is required as in most membrane separation processes. The pretreatment is done by the use of 1-10 μm filters, and it sometimes includes flocculation and sedimentation steps before filtration.

3.5.3 Demulsification

After emulsion liquid membrane extraction, the enriched internal phase is usually recovered and the membrane phase must be recycled repeatly. Therefore, demulsification of the loaded emulsion is necessary for the use of this separation process.

There are several methods available for emulsion breakage such as thermal demulsification, chemical treatment (Li et al., 1977) and centrifugation (Li, 1978). Chemical treatment involves the addition of a demulsifier to the emulsion. This method seems to be very effective. However, the added demulsifier will change the properties of the membrane phase and thus prohibit its reuse. In addition the recovery of the demulsifier by distillation is rather expensive. Therefore, chemical treatment is usually not suitable for breaking emulsion liquid membrane systems (Zhang, Huang and Chen, 1988). The various demulsification methods work by enhancing the slow, natural coalescence of the emulsion globules.

In order to make emulsion liquid membrane separations economical, a restraint imposed upon demulsification is that the membrane phase components can be recovered and reused. Electrostatic coalescence is the best technique available, widely used to separate dispersed aqueous droplets of internal phase from membrane phases. Liquid membranes are designed to be stable through out the time required for extraction so a high voltage is required to breakdown the emulsion in order to recover the solvent (Boey et al., 1987). However use of a high electric field gives rise to sparking which leads to deterioration of the solvent and surfactant or the formation of sponge like emulsion (Hsu and Li, 1985).

3.6 Advantages and Disadvantages of Emulsion Liquid Membrane

The main advantages of emulsion liquid membranes are summarized below (Julian, 1990) :

1. The specific surface area of emulsion liquid membranes is very high, giving rise to very fast transfer rates, because of the small droplet sizes.

2. Liquid membrane extraction is ideal for the separation of products which are in low concentration in fermentation broths, because the concentration difference is always maximized (Boey et al., 1987).

3. The solute can be simultaneously separated and concentrated by :

   a. Making the internal phase volume smaller than that of the external phase, and

   b. Ensuring that the internal phase reagent is sufficiently concentrated.

4. As mentioned above, in comparison of conventional solvent extraction, extraction and stripping can be carried out in one stage so reducing the equipment capacity and associated capital and running costs (Boey et al., 1987).

5. With respect to reactive extraction, liquid membrane extraction is more economical as much smaller quantities of the expensive extractant are required.

6. Emulsion liquid membrane systems are based on liquid-liquid extraction technology. This technology has been shown to easily scaled up industrial scale operation and for continuous use (Thien and Hatton, 1987 ; Likidis and Suchugerl, 1987).

7. Liquid membrane emulsion separations are little affected by solids which suggest application of this process as a primary separation step without the requirement of filtration (Thien et al., 1988).

8. Unlike chromatographic separations, ELMs do not require any pretreatment of the feed phase (Thien and Hatton, 1987).

Two disadvantages of ELMs are emulsion formation and breakage. There are two other phenomena associated with the operation of emulsion systems which can have a detrimental effect on the overall separation. There are leakage and swelling.

a. Leakage

In emulsion liquid membrane process, some of the extracted solute can leak back into the external phase. This phenomenon is accompanied by leakage of the internal phase reagent which can then transform the solute into a non-extractable form. The emulsion is designed so that it is stable under process conditions, but is also easy to break to recover the extracted solute. The degree of membrane leakage or breakdown is important in assessing the stability of liquid membranes. Membrane leakage in emulsion liquid membrane systems includes the rupture of the emulsion, leading to the short circuiting of the reagent and extracted solute in the internal phase to the external phase. As a result, the leakage causes a decrease of the driving force of mass transfer and increase of the external concentration thus lowering the extraction efficiency. The main factors governing membrane stability include the membrane formulation, the method of emulsion preparation, and the condition under which the emulsions are contacted with the external solute. The leakage rate are quite different, ranging from 0.2 - 10 % (Zhang et al., 1988; Shere and Cheung, 1988; Thien and Hatton, 1988).

b. Swelling

Emulsion swelling that increases the internal phase volume is a troublesome problem associated with the use of emulsion liquid membranes. It is a process by which water is transferred from the external phase into the internal droplet phase. The water transfer will (a) dilute the solute that has been concentrated in the internal droplets, thus preventing a highly concentrated solute solution from being obtained; (b)

reduce the driving force for solute extraction (Draxler and Marr, 1986; Yan Huang and Shi, 1987) (c) make the membrane thinner, leading to a less stable emulsion (Matsumoto et al., 1980; Magdassi and Garli, 1984; Ma and Shi, 1987); and (d) change the rheological properties of the emulsion to cause difficulties in emulsion transport and phase separation (Martin and Davies, 1977; Draxler and Marr, 1986).

Del Cerro and Boey (1988) summarized the possible mechanism for swelling as follows:

1. Emulsification of the external phase. This is more likely when excess surfactant is used and a high external phase to internal phase ratio is used.
2. Occlusion of part of the external phase through droplet coalescence.
3. Osmosis brought about as a result of the retatively high concentrations of reagent required for stripping.

Swelling can be reduced by careful choice of the surfactant used in the emulsion.

3.7 Solutes and Mechanism of Transport

The model solutes used in this study is berberine alkaloid with chemical structure as shown in Figure 3.7.

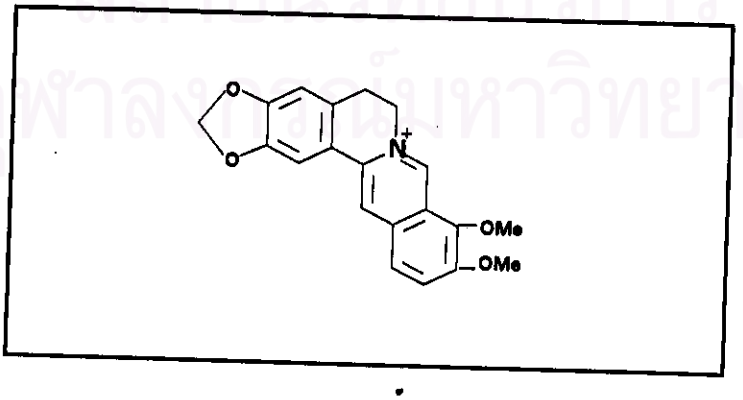

Figure 3.7 Chemical Structure of Berberine (Free Base)

Berberine alkaloid in the external phase was berberine free base form. The reaction in acid/base character as follow.

$$R_4N^+X^- \xrightarrow{NaOH} R_4N^+OH^- + Na^+X^- \quad ...(3.2)$$

$$R_4N^+OH^- \xrightarrow{HCl} R_4N^+Cl^- + H_2O \quad ...(3.3)$$

In this study, unfacilitated extraction occurs. The absence of a carrier in the membrane phase, implies the un-ionized berberine partition into the membrane phase and diffuses to the reaction front where it reacts with the internal phase reagent and prevents any back-diffusion across the membrane. Hydrochloric acid was used as the internal phase reagent. Figure 3.8 shows the simplified concentration profile for berberine in unfacilitated extraction assuming a two film model. In such a system, the factor controlling the solute yields and selectivity is the partition coefficient of the berberine. The extraction rate is controlled by the external phase mass transfer coefficient, the membrane phase diffusion coefficient, the diffusion distance and the concentration of the internal phase reagent.

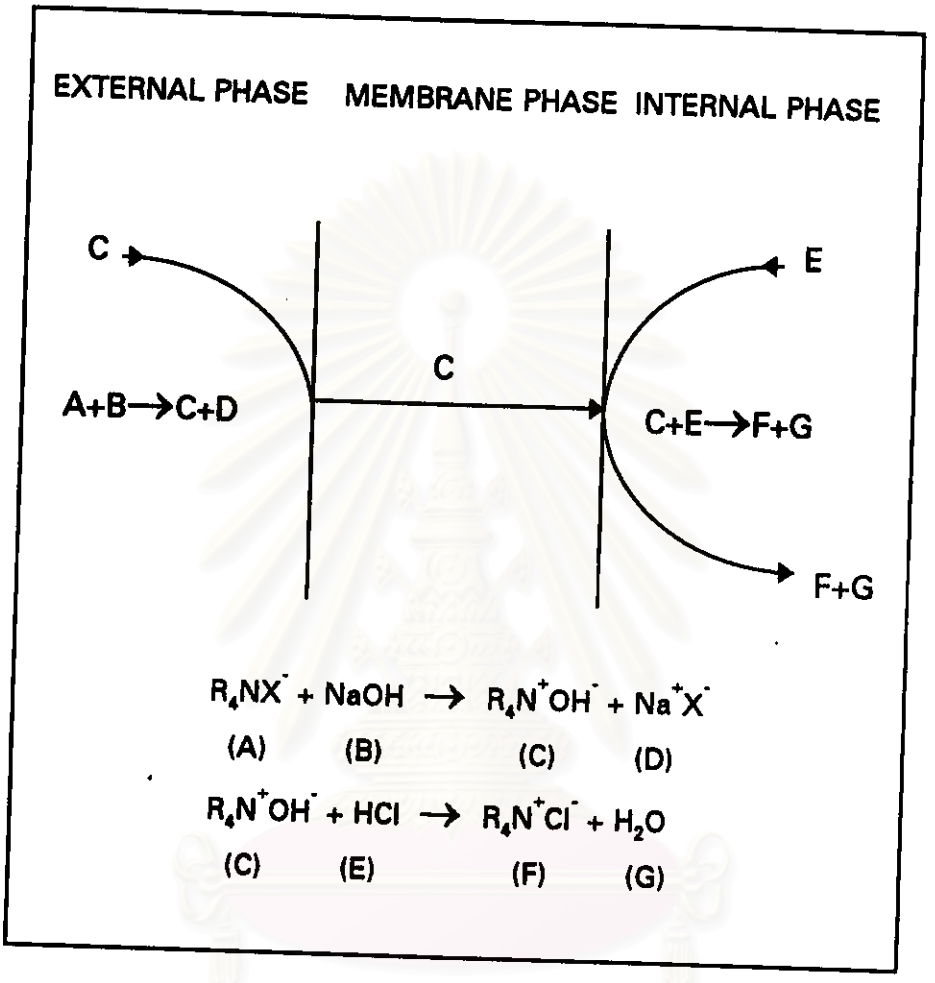

Figure 3.8 Mechanism Unfacilitated Extraction of Berberine