CHAPTER 3

THEORY

Emulsion Liquid Membrane System.

In chapter 2, Details about ELM have already been mentioned. There are 2 types of emulsion liquid membrane system; water/oil/water (w/o/w) and oil/water/oil (o/w/o). The emulsion liquid membrane system consists of three phases. In case of w/o/w system, the oil phase acts like a membrane between the internal aqueous phase and the external aqueous phases. The external phase is the feed solution and the internal phase is the concentrated product solution.

In order to form an emulsion liquid membrane, the internal phase is emulsified at a high shear into the solvent or membrane phase. Typically, the resulting emulsion has a mean internal phase droplet diameter of 1-10 μm. It is stabilized by addition of a surfactant to the organic phase. After emulsification the emulsion is dispersed into the continuous external phase under mild agitation, forming a dispersion of globules of 0.1-2 mm in diameter. The size is depended on the physical properties of the continuous and dispersed phases and the agitation speed (Figure 2.2).

As shown in Figure 2.2, the ELM system consists of three phases:

(1) an internal phase (water phase) which is encapsulated by a membrane phase.

(2) a membrane phase (oil phase) which forms a w/o (water in oil) emulsion with the internal phase.

(3) an external phase (continuous phase) in which the emulsion globules are dispersed. As a result of this, an emulsion in water dispersion is formed and the internal phase never directly contacts the external phase.

The solute of interest can be transported from the external aqueous phase to the internal phase by one of several mechanisms depending on the chemical nature of the solute including facilitated transport and simple diffusional transport. Different solutes have different solubilities and diffusion coefficients in the membrane, and these properties can be further modified by the addition of a selective carrier such as di (2-ethylhexyl) phosphoric acid (D2EHPA) to the solvent.

Extraction involves batch or continuous contact between the dispersed phase and the continuous feed stream. After sufficient contact time the desired solute is recovered by emulsion breakage and release of the internal phase.

Solutes and Mechanism of Transport.

The model solutes in this study are L-phenylalanine (Phe) and L-tryptophan (Trp) with chemical structure as shown in Figure 3.1. L-phenylalanine has a significant commercial market. It has been used as one of the two precursors of the non-nutritive sweetener Aspartame.

Like all α-amino acid, L-phenylalanine and L-tryptophan are zwitterions and its zwitterionic character imparts unique acid/base characteristics to the species. Equation (3.1) to (3.4) show dissociation character of amino acid. The dissociation ratio of L-phenylamine and L-tryptophan are shown in figure 3.2.

$$\underset{(A^{+})}{\mathrm{R\text{-}\underset{NH_3^+}{CH}COOH}} \; \underset{pH<3}{\overset{K_1}{\rightleftharpoons}} \; \underset{(A^{\pm})}{\mathrm{R\text{-}\underset{NH_3^+}{CH}COO^-}} + H^+ \qquad \text{------------- (3.1)}$$

$$\underset{(A^{\pm})}{\mathrm{R\text{-}\underset{NH_3^+}{CH}COO^-}} \; \underset{pH>9}{\overset{K_2}{\rightleftharpoons}} \; \underset{(A^{-})}{\mathrm{R\text{-}\underset{NH_2}{CH}COO^-}} + H^+ \qquad \text{------------- (3.2)}$$

$$K_1 = \frac{[A^{\pm}]\,[H^+]}{[A^+]} \qquad \text{-------------- (3.3)}$$

(Phe : $K_1 = 10^{-1.83}$ mol/dm^3 , Trp : $K_1 = 10^{-2.38}$ mol/dm^3)

$$K_2 = \frac{[A^-][H^+]}{[A^\pm]} \qquad \text{-------------- (3.4)}$$

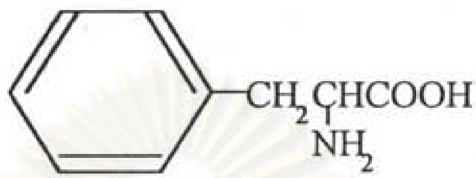
(Phe : $K_2 = 10^{-9.13}$ mol/dm^3 , Trp : $K_2 = 10^{-9.39}$ mol/dm^3)

Where A^+, $A^\pm$ and A^- are the cation, zwitterion and anion of amino acid , respectively. K_1 and K_2 are the dissociation constants 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 the oil and transport it to the internal phase. Di-(2-ethylhexyl) phosphoric acid or D2EHPA as shown in Figure 3.3, is one of the most preferable cation carrier in the ELM extraction. Thien et. al. (1988) reported the application of anionic carrier (Aliquat 336, a quaternary ammonium salt) for the separation of Phe. But in their system, removal of cells from the fermentation broth might be necessary, since the surface of microorganisms is usually negatively charged and could result in fouling of the membrane interface. In addition, organic acids are often seen in fermentation broth as impurities and could be transported in competition with Phe, therefore cation carrier seem to be referable.

D2EHPA is soluble in the membrane phase and it aqueous solubility is extremely low. As shown schematically in Figure 3.4, the D2EHPA first exists as a carrier/proton complex. When the carrier reaches the interface 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 3.4. The carrier /amino acid complex then diffuses though the membrane to the interface between the internal and membrane phases. Another ion exchange reaction takes place. The carrier/amino acid complex must release the A^+ and the carriers immediately protonated. These processes are repeated and the amino acid thus separated and concentrated in the internal phase.

L-phenylalanine



L-tryptophan

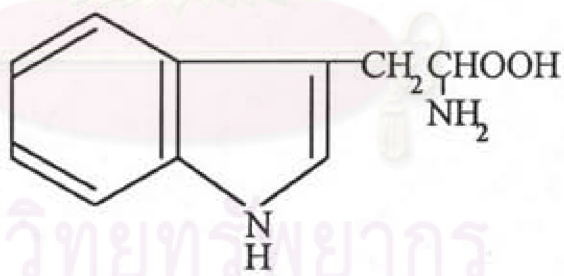


Figure 3.1 Chemical Structure of L-phenylalanine and L-ryptophan.

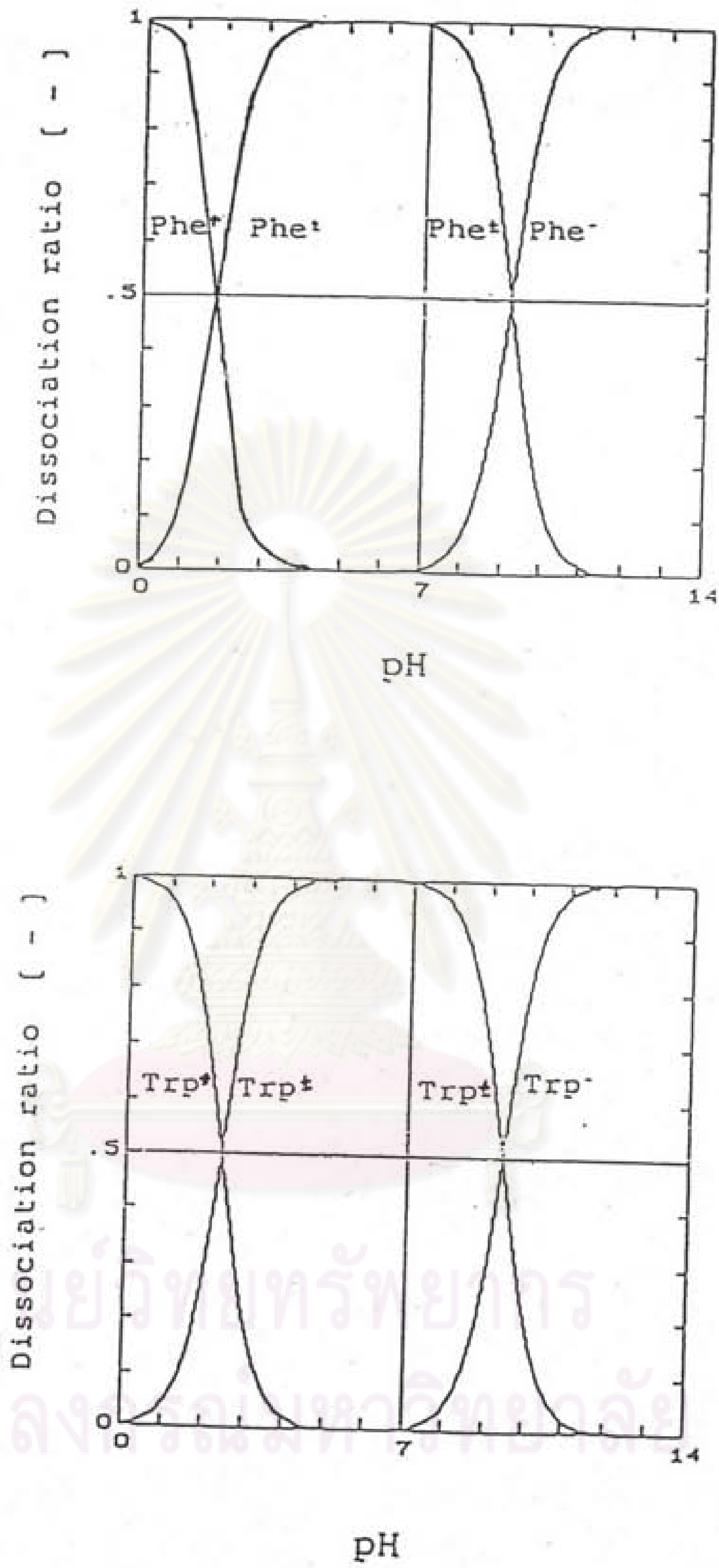


Figure 3.2 Dissociation Ratio of L-phenylalanine and L-tryptophan.

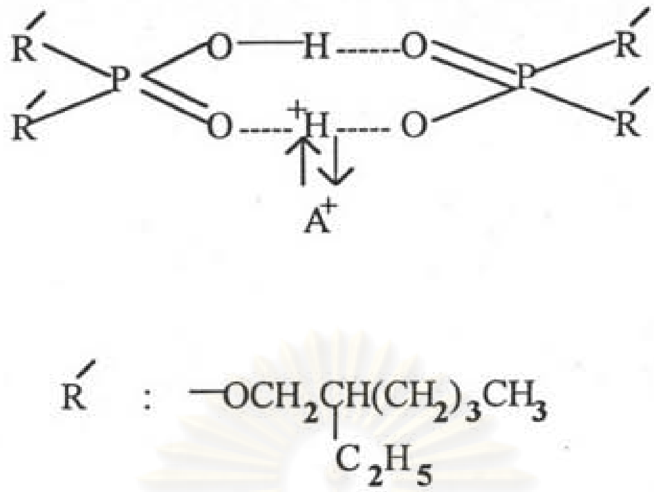
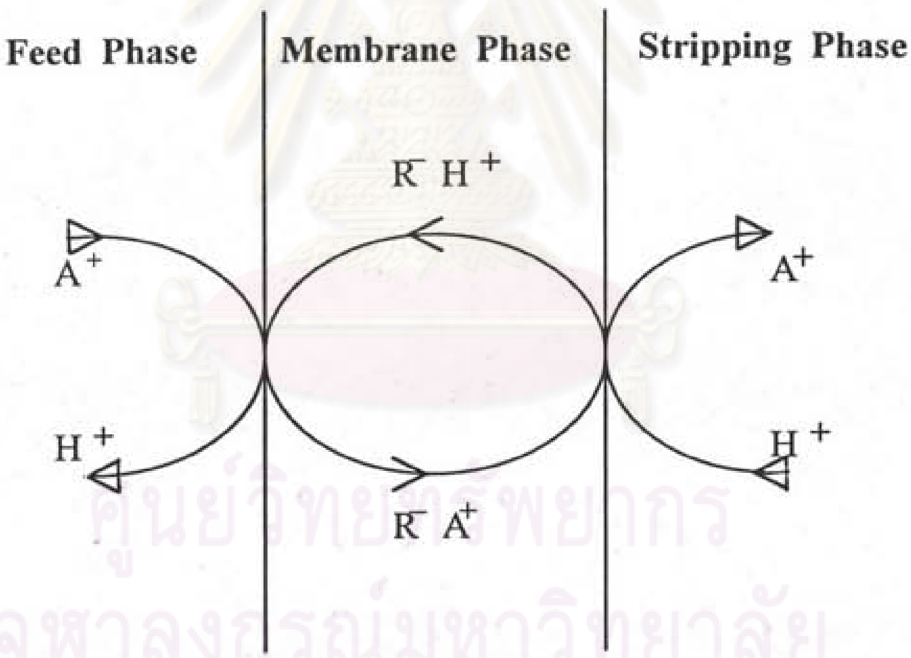


Figure 3.3 Di(2-ethylhexyl) Phosphoric Acid (D2EHPA).



$R^- H^+$: Carrier
A : Amino Acid

Figure 3.4 Schematic Diagram of the Transport Mechanism for Amino Acid.