CHAPTER 6

MECHANISM OF MASS TRANSFER

Mass Transfer Model.

Boey (1989) and Chaudhuri (1990) summarized the mechanism of mass transfer in liquid membrane as follows.

Mechanism of mass transfer in liquid membrane systems have been proposed in the literature to explain and predict the rate of solute transfer and the effect of operating parameters on this rate. The literature available on supported liquid membrane systems is vast. The mass transfer model of emulsion liquid membrane, in the main, are extended from the model of supported liquid membrane. The following assumptions are common to most supported liquid membrane models:

1. the phases on either side of the membrane are well mixed, therefore mass transfer resistance are negligible.
2. the membrane phase is stagnant.
3. the system is at steady-state.
4. the diffusion coefficients in the membrane phase are constant.
5. chemical equilibrium exists at both interface.

In most cases an "effective" diffusivity is used to account for the tortuous path of the diffusing species through the inert support.

Various model have been proposed for emulsion liquid membrane. Many of these models are developed for Type I Transport, but are also equally applicable for type II Facilitated Transport by assuming that the diffusion of the carrier complex across the membrane phase is rate limiting.

The five models that have been developed so far will be briefly described as follows.

1. Uniform Flat Sheet Model.

In this model, all the internal phase droplets containing the stripping reagents are coalesced into one large droplet. The membrane phase thickness is assumed to be so small in comparison with the globule diameter that the mass transfer area in the direction of solute transport can be considered to be constant., i.e. planar geometry can be assumed.

It is further assumed that the phases on either side of the membrane are well mixed, while the membrane phase itself is stagnant. Thus the model is similar to that of the supported liquid membrane (SLM).

2. Hollow Sphere Model.

This model is similar to the previous one but allows for the spherical geometry of the system. Thus the internal droplets are also assumed to be coalesced into a single well mixed droplet, but here, a spherical membrane of finite thickness surrounds this droplet.

3. Hollow Sphere-Advancing Front Model.

This model follows the lines of the Hollow Sphere model, except that , here, no mixing is assumed within the internal droplet. As a consequence, the diffusing species is removed first by the internal reagent adjacent to the membrane phase, and then has to penetrate further into the droplet as the reagent is consumed. Thus, a concentric reaction advances towards the center of the droplets as the stripping reaction progresses.

4. Immobilized Globule-Advancing Front Model.

This model is by far the most realistic in terms of geometry and configuration of the emulsion globule. The internal droplets are allowed to retain their heterogeneity (identity). The model further assumes that:

a) there is no circulation of the droplets , i.e. they are immobilized or fixed in space, and

b) that there is local chemical equilibrium between the membrane phase and the internal phase.

This model is commonly known as shrinking core model. The solute diffuses through the membrane phase whereupon it is removed by an irreversible chemical reaction in the internal droplets. A reaction front develops that advances into the center of the globules as the reagent within the outermost droplets is consumed.

5. Immobilized Hollow Spherical Globule-Advancing Front Model.

This is similar to the above model in that the internal droplets are also allowed to retain their shape and identity. A further assumption made, is that a thin distinct layer of membrane phase fluid surrounds the globule. A mass transfer resistance is assigned to this layer.

Literature on Proposed Model for Emulsion Liquid Membrane.

Over the past few years, while many papers have experimentally demonstrated the possibility of applying emulsion liquid membrane to separate various species, only a few papers have dealt with the mathematical modeling of such process.

Early attempts at modeling of real systems adopted the flat sheet model for its simplicity. Cahn and Li (1974) modeled Type 1 Facilitated Transport of phenol in emulsion liquid membrane in which the extraction rate was assumed to be proportional to the solute concentration difference between the internal and the external phase.

Matulevicius and Li (1975) proposed a hollow sphere model in which the mass transfer resistance was assumed to be limited to the peripheral shell of the emulsion globules and kept constant during the extraction process to describe phenol extraction by emulsion liquid membrane. Similar model were adopted by Gladek et. al. (1982).

Another improved approach, but more mathematically complex model, is to assume that the internal encapsulated droplets are immobilized and homogeneously distributed in the emulsion globule. This approach accounts for mass transfer contributions accompanying solute diffusing and reaction in an emulsion globule. Ho et. al. (1982), Kim et. al. (1983) and Stroeve and Varanasi (1984) used this approach to analyze the phenol removal from waste-water system. They assumed that solute removed from the bulk phase diffused through the globule to a reaction front, where it was removed instantaneously and irreversibly by reaction with an internal reagent. The reaction front advances towards the center as the reagent is consumed.

Kim et. al. (1983), assumed an additional thin outer liquid membrane layer which contained no internal droplets. The advancing front approach assumed that the reaction to be irreversible and the local solute concentration did not affect the amount of reagent to react and, that the reagent permanently traps reacted solute. It is incorrect in the real

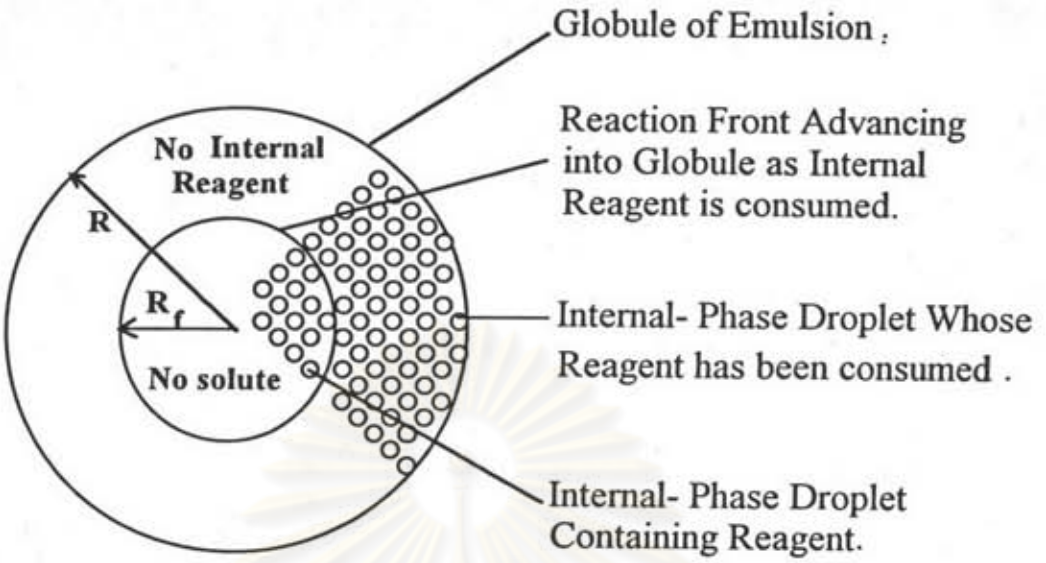


Figure 6.1 Schematic Diagram of Immobilized Globule-Advancing Front Model.

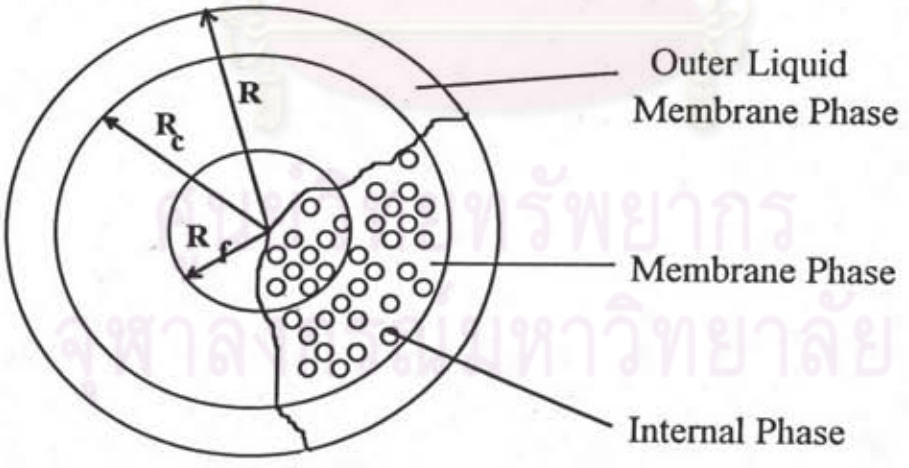


Figure 6.2 Schematic Diagram of Immobilized Hollow Spherical Globule-Advancing Front Model.

system.

Teramoto et. al. (1983) and Bunge and Noble (1984) have developed models which incorporated the more realistic assumption of reaction equilibrium. In the reversible reaction model locating the reaction front is unnecessary.

There has been more success with this model in explaining experimental results,, this basic model has been extended to account for poly dispersity of the internal phase droplets (Lorbach and Hatton, 1988) and reaction reversibility in Type I Facilitated Transport (Baird et. al., 1987).

Recently, Yan et. al. (1992) developed a model for Type I Facilitated Transport an emulsion liquid membrane by taking into account the mass transfer both inside and outside the emulsion globules and reaction between the diffusing component and the internal reagent. Datta et. al. (1993) proposed an advancing reaction front model with drop-size distribution for the case of Type 1 Facilitated Transport through an emulsion liquid membrane. The model takes into account the continuous phase and outer liquid membrane phase resistances along with diffusion through a composite emulsion drop. The computed results are found to be in excellent agreement with the experimental data of Ho et. al. (1982).

Teramoto et. al. (1991) proposed a permeation model for the extraction of tryptophan, phenylalanine and β-phenethylamine on the basis of immobilized hollow spherical globule-advancing front model, in which diffusional processes in the external aqueous phase and in the w/o emulsion globules, as well as extraction equilibria, are considered. They concluded that the experimental results were satisfactorily simulated by the proposed model.

Mechanism of Mass Transfer of Amino Acid.

The objective of this study concerning the mechanism of mass transfer of amino acid is to obtain the influence of external pH on the permeation rate by simulation.

Even though the advancing front model seemed to be regarded as the most realistic model used to represent emulsion liquid membrane system. Many assumptions and also many unknown parameters are required in the model. Many experiments have to be performed in order to get the values of parameters that can be applied in a certain condition. The mechanism of mass transfer of amino acid in emulsion liquid membrane seem to be very complicated especially on the surface area of

membrane seem to be very complicated especially on the surface area of mass transfer. It involved many small droplets of globules which varies on the stirring condition and also very difficult to measure the diameter in order to get the right value. Furthermore, during extraction the swelling and breakage of emulsion will occur. These phenomena made the system more complicated. At present, no model can really describe the mechanism of mass transfer in emulsion liquid membrane without many assumptions. Therefore the simplest model will be proposed in this study.

The most simplest model is the uniform flat sheet model. In this model, the internal phase droplets containing the stripping reagents are coalesced into one large droplets. The membrane phase thickness is assumed to be very small compared to the globule. The radius curvature can be neglected, therefore planar geometry can be assumed. It is further assumed that the phase on each side of the membrane are well mixed, while the membrane phase itself is stagnant. Thus the model is similar to that of the supported liquid membrane.

From the study of equilibrium extraction of amino acids in chapter 4, the following equations can be obtained:

$$A^+ + 2\,\overline{(HR)_2} \quad \Leftrightarrow \quad \overline{AR\,(HR)_3} + H^+ \qquad \text{.....(6.1)}$$

The schematic diagram of the permeation mechanism of amino acids through a liquid membrane containing D2EHPA as a cation carrier is illustrated in Figure 6.3 Amino acid ion in the feed solution diffuse toward the interface (x = 0), where complex formation between amino acid ion and 2 mole of dimeric D2EHPA occurs. This complex $AR(HR)_3$ then diffuses through the membrane toward the interface x = l, where amino acid ion is stripped back to the stripping solution. This step regenerates the D2EHPA carrier which then diffuses back to the interface x = 0, after which the entire process is repeated. Such a process is called "counter-transport". It is able to transport amino acid ion from a low-concentration solution to a high - concentration solution.

The concentration profile across the permeation cell is schematically shown in Figure 6.4. It is assumed that linear concentration gradients exist through out the system. The resistance of hydrogen ion diffusion in both aqueous solutions and of amino acid ion in the stripping solution are also assumed to be negligible.

In quasi-steady state, the permeation rates of amino acid are involved the following equation;

1. Permeation rate of amino acid in the feed phase.

$$J_{A,f} = \frac{(D_{A,f})}{\delta} ([A^+]_f - [A^+]_o)$$

$$J_{A,f} = (k_{A,f}) ([A^+]_f - [A^+]_o) \quad \text{..... (6.2)}$$

2. Interfacial reaction rate at the interface between feed phase and membrane phase.

$$R_1 = k_1[A+]_o[\overline{(HR)_2}]^2_o - k_{-1} [\overline{A+}]_o [H+]_o \quad \text{..... (6.3)}$$

3. Permeation rate of amino acid complex in the membrane phase.

$$J_C = \frac{(D_C)}{\tau l} ([\overline{A^+}]_o - [\overline{A^+}]_l) \quad \text{..... (6.4)}$$

4. Interfacial reaction rate at the interface between membrane phase and stripping phase.

$$R_{-1} = k_{-1}[\overline{A^+}]_l[H^+]_l - k_1[A^+]_l[\overline{(HR)_2}]^2_l \quad \text{..... (6.5)}$$

5. Permeation rate of amino acid in the stripping phase.

$$J_{A,S} = \frac{(D_{A,s})}{\delta} ([A^+]_l - [A^+]_s)$$

$$J_{A,S} = k_{A,S} [A^+]_l - [A^+]_s \quad \text{..... (6.6)}$$

Where :

J_A = permeation rate of amino acid in the aqueous phase.
D_A = diffusivity of amino acids.
D_C = diffusivity of amino acid-D2EHPA complex.
$[A^+]$ = cation of amino acid.

$\overline{[A^+]}$ = concentration of amino acid-D2EHPA complex or $AR.(HR)_3$ in the membrane phase.

$\overline{(HR)_2}$ = dimeric form of D2EHPA in the membrane phase.
τ = membrane constant.
l = thickness of the membrane.
δ = thickness of the aqueous film.
k_1, k_{-1} = interfacial reaction rate constant.

subscripts f, o, l, s refer to positions shown in Figure 6.4

When the quasi-steady state is reached,

$$J = J_{A,f} = R_1 = J_c = R_{-1} = J_{A,S}$$

From equation (6.2) to (6.6), the following equation (6.7) permeation rate of amino acid can be derived based on the assumption that all species have an equal diffusivity in the membrane and D2EHPA carrier and the amino acid-D2EHPA complex are soluble only in the liquid membrane.

$$J = \frac{\dfrac{\overline{[(HR)_2]}_0^{\,2}[A^+]_f}{[H^+]_o} - \dfrac{\overline{[(HR)_2]}_l^{\,2}[A^+]_s}{[H^+]_l}}{\dfrac{\overline{[(HR)_2]}_o^{\,2}}{k_{A,f}[H^+]_o} + \dfrac{1}{k_1}\left\{\dfrac{1}{[H^+]_o} + \dfrac{1}{[H^+]_l}\right\} + \dfrac{\overline{[(HR)_2]}_l^{\,2}}{k_{A,s}[H^+]_l} + \dfrac{k_{-1}(\tau l)}{k_1 D_c}} \quad \text{..... (6.7)}$$

If the membrane diffusion control is assumed in this case. The permeation rate of amino acid will be as follow:

$$J = \frac{k_1}{k_{-1}}\frac{D_c}{\tau l}\left[\frac{\overline{[(HR)_2]}_o^{\,2}[A^+]_f}{[H^+]_o} - \frac{\overline{[(HR)_2]}_l^{\,2}[A^+]_s}{[H^+]_l}\right] \quad \text{..... (6.8)}$$

Since, $K_{ex} = \dfrac{k_1}{k_{-1}}$

$$J = K_{ex}\frac{D_c}{\tau l}\left[\frac{\overline{[(HR)_2]}_o^{\,2}[A^+]_f}{[H^+]_o} - \frac{\overline{[(HR)_2]}_l^{\,2}[A^+]_s}{[H^+]_l}\right] \quad \text{..... (6.9)}$$

At the very initial state of extraction, $[A^+]_s$ can be assumed to be zero.

Therefore, the equation will be:

$$J = \frac{D_c K_{ex}\overline{[(HR)_2]_o}^{2} [A^+]_f}{\tau l \quad [H^+]_o} \qquad \text{..... (6.10)}$$

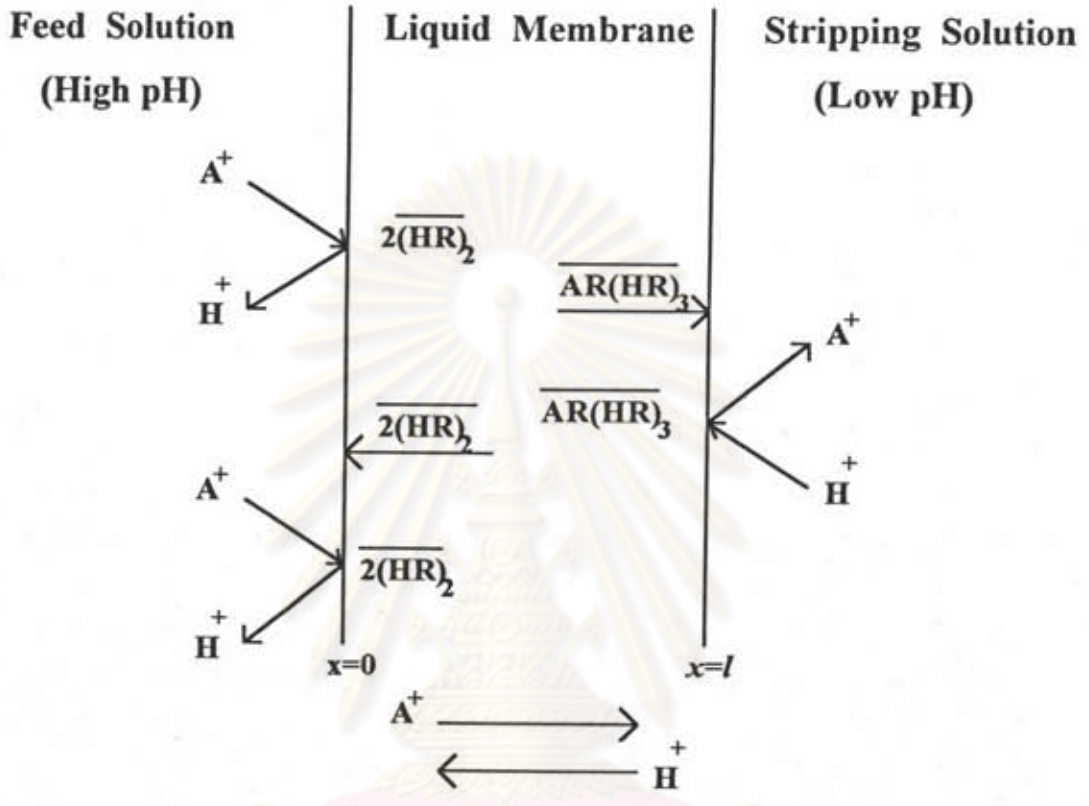
The equation (6.10) is the very simple model equation to predict the influence of external pH on the permeation rate at the initial state of extraction.

From this simple model, it can be seen that the permeation rate of amino acid is inversely proportional to the initial pH value of feed phase. The initial extraction rate of amino acid at lower pH will be less than the initial extraction rate of amino acid at higher pH. This prediction is true in the real extraction. Therefore, the trend from the influence of pH in the feed solution on the permeation rate can be obtained from this simple permeation model.

The results of calculation on inititial permeation rate of 0.006M phenylalanine at pH 2, 3 and 5 from model equation and experimental data are summarized in Table 6.1. The initial permeation rates at pH 2,3 and 5 which were calculated from equation (6.10) are shown in Figure 6.5. As shown in Figure 6.6, J**a* is plotted against pH. In this case "*a*" which is the mass transfer area of liquid membrane was assumed to be constant. Figure 6.6 shows results from the experimental data which shows similar trend as in Figure 6.5. However, the results from experimental data shows some variation from the model equation. this may be due to the assumption that there are no mass transfer resistances both in the external and internal aqueous phase. The other reason for this variation may be from the experimental data that were used for initial rate calculation which may not really be initial rate data. However,we can conclude that the initial permeation rate at pH 5 is better than pH 3, and the initial permeation rate at pH 3 is better than pH 2. The prediction of initial permeation rate trend from the model equation shows the similar result as from experimemtal data.

Example of Calculation.

According to equation (6.10), the permeation rate at the initial state can be calculated as follows:



Extraction : x=0 $A^+ + \overline{2(HR)_2} \longrightarrow \overline{AR(HR)_3} + H^+$

Stripping : x= *l* $\overline{AR(HR)_3} + H^+ \longrightarrow A^+ + \overline{2(HR)_2}$

Figure 6.3 Uniform Flat Sheet Model for Amino Acid Permeation.

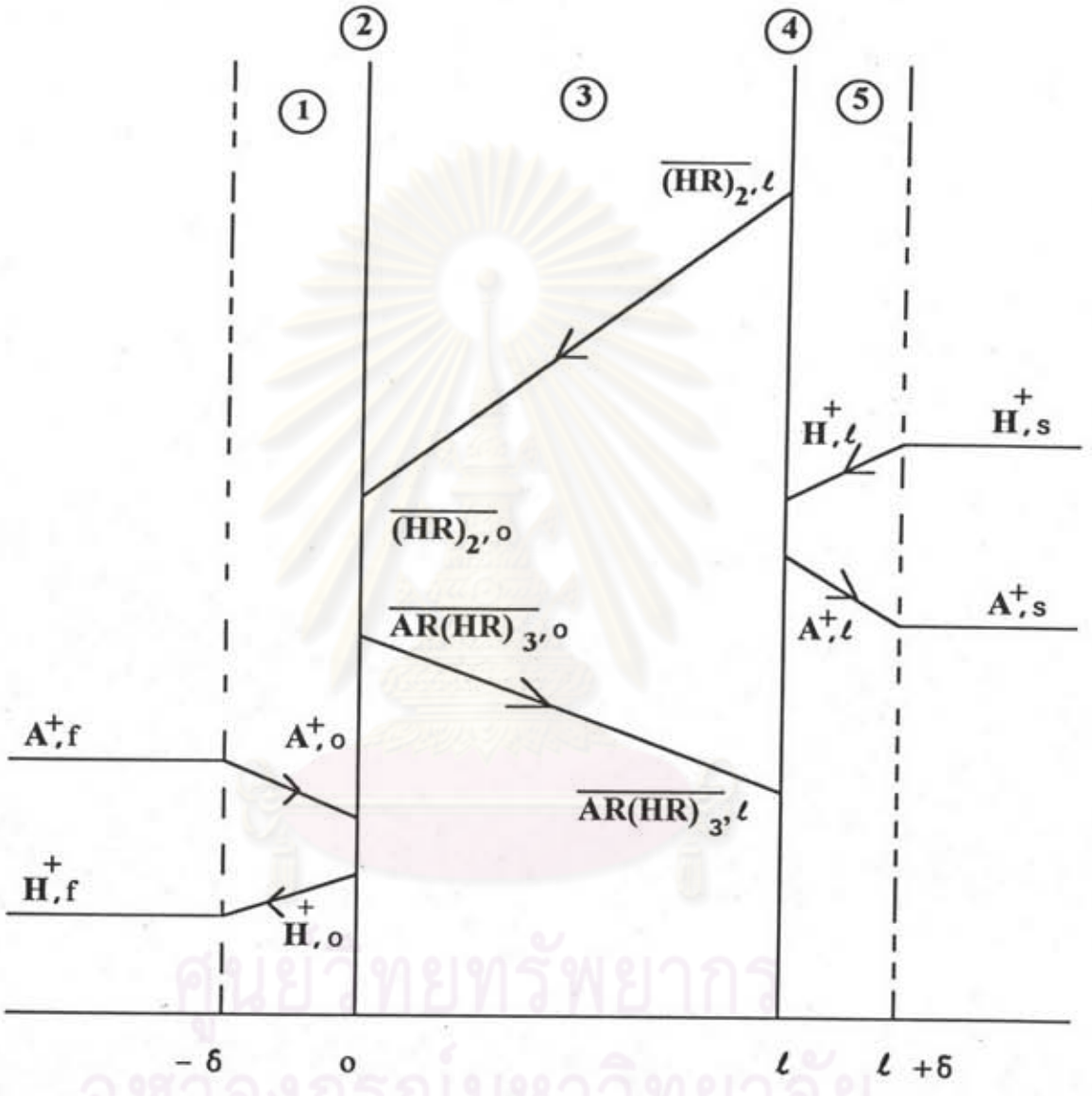


Figure 6.4 Schematic Concentration Profile of Amino Acid Permeation.

1. Calculation of $[A^{\pm}]$ in the Feed Phase.

$A_T = A^{\pm} + A^{+}$ ..... (a)

A_T = total amount of amino acid = 0.006 M

$A^{\pm}$ = zwitterion ion of amino acid

A^{+} = cation of amino acid

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

K_1 = dissociation constant of amino acid, mol/dm^3

K_1 for Phenylalanine = $10^{-1.83}$ mol/dm^3

At pH 2,

$$10^{-1.83} = \frac{[A^{\pm}][10^{-2}]}{[A^{+}]}$$

$$[A^{\pm}] = 1.479\,[A^{+}] \quad \text{..... (c)}$$

From (a); $0.006 = [A^{\pm}] + [A^{+}]$ ..... (d)

From (c) and (d) ; $[A^{+}] = 2.42 \times 10^{-3}$ mol/dm^3

Therefore, $[A^{+}]$ in the feed phase at pH2 = 2.42 mol/m^3

2. Calculation of Membrane Thickness.

In this experiment, 25 ml of internal phase and 25 ml of membrane phase was emulsified to make the emulsion.

Based on the assumption that the internal phase is coalesced into a single droplet with volume of 25 ml and the outer spherical droplet will be 50 ml in volume, the thickness of the membrane, l, can be calculated as follow:

a) Diameter of Inner Sphere (D_i).

Volume of inner sphere = 0.025 dm^3

$$\frac{1}{6}\pi D_i^3 = 0.025 \times 10^{-3} \quad m^3$$

$$D_i = \sqrt[3]{0.025 \times 10^{-3} \times 6 / \pi}$$

$$D_i = 0.0363 \quad m$$

b) Diameter of Outer Sphere (D_o).

Volume of outer sphere = 0.050 dm^3

$$\frac{1}{6}\pi D_o^3 = 0.050 \times 10^{-3} \quad m^3$$

$$D_o = \sqrt[3]{0.050 \times 10^{-3} \times 6 / \pi}$$

$$D_o = 0.0457$$

membrane thickness (l) $= \frac{D_o - D_i}{2} = \frac{0.0457 - 0.0363}{2}$ m

$$l = 4.7 \times 10^{-3} \quad m$$

3) Calculation of Permeation Rate from the Model Equation.

$$J = D_c \cdot \frac{K_{ex}\overline{[(HR)_2]}_o[A^+]_f}{\tau l \quad [H^+]_o} \qquad \text{..... (6.10)}$$

K_{ex} = 0.167 x 10^{-3} m^3/mol (from this study)

$\overline{(HR)_2}$ = 0.072 mol/dm^3 = 72 mol/m^3

$[A^+]_f$ at pH2 = 2.42 mol/m^3

$[H^+]_o$ = 10^{-2} x 10^3 mol/m^3

$$l = 4.7 \times 10^{-3} \text{ m}$$

D_c which is the diffusivity of the complex in the membrane phase was reported by Teramoto et. al. (1991) at the other concentration of carrier. However, the D_c for 0.072 M of carrier can be interpreted to be 1.65×10^{-10} m^2/s. τ (the membrane constant) will be assumed to be one.

$$J = \frac{1.65\times10^{-10}}{4.7\times10^{-3}} \times \frac{[0.167\times10^{-3}][72]^2[2.42]}{0.01\times10^{3}} \quad \text{mol/m}^2\text{ s}$$

$$J = 7.36\times10^{-9} \quad \text{mol/m}^2\text{ s}$$

Table 6.1 Calculated and Experimental Value of Initial Permeation Rate of 0.006 M Phenylalanine .

pH	Experimental Result $J*a$ (mol/s)	Model Equation J ($mol/m^2/s$)
2	4.34×10^{-6}	7.36×10^{-9}
3	7.28×10^{-6}	11.49×10^{-9}
5	10.78×10^{-6}	12.23×10^{-9}

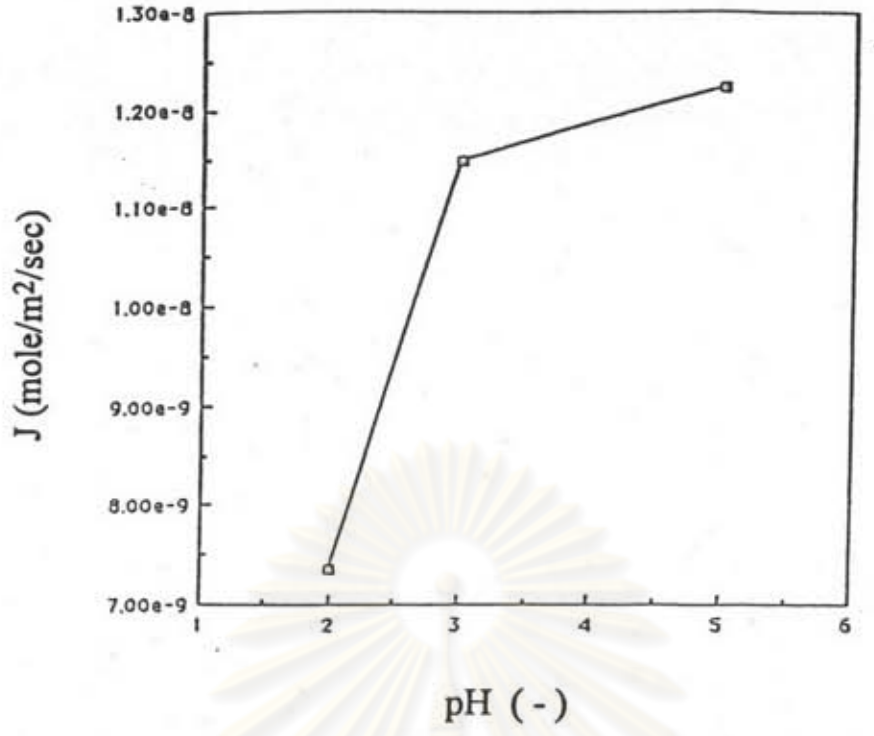


Figure 6.5 J vs. pH (Model Equation).

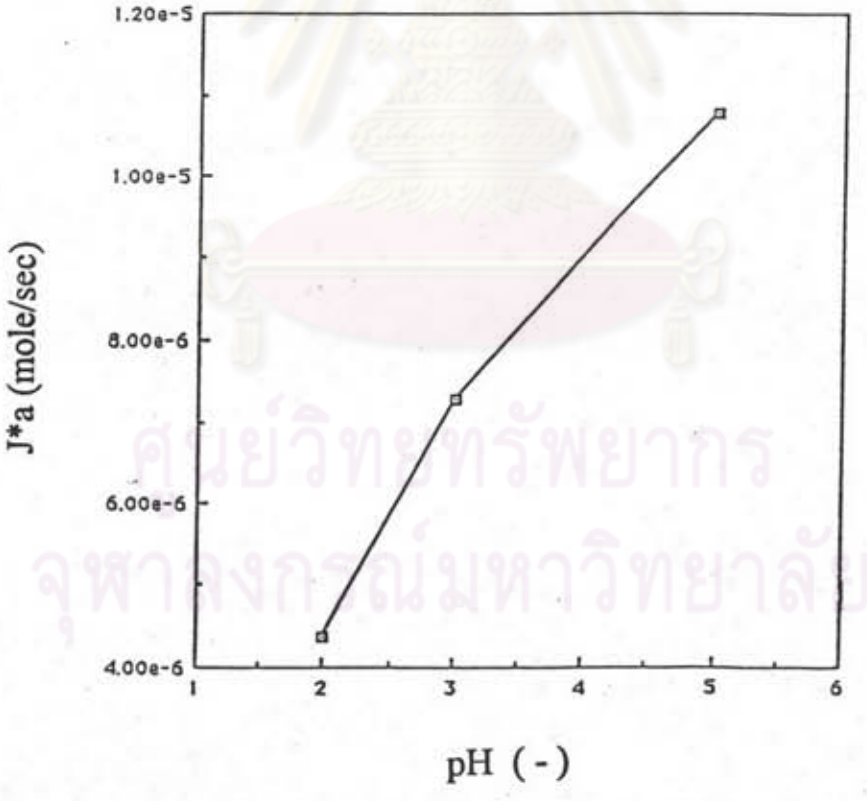


Figure 6.6 J*a vs. pH (Experimental Result).