CHAPTER 3

THEORY

Membranes have been a source of interest for separation process for biotechnology. Membrane processes have the properties that they are technically simple, have high efficiency, and in the case of solid membrane, the component to be separated are not altered chemically or thermally (Marr and Kopp,1982).

Liquid membrane technology refers to those processes in which an extraction process occurs by means of a selective liquid separating phase; the liquid membrane. The transport of a dissolved solute through this liquid membrane gives rise to the process liquid membrane extraction (Marr and Kopp,1982).

In liquid membrane systems, the membrane phase always separates two immiscible phases. The feed phase is the solution containing the solute and the stripping phase into which this solute is extracted after passing through the membrane. In most systems of interest the membrane phase has been an organic solvent with the feed and stripping phases aqueous liquids.

Liquid membranes can be classified by configuration of the membrane phase which can be either supported liquid membrane and emulsion liquid membrane. Supported liquid membranes have membrane areas of 100-200 m^2/m^3 of equipment volume, whilst emulsion-liquid membranes have surface area of 1000-3000 m^2/m^3 (Marr and Kopp,1982)

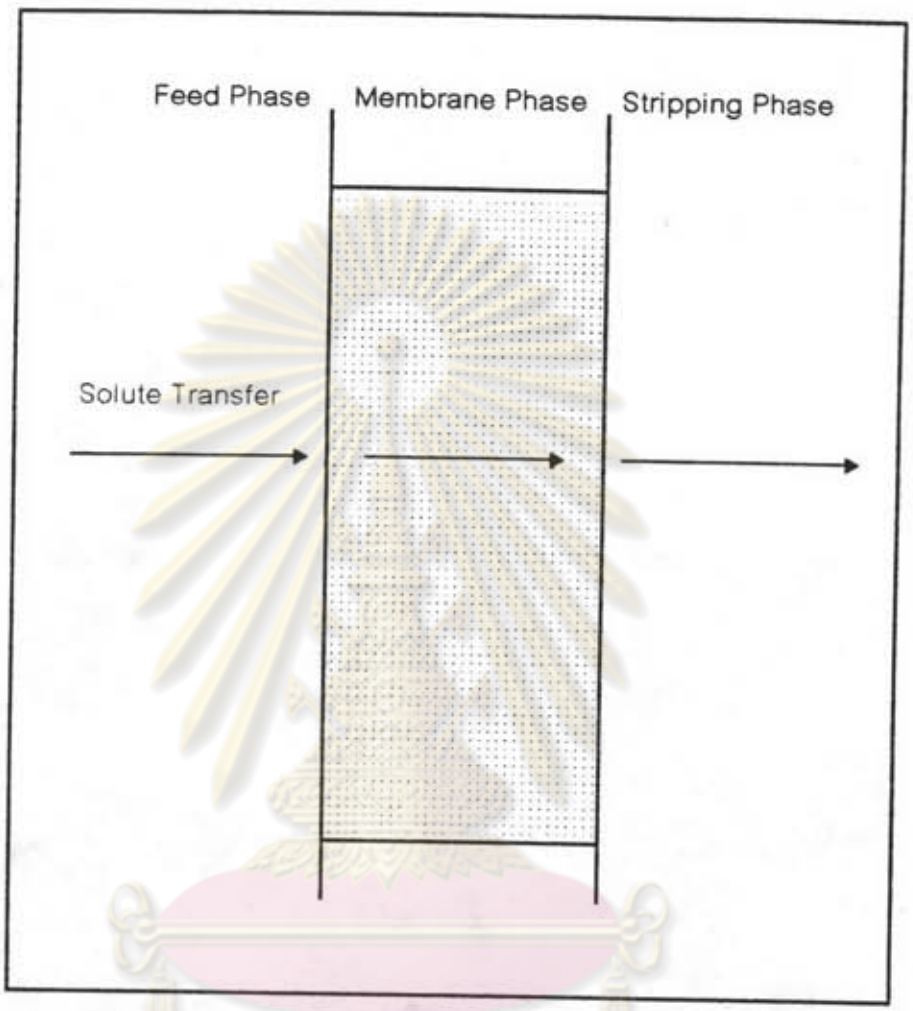


Figure 3-1. Schematic Diagram of Liquid Membrane System.

Supported Liquid Membrane

A supported liquid membrane can be achieved by impregnating a porous solid film with an organic solvent, which is held in place by capillary forces that exists within the pores. The membrane separates an aqueous phase, initially containing the solute of interest, from another aqueous phase into which the solute is extracted, the stripping phase, as shown in Figure 3-2.

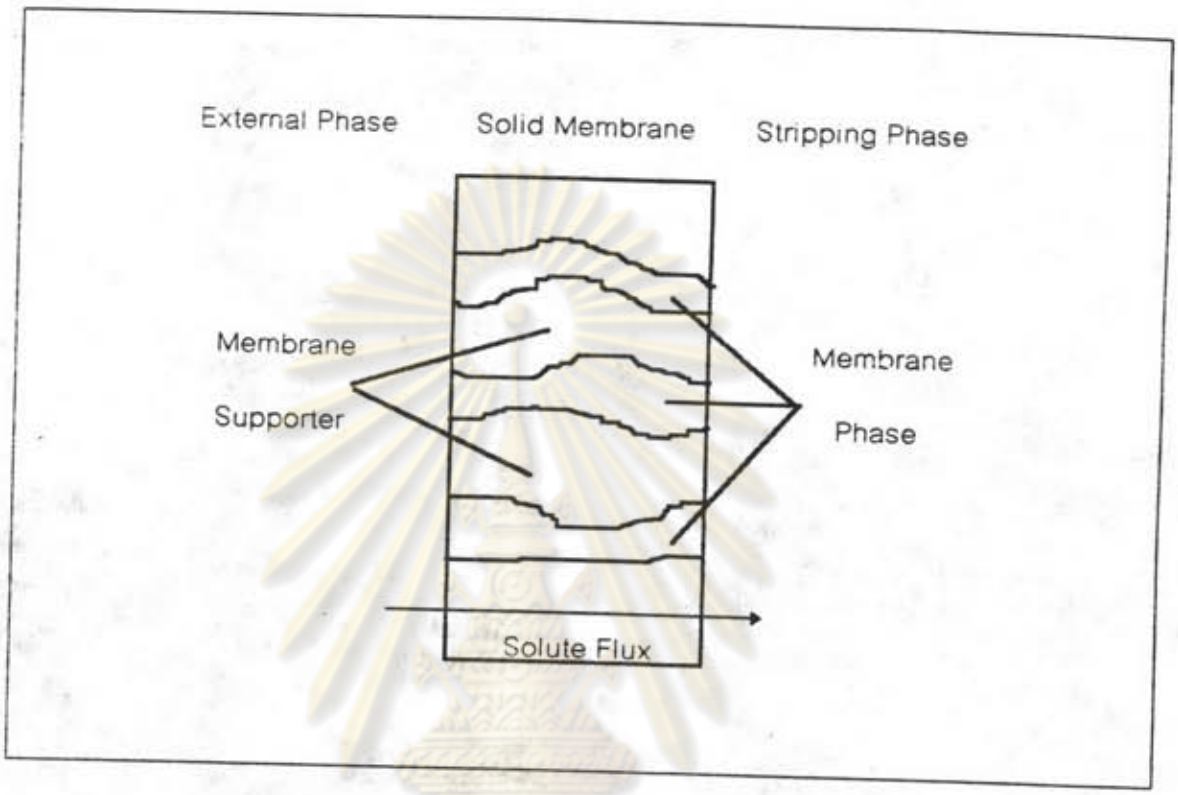


Figure 3-2 Schematic Diagram of a Supported Liquid Membrane.

Extraction occurs because of the difference in chemical potential(concentration) that exists between the two aqueous phases.

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 supports used are generally microporous polymeric films made of polypopylene, polysulfone, or other hydrophobic materials. Typical dimensions are, a membrane thickness of 25-50 μm, with pore size between 0.02-1.0 μm.

Compared to emulsion liquid membrane, supported liquid membrane has an advantage in that there is no emulsion to be prepared, or to be broken in order to recovery the product. However, one of the main disadvantage is that supported liquid membranes have a much thicker. This results in a much larger equipment capacity to achieve the same separation. The other disadvantages include the necessity for frequent charging of the membrane liquid due to the wash out of the immobilized membrane phase from the support pores(Denesi et.al,1987) and also a low solute flux.

The use of supported liquid membrane has mainly been applied to the separation of metal ions. Further details on the application can be found in work by Denesi(1987), Denesi and Rickert(1986).

Emulsion Liquid Membrane

The emulsion liquid membrane is a liquid phase involving an emulsion configuration. Emulsion liquid membranes, also called surfactant liquid membrane or liquid surfactant membranes, are essentially double emulsions, i.e., water/oil/water (W/O/W) systems or oil/water/oil (O/W/O) systems. For the W/O/W systems, the oil phase separating the two aqueous phases is the liquid membrane. For the O/W/O systems, the aqueous phase is the liquid membrane that separating the two oil phases.

1. General Description of Emulsion Liquid Membrane

Emulsion liquid membranes are usually prepares by first forming an emulsion between two immiscible phases, and then dispersing the emulsion in a third phase by agitation for extraction. The membrane phase is the liquid phase that separates the encapsulated, internal droplets in the emulsion from external, continuous phase, as shown in figure 3-3.

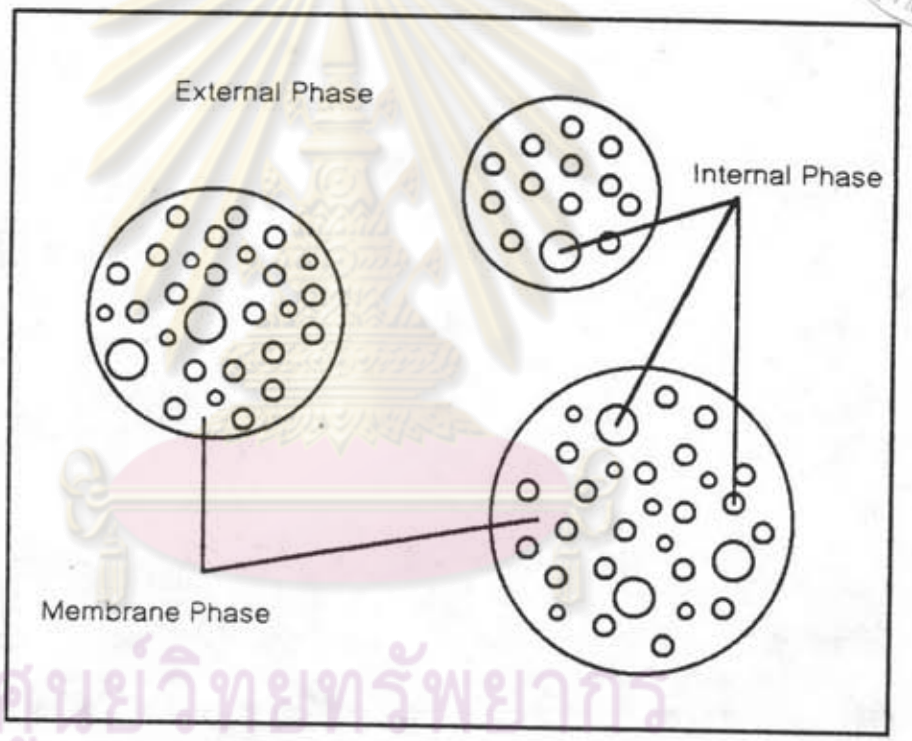


Figure 3-3 Schematic of an Emulsion Liquid Membrane System.

In general, 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. Therefore, the emulsion is of the W/O type if the

external phase is water, and it is O/W type if the external phase is oil. To maintain integrity of the emulsion during the extraction process, the membrane phase generally contains some surfactant and additive as stabilizing agents, and it also contains a base material that is a solvent for all the other ingredients.

Typically, the encapsulated, internal droplets in the emulsion are 1 to 3 μm in diameter to provide a good emulsion stability for emulsion liquid membrane extraction. When the emulsion is dispersed by agitation in the external phase during the extraction process, many small globules of the emulsion are formed. The size of the globules depends on the characteristics and concentration of the surfactant in the emulsion, the viscosity of the emulsion, and the intensity and mode of mixing. Usually the globules size is controlled in the range of 100 to 2000 μm in diameter. Thus, a very large number of emulsion globules can be formed easily to produced a very large mass transfer area adjacent to the external phase. Each emulsion globules contains many 1 to 3 μm internal droplets. Thus, the internal mass transfer surface area, typically 10^6 m^2/m^3, is even much larger than the external mass transfer surface area. Therefore, a rapid mass transfer in the emulsion liquid membrane process can occur from either the external phase to the internal phase or vice versa.

Separation of mixtures can be achievable by selective diffusion component through the membrane phase into the receiving phase of lower equivalent concentration. Surfactant and additive included in the membrane phase can control the selectivity and permeability of the membrane. An individual component can be trapped and concentrated in the internal phase for later disposal or recovery. Once

separation is achieved, the emulsion and external phases are separated, usually by settling as in conventional solvent extraction. The extracted component can be recovered from "loaded" internal phase of the emulsion by breaking the emulsion, usually by the use of an electrostatic coalescer(Wang and Zhang,1988; Marr, Bart and Draxler, 1990). From breaking the emulsion, the membrane phase recovered can them be recycled to emulsification step for the preparation of the emulsion with a regenerated or fresh reagent phase.

2. Liquid Membrane Extraction : A Form of Solvent Extraction

Liquid-liquid extraction is a separation technology which has found wide application in the separation of biomolecules. This has mainly involved organic/aqueous systems, but more recently, aqueous-aqueous extraction is becoming more widespread (Abbott and Hatton, 1988). This operation relies on the partitioning of the required solute between an aqueous and organic phase. The equilibrium governing this phenomenon can be related by means of the distribution coefficient, K_{ol}

$$K_{ol} = \frac{C_2}{C_1} \qquad \text{..... (3.1)}$$

where C_2 is the concentration of the solute in the extracting solvent phase which is usually an organic liquid. C_1 is the concentration in the aqueous product stream. After the solute has partitioned into the organic solvent, the phases are separated and the solute is usually re-extracted or stripped back into an aqueous phase.

An analogy may be drawn between emulsion liquid membrane extraction and solvent extraction (del Cerro and Boey, 1988). 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 value of K_{oi} can be increased by alteration of conditions such as pH, or by the introduction of an extractant into the organic phase, with increases the solute solubility in the organic phase (Likidis and Schugerl, 1987). These improvements in 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 requirement for an emulsion breakage operation to recover the extracted product (Chaudhuri, 1990).

3. Principles of Separation

In a liquid membrane process mass transfer occurs in all three phases. In the external phase the solute transfer across the interface with the membrane, then diffuses through the membrane phase. At the interface with the internal phase the solute transfer into the small droplets of the internal phase. Any reaction at this interface is usually assumed to be instantaneous because of the high specific interfacial area of the small droplets, so it is unlikely that mass transfer will be limited by the solute/reagent reaction(Ho et. al., 1982). As mentioned above, the membrane phase confers selectivity on liquid membrane processes and consequently the mechanism of solute transport across this phase is of prime

importance. There are two principle modes of transport across the membrane phase (Matulevicius and Li, 1975; Chan and Lee, 1984).

3.1 Unfacilitated Transport

This is the simplest case of solute transport through the membrane phase and is a diffusion process. The solute is initially in the bulk of the external phase and diffuses to the interface with the membrane phase. Here it partitions into the membrane and diffuses across to the interface with the internal phase into which it partitions, the driving force for transport is the chemical potential difference in the solute across the membrane phase.

The driving force can be manipulated by the inclusion in the internal phase a chemical reagent which reacts with the solute. This has a two-fold effect; first, the solute is now in a different chemical form which if it is in soluble in the organic solvent, cannot back-diffuse. Second, because the solute is now in a different form, the concentration of the transportable species in the internal phase, is effectively zero and hence the concentration gradient is maximized, thus enhancing mass transfer.

Thein et.al.(1985) point out that unfacilitated transport is only applicable to uncharged solutes, as charged species will be insoluble in the non-polar membrane solvent.

3.2 Facilitated transport

This form of transport is of greater importance in any potential liquid membrane separation. Its application is for membrane-insoluble materials, such as charged species, e.g. metal ions, organic acids and zwitterions. By introducing a

'carrier' molecules into the membrane phase, the solute solubility is increased by the reversible formation of a membrane-solute carrier-solute complex. This results in faster mass transfer rates, selectivity is introduced into the extraction as the carrier-solute reaction can be selective(Cussler,1984). The carrier must be insoluble in water and must be also be specific for the solute of interest. The solute is transport across the membrane by the formation of a complex as follows(Lobarch and Marr, 1987).

1. At the interface between the external phase and membrane phase the solute A, reacts with the carrier complex BC, to form the complex AC, and liberates B in the external phase. This complex is insoluble in either aqueous phase but is soluble in the membrane phase.

2. The carrier-solute complex (AC) diffuses across the membrane to the interface with the internal phase.

3. 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 a counter-ion B, in the internal phase. Hence the solute A is released into the internal phase reagent.

4. The carrier reacts with the counter-ion to form the carrier-counter-ion complex BC, which then diffuses back through the membrane to the exterior interface where the counter-ion released, Haunch completing the process.

Although Lobarch and Marr(1987) state that the driving force of the difference between the activities of the counter-ion in the internal and external

phase, it is more process is known as counter transport(Figure 3-4).

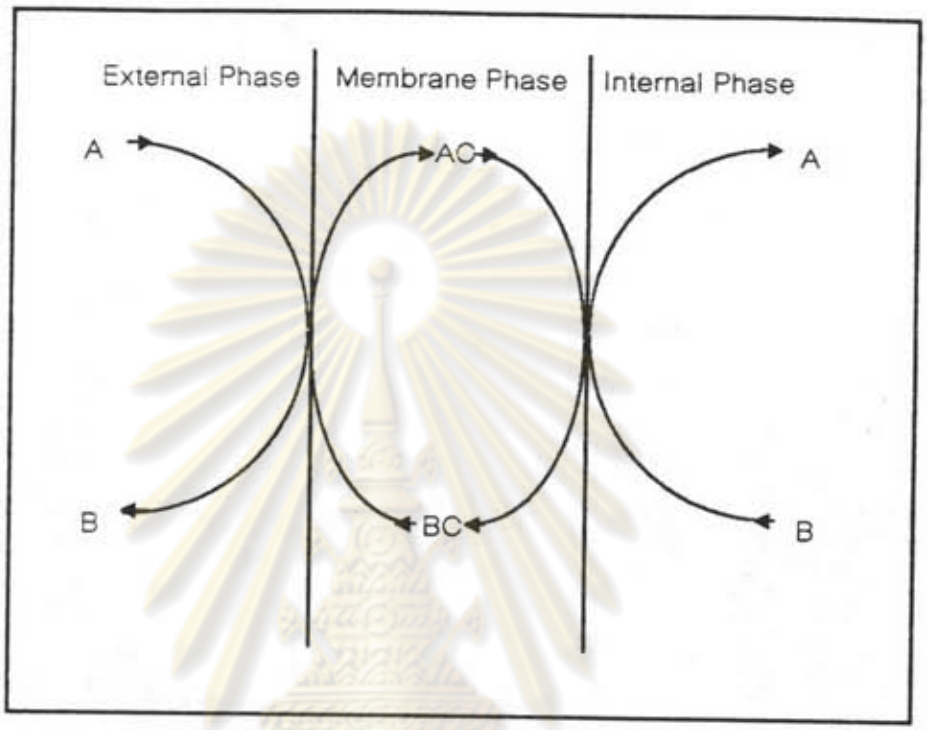


Figure 3-4. Schematic of Counter Transport of Solute A by Carrier C.

The second, less common mode of facilitated transport is known as co-transport (Figure 3-5). This is characterized by the carrier (C) reacting reversibly with the solute A, and a second species B, and transporting them in one direction across the membrane. Thereforee two coupled fluxes exist across the membrane in the same direction (Cussler, 1984).

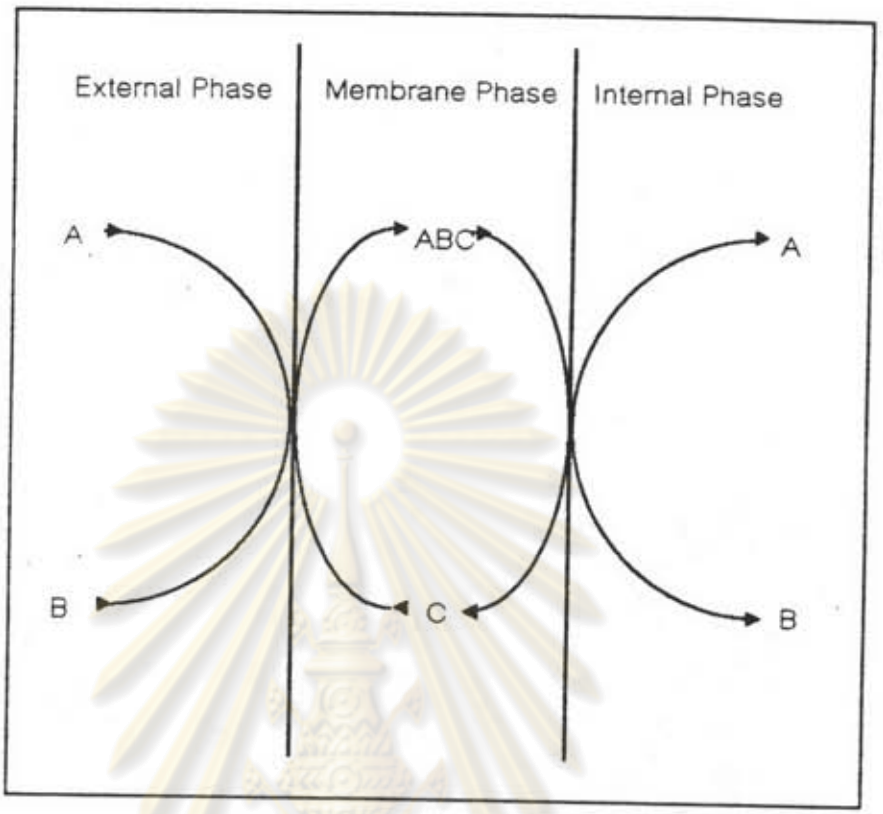


Figure 3-5. Schematic of Co-Transport of Solute A and B by the Carrier C.

4. Process Considerations

An emulsion liquid membrane process includes three steps :

1) emulsification

2) dispersion/extraction/settling

3) demulsification (breaking of emulsion)

4.1. Emulsification.

4.1.1 Membrane Formulation.

For unfacillitated transport, the membrane phase consists only of a diluent and a surfactant to stabilize the primary emulsion. No extractant is needed for unfacilitate transport because the solute transport across the membrane is accomplished through its physical solubility and then diffusion in this membrane. However, for facilitation transport, an extractant and its associated stripping agent must be incorporate into the membrane and internal phase, respectively, in order to achieve a coupled extraction/stripping process.

4.1.2 Extractants/Stripping Agents.

When choosing extractants, the selected extractant and its complex must be soluble in the membrane phase, but insoluble in the external and internal phase. Precipitates are also not allowed to form either within the membrane or at the interfaces. Otherwise, the membrane process will fail.

Generally, the selection of the extractant/stripping agent system is based on the thermodynamic and kinetic considerations. Thermodynamically, the selected extractant should favor the distribution of the solute from the external phase to the membrane phase.

A thermodynamic condition exists under which the liquid membrane process can be operated while solvent extraction cannot. A solvent extraction process need 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.

Kinetically, The selected extractant and stripping agent should usually exhibit fast reactions for both extraction and stripping . But it is interesting to note that because its much higher interfacial area for stripping than that for extraction, and emulsion liquid membrane process is capable of coping with the situation in which the extractant has relatively fast extraction kinetics but the stripping agent has extremely low stripping kinetics.

According to functional groups, the extractants are generally devided into three classes : acidic extractants, basic extractants, and neutral extractants.

- Acidic Extractants.

To extract a cation from an aqueous solution, it must be combined with an anionic species to form an uncharged species. Acidic extractants are most effective for extracting cations by exchanging their protons for the cations for liquid membranes cation extraction. Commonly used acidic extractants can be classified into three groups: Chelating extractants, Alkylphosphorus compounds, and Ionized crown ethers.

- Basic Extractants.

Basic extractants are used for extraction of anionic or neutral metal complexes, These extractants can be regarded as "liquid anion exchangers" i.e., the high molecular weight primary amines, secondary amines, tertiary amines and the quaternary ammonium salts.

- Neutral Extractants.

Neutral extractants often extract uncharged metal complexes or cations together with the coupled anions in order to maintain the electrical neutrality.

4.1.3 Surfactants

The surfactant is the key component for forming a stable emulsion. In emulsion liquid membranes , the overwhelming majority involves W/O/W double emulsion systems. But as membranes have become commercialized, their industrial applications have required more of the surfactants than their major contribution to membrane stability. An ideal surfactant should process the following properties :

1. It carries virtually no water during operation so as to alleviate osmotic swelling.

2. It does not react with the extractant in the membrane phase ; if any, the reaction should promote the extraction process rather than catalyze the decomposition of the extractant.

3. It has a low interfacial resistance to mass transfer .

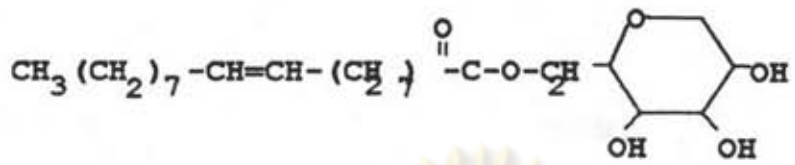
4. It does not inhibit demulsification.

5. It is soluble in the membrane phase but insoluble in the external and internal phase.

6. It is stable against acids , bases , and bacteria.

In addition , the selected surfactant should be cheap and nontoxic for economic and environmental considerations .

SPAN 80 (Sorbitan monoleate) is a nonionic surfactant with a molecular weight of 428. Its structure is :



During extraction operations , the membranes incorporated with SPAN 80 show less resistance to mass transfer than those with other surfactants SPAN 80, however, suffers from some drawbacks. It is good carrier for water molecules and therefore favors the osmotic swelling of emulsion. Another disadvantage of SPAN 80 as an emulsifier lies in its poor chemical stability, especially when the NaOH is incorporated into the internal phase.

4.1.4 Diluents

The diluent is the main membrane component in which both extractant and surfactant are dissolved. Although the diluent is normally regarded as an "inert" component, it does affect the membrane properties, such as distribution coefficient and diffusion coefficient, and can have significant impact on the effectiveness of the membrane system. From the viewpoint of industrial application, an ideal diluent should;

1. Have low solubility in the internal and external aqueous phase so as to minimize the solvent loss.

2. Be compatible with extractant and surfactant without the formation of new phases.

3. Have a moderate viscosity (In solvent extraction , an as-low-as possible viscosity is desired for the diluent for fast mass transfer. For emulsion liquid

membranes, however, a much lowered diluent viscosity would reduce the membrane strength, resulting in membrane instability.)

4. Have a sufficient density difference from the aqueous phase for the fast settling operation.

5. Be both cheap and readily available from a number of alternative sources.

6. Have low toxicity and a high flash point for safety reasons.

Based on the above considerations, aliphatic diluents are generally preferred to aromatic diluents because the aliphatic diluents usually can meet most of the above mentioned requirements.

4.1.5 Carrier Species

A carrier species is used to enhance solute solubility and selectivity in facilitated transport. There are two classes of carrier molecules, charged and uncharged, but common criteria for both are that carrier and its complexes must be insoluble in the aqueous phases.

4.1.6 Emulsion Preparation

To prepare a stable emulsion, the mean diameter of the dispersed internal droplets should be as small as 1 to 3 μm, which requires a high input of energy density to the water-oil system for emulsification. In laboratory studies, emulsions are usually made by high speed agitators with stirring rates up to 20000 rpm.

4.2 Dispersion/Extraction/Settling

The separation for an emulsion liquid membrane process includes dispersion, by which the coupled extraction/stripping is achieved, and settling,

which realizes the phase separation between the loaded emulsion and the aqueous raffinate because of their density difference. Before dispersing the emulsion into the feed, the pretreatment of the feed is required as in most separation processes. The pretreatment is typically done by the use of 1-10 μm filters, and it sometimes includes flocculation and sedimentation steps before filtration. During the dispersion operation, the emulsion is dispersed by agitation in the external phase and many small globules of emulsion are formed. Normally, the size of emulsion globules is controlled in the range of 0.1 to 2.0 mm in diameter. Each emulsion globule contains many tiny encapsulated droplets with a typically size of 1 to 3 μm in diameter. Such a large number of emulsion globules together with the numerous pre-encapsulated droplets provides large interfacial areas for both extraction and stripping. After the separation is completed, phase separation of the loaded emulsion from the external raffinate takes place in the settler. The settling is similar to that for conventional solvent extraction.

4.3 Demulsification

After liquid membrane extraction, the membrane phase must be recycled repeatedly, and the enriched internal phase is usually recovered. Thereforee, demulsification of the loaded emulsion is unavoidable for the use of this separation process, although a few exceptions use this technology without breaking the emulsion in some special cases(Dines,1982).

Two principle approaches for the demulsification of the loaded emulsion are chemical and physical treatments. 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. Thereforee, chemical treatment is usually not suitable for breaking liquid membrane emulsions. Physical treatment methods include heating, centrifugation, ultrasonic, solvent dissolution, high shear, and the use of high voltage electrostatic fields.

5. Advantages and Disadvantages of an Emulsion Liquid Membranes.

Noppaporn Panich (1994) has summarized the advantages and disadvantages of emulsion liquid membranes as follows:

5.1 Advantages.

The main advantages of emulsion liquid membranes are summarized below:

1. Because of the small droplets size, the specific surface area of emulsion liquid membranes is very high, giving rise to very fast transfer rates.

2. Because the concentration difference is always maximized, the liquid membrane extraction is deal for the separation of products that are in low concentration in fermentation broth (Boey et.al.,1987).

3. The solute can be simultaneously separated and concentrated by making the internal phase reagent is sufficiently concentrated and ensuring that the internal phase reagent is sufficient concentrated.

4. As mentioned above, in comparison to conventional solvent extraction, extraction and stripping can be carried out in one stage, hence 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 tne expensive extractant are required.

6. Emulsion liquid membrane systems are based on liquid-liquid extraction technology. This technology has been shown that it can easily scaled up to an industrial scale operation and a continuous process (Thein and Hatton, 1987; Likidis and Schuger, 1987).

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

8. Unlike chromatographic separations, emulsion liquid membranes do not require any pre-treatment of the feed phase (Thien and Hatton, 1987).

5.2 Disadvantages

Besides the two disadvantages of emulsion liquid membrane, i.e., emulsion formation and breakage, there are two other phenomena associated with the operation of emulsion system that can have a detrimental effect on the overall separation.

5.2.1 Leakage

During solute extraction, some extracted solute can leak back into the external phase. Usually this is accompanied by leakage of the internal phase reagent which can then transform the solutes into a non-extractable form. This is primarily an emulsion formulation problem. 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 emulsion breakage is small, less than 2% occurs during the initial stages of extraction (Thien and Hatton, 1987).

5.2.2. Swelling

Emulsion swelling is a process by which water is transferred from the external droplet phase. The water transfer will: dilute the solute that has been concentrated in the internal droplets, reduce the driving force for solute extraction, make the membrane thinner (leading to a less stable emulsion), and change the rheological properties of the emulsion to cause difficulties in emulsion transport and phase separation.

The two types of emulsion swelling that can occur are osmotic swelling which is driven by differences in the osmotic pressure between the external and internal phases and swelling attributed to the entrainment of the external aqueous phase which due to the repeated coalescence and redispersion of emulsion globules during the dispersion operation.

Solutes and Mechanism of Transport.

The model solute in this study is L-lysine with chemical structure is shown in figure 3-6.

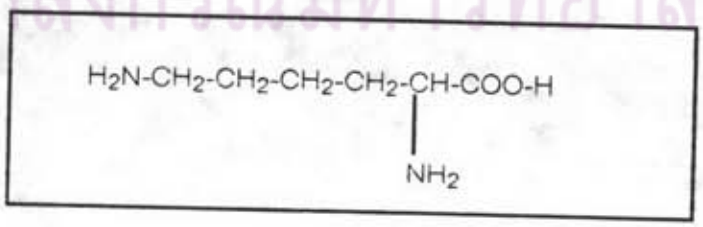
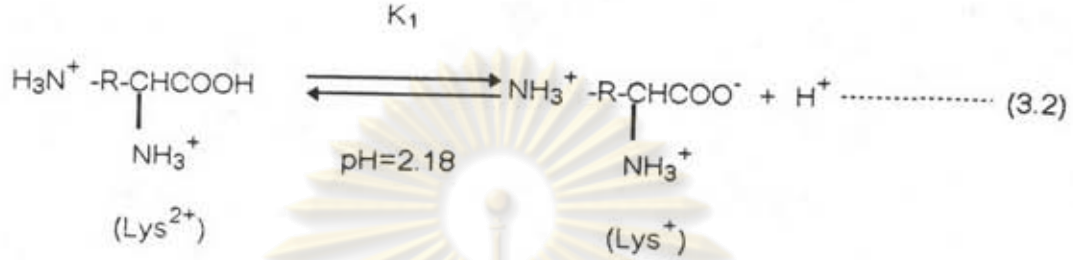
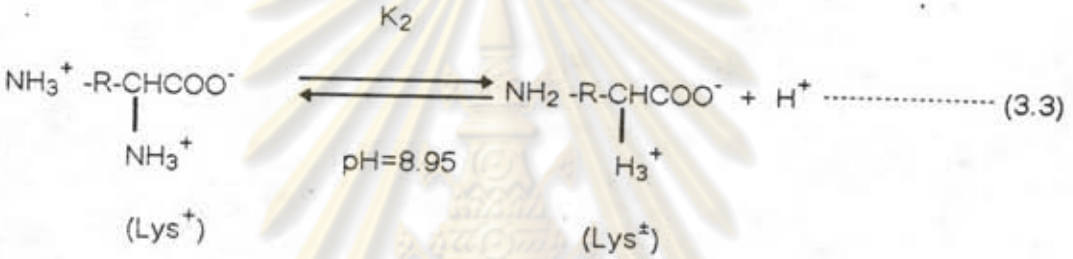


Figure 3-6 Chemical Structure of L-lysine.

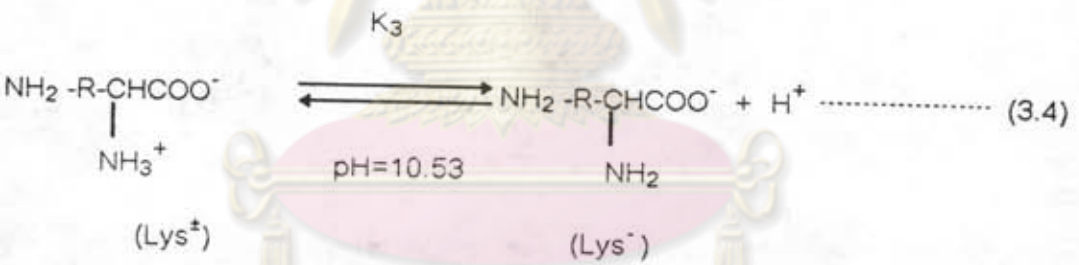
All α-amino acids, included L-lysine, are zwitterions which its character imparts unique acid/base characteristics to the species. The dissociation character of amino acid has shown in equation 3.2 to 3.5.



(3.2)



(3.3)



(3.4)

$$K_1 = \frac{[H^+][A^+]}{[A^{2+}]} \quad \text{.....} \quad (3.5)$$

For L-lysine : $K_1 = 10^{-2.18}$ mol/dm^3

$$K_2 = \frac{[A^{\pm}][H^+]}{[A^+]} \quad \text{.....} \quad (3.6)$$

For L-lysine : $K_2 = 10^{-8.95}$ mol/dm^3

$$K_3 = \frac{[A^-][H^+]}{[A^\pm]} \qquad \text{..... (3.7)}$$

For L-lysine : $K_3 = 10^{-10.53}$ mol/dm^3

Where A^+, $A^\pm$, and A^- are the cation, Zwitterion and anion of amino acid, respectively K_1, $K_2$and K_3 are the dissociation constant of amino acid.

Since amino acid is insoluble in the oil phase, an ion exchange carrier must be added to the membrane phase in order to solubilize amino acid into oil and transport it to the internal phase. Di-(2-ethylhexyl)phosphoric acid or D2EHPA is one of the most preferable cation carrier in the emulsion liquid membrane extraction, the structure of D2EHPA showed in figure 3-7.

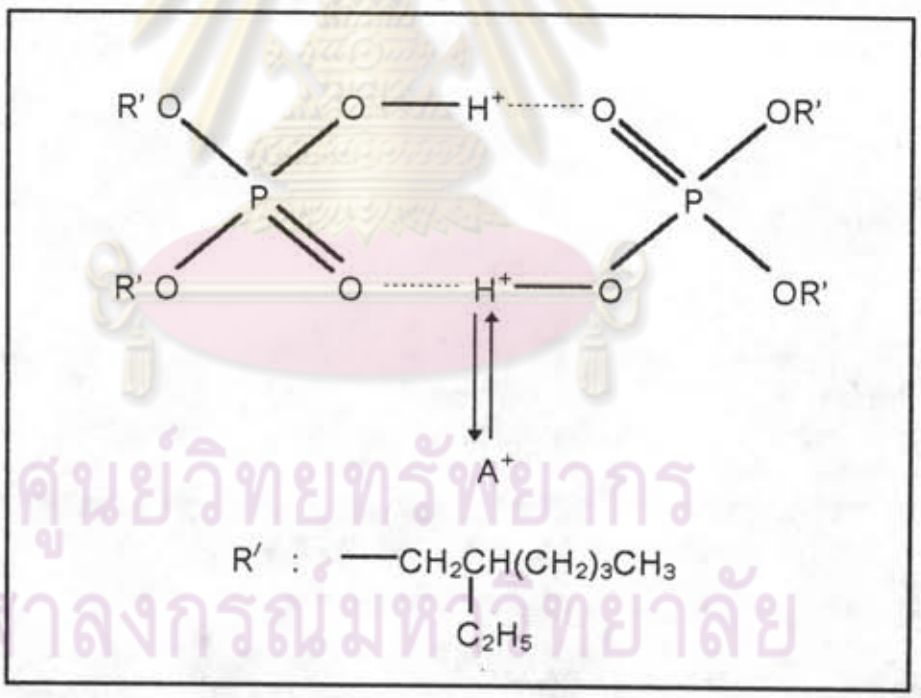


Figure 3-7. Structure of Di-(2-ethylhexyl)-phosphoric acid in monomeric form. (Noppaporn Panich, 1994)

D2EHPA is soluble in the membrane phase and it aqueous solubility is extremely low. As shown in figure 3-8, the D2EHPA first exists as a carrier/proton complex. When the carrier reaches the interfacial between the external and the membrane phases, an ion exchange reaction takes place and the carrier makes a complex with amino acid. Although the actual structure of complexes can be complicated, a simplified structure is shown in figure 3-8. The carrier/amino acid complex then diffuses through the membrane phase to the interface between the internal and the membrane phases. Another ion exchange reaction takes place. The carrier/amino acid complex must release the Lys^+ and the carriers immediately protonated. These processes are repeated and the amino acid thus separated and concentrated in the internal phase.

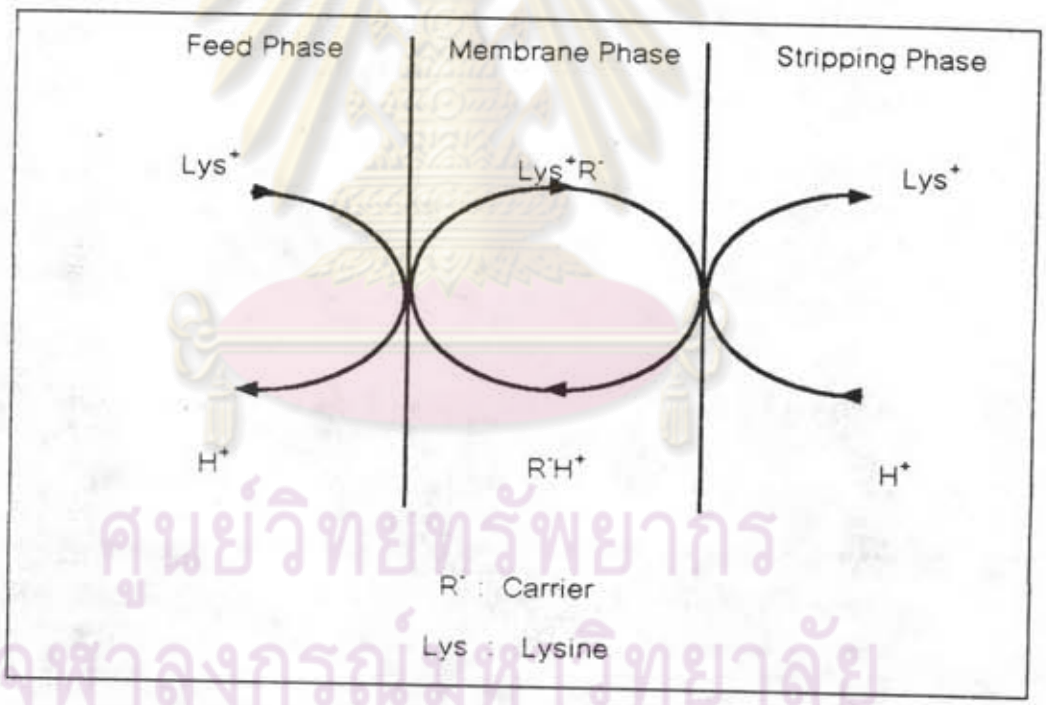


Figure 3-8. Schematic Diagram of the Transport Mechanism for L-lysine.