CHAPTER 6
MECHANISM OF MASS TRANSFER

6.1 Mass Transfer Model

This chapter describes the theory behind batch extraction with emulsion liquid membranes. The theory of batch extraction may be classified into two categories : 1) diffusion type mass transfer models for Type 1 Unfacilitated Transport and 2) carrier facilitated transport models for Type 2 Facilitated Transport (Lorbarch and Marr, 1987 and Ho, 1990).

Mechanism of mass transfer in ELM systems have been proposed in the literature to explain and predict the rate of berberine transfer and the effect of operating parameters on this rate. The following assumptions of ELM models are:

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 coefficient in the membrane phase are constant.
5. Chemical equilibrium exists at both interface.

In this experiment, it was studied batch extraction with ELM of crude berberine solution in Type 1 Unfacilitated Transport. Therefore, the diffusion-type mass transfer models for Type 1 Unfacilitated Transport will be briefly described.

6.2 Diffusion-Type Mass Transfer Model for Type 1 Unfacilitated Transport

In this type, reaction in the internal phase of ELM system maintains a solute concentration of effectively zero. This is the minimization of the diffusion species in the internal phase, resulting in the maximization of the driving force for the diffusion of the solute in the membrane phase from the external phase to the internal phase. The diffusion process may be described by two methods: 1) the spherical shell approach and 2) the emulsion globule approach as follows.

6.2.1 Spherical Shell Approach

This approach assumes that the resistance of mass transfer is diffusion in the spherical shell of membrane phase of the constant thickness between the external and internal phases. The schematic of shell is shown in Figure 6.1 the example of phenol extraction with the internal phase containing NaOH for the conversion of phenol to sodium phenolate (Hatton, Lightfoot, and Li, 1982, Chan and Lee 1984, 1987).

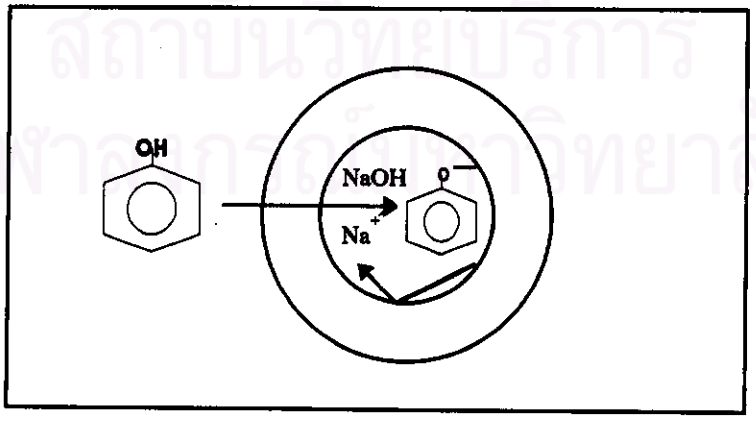

Figure 6.1 Schematic of Type 1 Unfacilitated Transport Mechanism

Mass Transfer Mechanism

In the spherical shell model of Ho and Li (1984), solute can transfer from the external phase to the internal phase only by diffusion transport. These mechanisms are shown schematically in Figure 6.2 in which the globule of the emulsion is represented by a hollow sphere with the membrane phase separating the internal phase from the external phase.

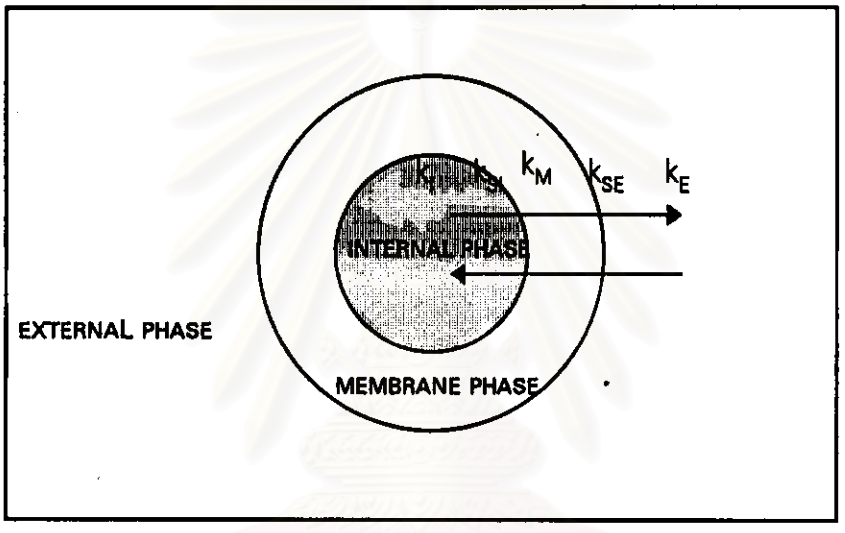

Figure 6.2 Schematic of Simplified Mass Transfer Mechanism

The concentration driving force of solute is higher for the external phase than for the internal phase, the direction of the diffuse transport will be from the external. This diffuse transport includes 5 steps:

Step 1. Mass transfer from the bulk of external phase to interface adjacent to the external phase.

Step 2. Interfacial mass transfer across this interface.

Step 3. Diffusion in the membrane phase from this interface to the second interface, adjacent to the internal phase.

Step 4. Interfacial mass transfer across the second interface.

Step 5. Mass transfer from the second interface to the internal phase.

6.2.2 Emulsion Globule Approach

The model is the most realistic in terms of geometry and configuration of the emulsion globule. The model does not take the diffusion of solute in emulsion globules into account. This can result in variation of the mass transfer coefficient with time, particularly for a long contact time (Cahn and Li, 1974). These models do not account for the effect to the rate at which the internal reagent is consumed either. They proposed the diffusion process be described in terms of a boundary at which the reaction occurs and which more forward the center of the emulsion globule as the interphase reagent is consumed. Ho et al. (1982) has developed a more rigorous and accurate model base on first principles as called Advancing Front Model. The model assumes the following:

a. There is no circulation of the droplets, i.e. the droplets are fixed in space.

b. There is local chemical equilibrium between the membrane phase and internal phase.

This model is shown in Figure 6.3. It is commonly known as **Shrinking Core Model**. The solute is taken from the external phase via dissolution in the membrane phase diffuses through to the globule to a reaction front where it is removed by reaction with the internal reagent. The reaction is assumed to be instantaneous and irreversible. The reaction front separates the inner region containing no solute from the outer region in which the internal reagent has been consumed and contained no reagent. This reaction front advances toward the globule center as the internal reagent is consumed.

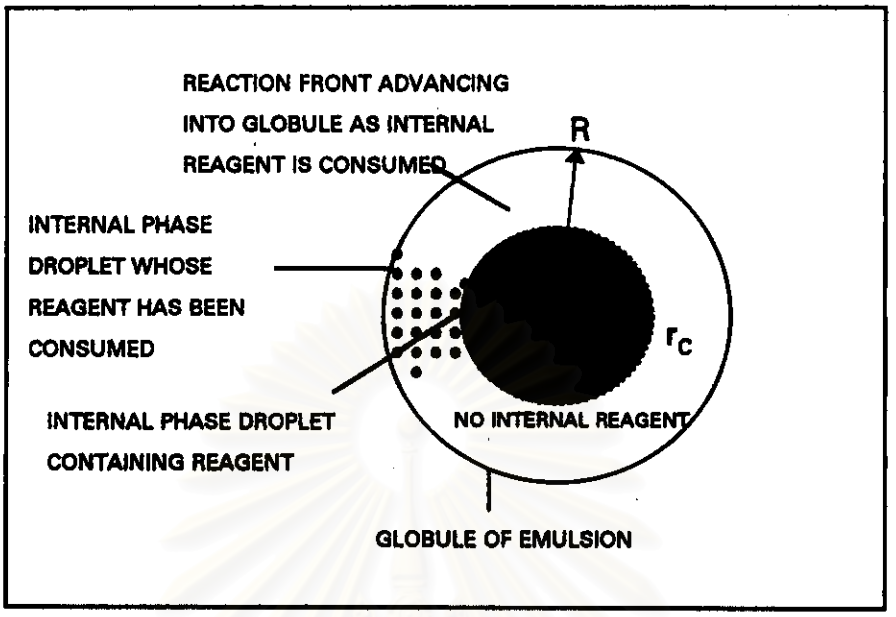

Figure 6.3 Schematic of the Advancing Front Model

6.3 Literature Review on Proposed Model for ELM

Cahn and Li (1974) had proposed the spherical shell approach assumes that mass transfer rate to be directly proportional to the average solute concentration difference between the continuous feed phase and the internal reagent phase and the proportionality, the overall mass transfer coefficient, to be constant. However contrary to the constant, and the effective overall mass transfer coefficient that they obtained varied with time. They also used this model for the analysis of pure permeation processes in the separation of hydrocarbon liquid phase was an aqueous medium.

Matulevicius and Li (1975) suggested the diffusion in a single drop. For spherical shell model, they formulated and solved the unsteady-state equations. In the model, solute diffuses from the surface of the globule to some fixed interior position where it is removed by the reaction with the internal reagent. In assuming that an

ELM globule can be represented by a single drop. An effective number thickness needs to be assigned to account for the mass transfer resistance in the globule.

Stelmaszek and Szust (1981,1982) took a similar modeling of spherical shell approach and applied the model to the separation of benzene from hexane and the extraction of phenol.

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, that the reagent permanent traps reacted solute. It is incorrect in the real system.

Ho and Li (1984) developed a more general mathematical model with overall mass transfer coefficients for extraction and leakage.

Krishna, Gaswami and Sharma (1987) investigated the effect of the breakage on selectivity in the separation of hydrocarbon mixtures.

Yan et al. (1992) developed a model for Type 1 Unfacilitated 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.

Datla et al. (1993) proposed an advancing reaction front model with drop-size distribution for the case of Type 1 Unfacilitated Transport through ELM. The model takes into account the continuous phase and outer liquid membrane phase resistance 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).

False and Stroeve (1984) and Stroeve and Varanasi (1984) extented the advancing front model to include external phase mass transfer resistance. They obtained zero and first-order perturbation solutions, and they showed that their results

reduce to those of the advancing front model when the external mass transfer resistance becomes negligible.

Kim, Choi and Ihm (1983) and Teramoto and Matsuyama (1986) included an additional mass transfer resistance in the peripheral thin membrane layer of the emulsion next to the external phase. This additional resistance is necessary for compensating their technique of volume-averaging the membrane and internal phase diffusivities, which underestimates the diffusion resistance in the emulsion globule.

6.4 Mechanism of Mass Transfer of Berberine

In this study, model is presented for unfacilitated extraction of berberine by ELM system, using the two film theory. There are two mass transfer resistances for ELM extraction. One is the resistance to the transfer of berberine from the bulk of the external phase to the emulsion globule interface (external phase resistance), the second is the resistance to berberine diffusion through the globule to the reaction front (membrane phase resistance). For planar geometry the membrane phase mass transfer resistance is equal to L/D , when D is the berberine diffusion coefficient through the membrane phase and L is the diffusion distance to the reaction front.

In this system the factor controlling the berberine yield and selectivity is the distribution (partition) coefficient of the free base. The extraction rate is controlled by the external phase mass transfer coefficient, the diffusion distance and the concentration of the internal phase reagent.

The experimental conditions used at room temperature were synthetic berberine and crude berberine. The transfer of berberine from the bulk of the external phase to the interface with membrane can be described by the equation:

$$j_{B,E} = k\left(C_B - C_{B,Ei}\right) \qquad \text{... (6.1)}$$

where $j_{B,E}$ is the berberine flux through the external phase; mol/cm^2 s

k is the external phase mass transfer coefficient; cm/s

C_B is the berberine concentration on the external phase; M

$C_{B,Ei}$ is the berberine concentration on the external phase/membrane interface; M

Assuming a shrinking core model [Figure 6.4], then for a planar geometry the diffusion of berberine through the membrane phase to the internal phase reagent reaction front is given by

$$j_{B,M} = \frac{D_B}{L}\left(C_{B,Mi} - C_{B,L}\right) \qquad \text{... (6.2)}$$

where $j_{B,M}$ is the berberine flux through the membrane phase; mol/cm^2 s

D_B is the diffusion coefficient of berberine in the membrane phase; cm^2/s

L is the diffusion distance to the reaction front; cm

$C_{B,Mi}$ is $C_{B,Ei}$; M

$C_{B,L}$ is the berberine concentration at L; M

Use of planar geometry is only valid for diffusion at the periphery of the emulsion globule where the effects of curvature are small. However, as the diffusion progresses into the emulsion globule, the effect of curvature cannot be neglected. Therefore, the system should be described by diffusion into a sphere [Figure 6.5].

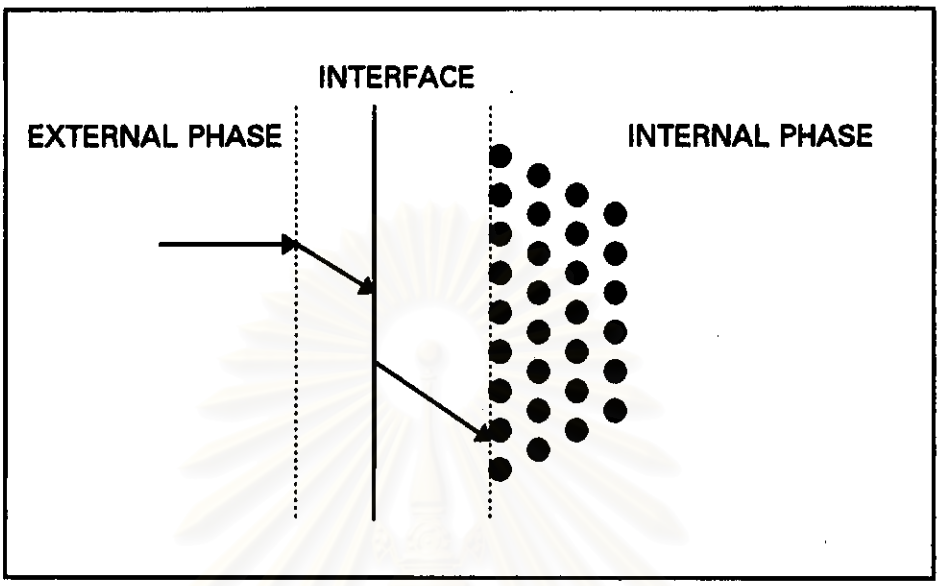

Figure 6.4 Unfacilitated Transport of Berberine Assuming a Two Film Model

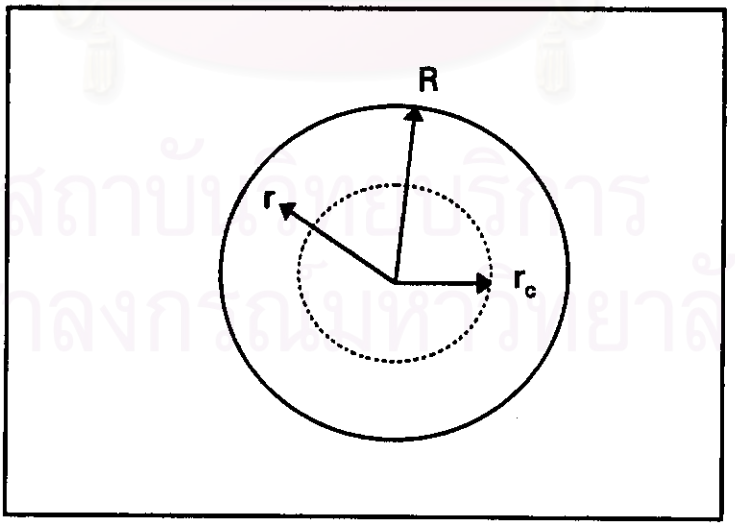

Figure 6.5 Shrinking Core Model of an Emulsion Globule

The emulsion globule of radius R, with the reaction front at r_c. Assumption at steady state of diffusion into the emulsion globule, the reaction front move slowly in comparison to the solute diffusion. So the rate of diffusion in the globule without considering swelling is

$$N = 4\pi r^2 D_B \frac{dC_B}{dr} \qquad \text{... (6.3)}$$

At steady state, the diffusion of berberine through a small layer of thickness δr is

$$N|_r - N|_{r+\delta r} = 0 \qquad \text{..... (6.4)}$$

Substituting from Eq. (6.3) and take limit $\delta r \rightarrow 0$

$$\frac{d}{dr}\left(r^2 D_B \frac{dC_B}{dr}\right) = 0 \qquad \text{..... (6.5)}$$

Intergrating Eq. (6.5) with the boundary conditions

at $r = R$, $C_B = C_{B,Mi}$ at $r = r_c$, $C_B = C_{B,L}$

The gradient in Eq. (6.3) can be found by differentiating the concentration radius profile, which when substituted into Eq. (6.3) give the flowrate of berberine in the globule :

$$N = \frac{4\pi R r_c D_B}{L}\left(C_{B,Mi} - C_{B,L}\right) \qquad \text{..... (6.6)}$$

where $L = R - r_c$

The berberine flux at the periphery of the emulsion globule ($j_{B,M}$) can be found by dividing the flowrate by the globule surface area

$$j_{B,M} = \frac{r_o D_B}{RL}\left(C_{B,Mi} - C_{B,L}\right) \qquad \text{..... (6.7)}$$

There is a steady state at the extraction phase/membrane phases interface and so that the berberine flux through the external and membrane phase are equal. Also, the berberine on either side of the interface must be at equilibrium. So that

$$K_D = \frac{C_{B,Mi}}{C_{B,Ei}} \qquad \text{..... (6.8)}$$

where K_D is the distribution (partition) coefficient

The internal phase reaction between berberine and hydrochloric acid is assumed to be instantaneous and irreversible. Therefore the berberine concentration at reaction front can be taken to zero i.e. $C_{B,L}$ equal to 0

Combination Eq (6.1),(6.7) and (6.8), the interfacial concentration of berberine can be eliminated

$$C_{B,Ei} = \frac{kC_B}{k + \frac{r_o D_B K_D}{RL}} \qquad \text{..... (6.9)}$$

Then the overall mass transfer coeffcient (K_0) can be defined as

$$\frac{1}{K_0} = \frac{1}{k} + \frac{RL}{r_o D_B K_D} \qquad \text{..... (6.10)}$$

A mass balance on the external phase, assuming constant volume; gives

$$V_E \frac{dC_B}{dt} = -Aj = -kA(C_B - C_{B,Ei}) \qquad \text{..... (6.11)}$$

The boundary condition was at t = 0, $C_B = C_{BO}$

where V_E is the volume of the external phase; cm^3

A is the surface area of the emulsion globules; cm^2

Substituting the interfacial concentration of berberine (Eq. 6.9) into the rate of equation and rearranging gives the rate berberine extraction from the extraction phase as

$$\frac{dC_B}{dt} = -\frac{kAC_B}{V_E}\left(1 - \frac{k}{k + \frac{r_c D_B K_D}{RL}}\right) \qquad \text{..... (6.12)}$$

In this equation (Eq. 6.12), the rate of extraction depends on both the external phase mass transfer process and the membrane phase diffusion. It predicts that when the diffusion distance is very small i.e. at low extraction time, the external phase mass transfer will dominate the rate of extraction. The diffusion resistance will increase due to the increase in diffusion distance in the membrane as extraction proceeds, because of the shrinking core of material reagent.

In order to follow the concentration profile, it is necessary to predict the diffusion distance in to the globule. Therefore this simple model, the diffusion distance can be determined by calculating the fraction of the internal phase reagent. The assumption of this model are; the globules and droplets are monodisperse, the internal

phase reagent concentration is independent of position in the droplet, the relative phase volume remain constant under extraction concentrations, and the emulsion globules are homogeneously dispersed in the external phase so that berberine transfer into the globules is uniform. Therefore

$$z = \left(\frac{r_C}{R}\right)^3 \qquad .....(6.13)$$

where z is the fraction of the initial charge of stripping reagent which remains when the berberine concentration in the external phase is C_B.

r_C is the radius of the unreacted core in the emulsion droplet; cm

R is the emulsion globule radius; cm.

When no reaction has taken place z = 1. The diffusion distance to the reaction front is

$$\frac{L}{R} = 1 - z^{1/3} \qquad .....(6.14)$$

where L is the diffusion distance to the raction front; cm

By mass balance, the amount of berberine extracted at time t is equal to V_E (C_{B0}- C_B). The amount of internal reagent used is χV_E (C_{B0}- C_B), where χ is the stoichiometric coefficient belonging to the internal reagent to berberine in the internal reaction.

$$R_4N^+OH^- + \chi\,HCl \longrightarrow R_4N^+Cl^- + H_2O$$

where χ is equal to 1. The fraction of reagent left is

$$z = \frac{V_I C_{HCl0} - \chi V_E (C_{B0} - C_B)}{V_I C_{HCl0}} \qquad .....(6.15)$$

where C_{B0} is the initial berberine concentration; M

C_B is the concentration of berberine in the external phase at time t

V_I is the internal phase volume; cm^3

C_{HCl0} is the initial hydrochloric acid concentration; M

Substituting the expression of z into Eq. (6.14)

$$\frac{L}{R} = 1 - \left\{ 1 - \frac{\chi \phi C_{B0}}{C_{HCl0}} \left(1 - \frac{C_B}{C_{B0}} \right) \right\}^{\frac{1}{3}} \qquad .....(6.16)$$

where ϕ is the external phase/internal phases volume ratio

Under conditions of swelling, using of Eq.(6.16) is not valid as the emulsion globule radious (R), and the external phase/internal phases volume ratio (ϕ), will change with time as a result of change in the emulsion volume. So the model must be developed. The assumptions are the emulsion volume containing the unreacted hydrochloric acid solution was proportional to the fraction (z) of unreacted hydrochloric acid solution, the diffusion distance was the difference between the emulsion globule radius (R) and the radius of the unreacted core (r_C), the volume change of external phase in this experiment was negligible. The unreacted fraction of the internal phase reagent was determined by a mass balance between the initial amount of hydrochloric acid present and the amount of berberine removed from the external phase. Then z was defined as in Eq.(6.15) and the diffusion distance L, is given as in Eq. (6.14). So that L/R will be the same as Eq.(6.16), from which the diffusion distance into the emulsion globule can be estimated as a fraction of the globule radius. However,

swelling will lead to an increase in the size of the emulsion globule. The growth of the globule radius can be determined from the emulsion volume.

$$R = \left(\frac{\frac{3}{4} V_{emul}}{\pi N_{emul}} \right)^{\frac{1}{3}} \qquad .....(6.17)$$

where V_{emul} is the emulsion volume; cm^3

N_{emul} is the number of globules in the emulsion

The following assumptions, it is assumed that the globules and the dropletes are monodisperse, the internal phase concentration is independent of position in the droplet, and no droplet or globule leakage occurs.

The swelling will affect the predicted diffusion distance , will depend on the choice of water transport model. The shrinking core model assumes that swelling occurs by the progressive dilution of internal phase droplets from the emulsion globule periphery towards the centre. That is the outer most droplets increase in size first, and the inner droplets remain the same size; it is assumed that berberine extraction is faster than water transport. From $L = R - r_c$ (The diffusion distance is defined as the distance from the external/membrane phases interface to the unreacted hydrochloric acid at the core), r_c will not be affected by swelling, only decreases as a result of berberine extraction. Therefore the term L/R [Eq.(6.16)] does not give the true diffusion distance. The diffusion distance of berberine through the emulsion globule can be described from Figure 6.6. The distance of berberine diffuses equal to the increase in the globule radius (R) due to swelling. There is the diffusion distance (L) from the initial globule radius (R_0) to the reaction front (r_c). The total diffusion distance is given by

$$L_{TOT} = L + (R - R_0) \qquad .....(6.18)$$

The diffusion distance obtained from Eq.(6.18) can be substituted into Eq.(6.12) to obtain the interfacial berberine concentration and the berberine extraction rate. The way to calculate this was shown in Appendix E and the computer program of this model, which is written in Q Basic in Appendix F.

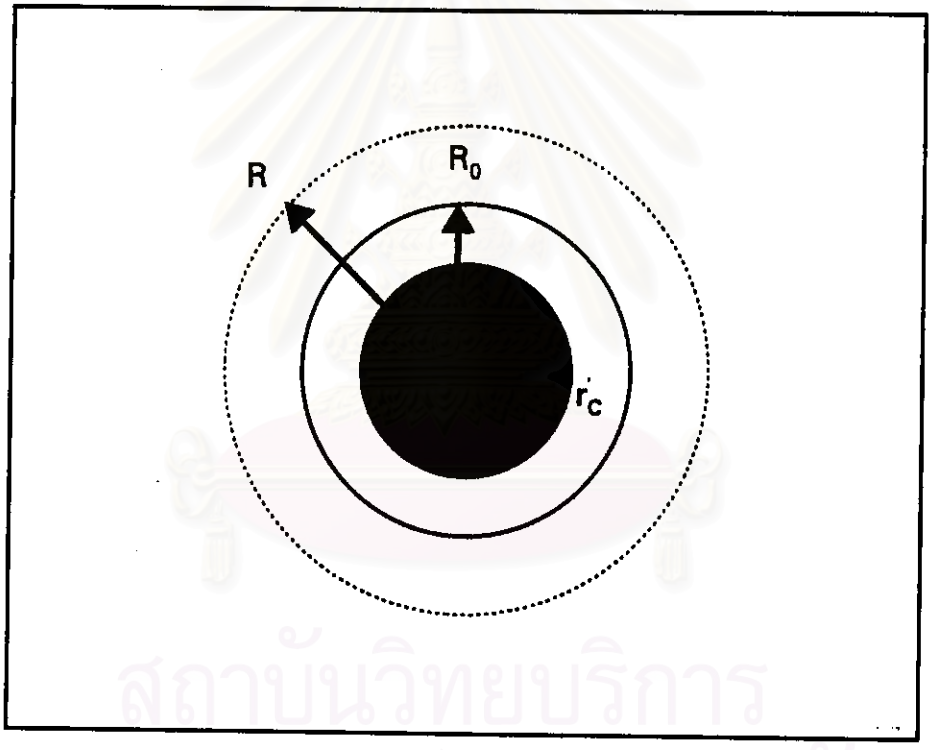

Figure 6.6 Schematic Representation of Emulsion Globule Showing the Initial Radius; R_0, the Globule Radius as a Result of Swelling; R, and the Reaction Front Radius; r_c

6.5 Comparison with Theory for Unfacilitated Transport of Berberine

Theory for Unfacilitated Transport of Berberine was developed. The main assumptions can be summarized as follow: the emulsion globules have a uniform size and any breakage on leakage is negligible; berberine partitions into the solvent and diffuses to the internal phase where it is removed by an instantaneous internal reagent; as stripping occurs the reaction front recedes into the emulsion. The removal rate of berberine from the external phase can be represented by Eq. (6.12).

The external phase mass transfer coefficient (k) can estimate from the correlation for mass transfer in dispersions (Calderbank and Moo-Young, 1961).

$$Sh = 2.0 + 0.31\ Ra^{1/3} \qquad .....(6.19)$$

where Sh is the Sherwood number which is equal to kd/D_E

Ra is the Raleigh number which is equal to $d^3\Delta\rho g/\mu_\epsilon D_E$

d is the emulsion globule diameter; cm

D_E is the diffusion coefficient of berberine in the external phase; cm^2/s

$\Delta\rho$ is the density difference between the emulsion and the external phases; g/cm^3

g is the acceleration due to gravity, cm/s^2

μ_ϵ is the external phase viscosity; cP

The external phase mass transfer coefficient was estimated using Eq.(6.19) and the diffusion coefficient of berberine in the external phase was calculated using the Wilke-Chang correlation (Wilke and Chang, 1955), and the globule size estimated by experimental observation. The mass transfer coefficient was determined to be $7.4359*10^{-6}$ cm/s. The detailed calculation is presented in Appendix F. The influence of the variables in Eq.(6.16) on the mass transfer coefficient was determined by altering the variable values by ±10% and no the effect on k. The results are shown in the Table 6.1

Table 6.1 Calculation Variables Effect with Mass Transfer Coefficient from the Model of Unfacilitated Transport with No Swelling

Variable	Initial Value	Change	Change in k
Globule diameter	0.04 cm	10%	2.95%
Diffusion coefficient	10^{-6} cm/s	10%	10%
Density difference	0.1967 g/cm^3	10%	2.42%
External phase viscosity	1cP	10%	10%

6.6 Results and Discussion

The theoretical model was evaluated using the parameter values from Appendix E. It was fitted by eye to the experimental results at high pH (due to low swelling) as shown in Figure 6.7 by using the partition coefficient, giving values of various pH from Chapter 4 and 0.04 cm of globule radius. The diffusion coefficient of berberine in

external phase and membrane phase were calculated from Wilke-Change correlation. They were $4.7506*10^{-6}$ and $2.0781*10^{-5}$ cm^2/s, respectively. With these values good agreement is observed between the theoretical and experiment results. The theoretical model was calculated as in Appendix F. For lower pH, the predicted concentration-time profile is not agree with the experimental results as well as for previous simulations. The initial rate are very close, the final berberine concentration is predicted to be lower than the experimental value. This may be attributed to slightly lower initial hydrochloric acid solution in the internal phase. In case of low pH, the water transport to the emulsion globule was higher than the rate of extraction, so the duffusivity of water and the partition coefficient to the membrane phase should be calculated. In this model, it was assumed constant and the external phase volume was also constant too.

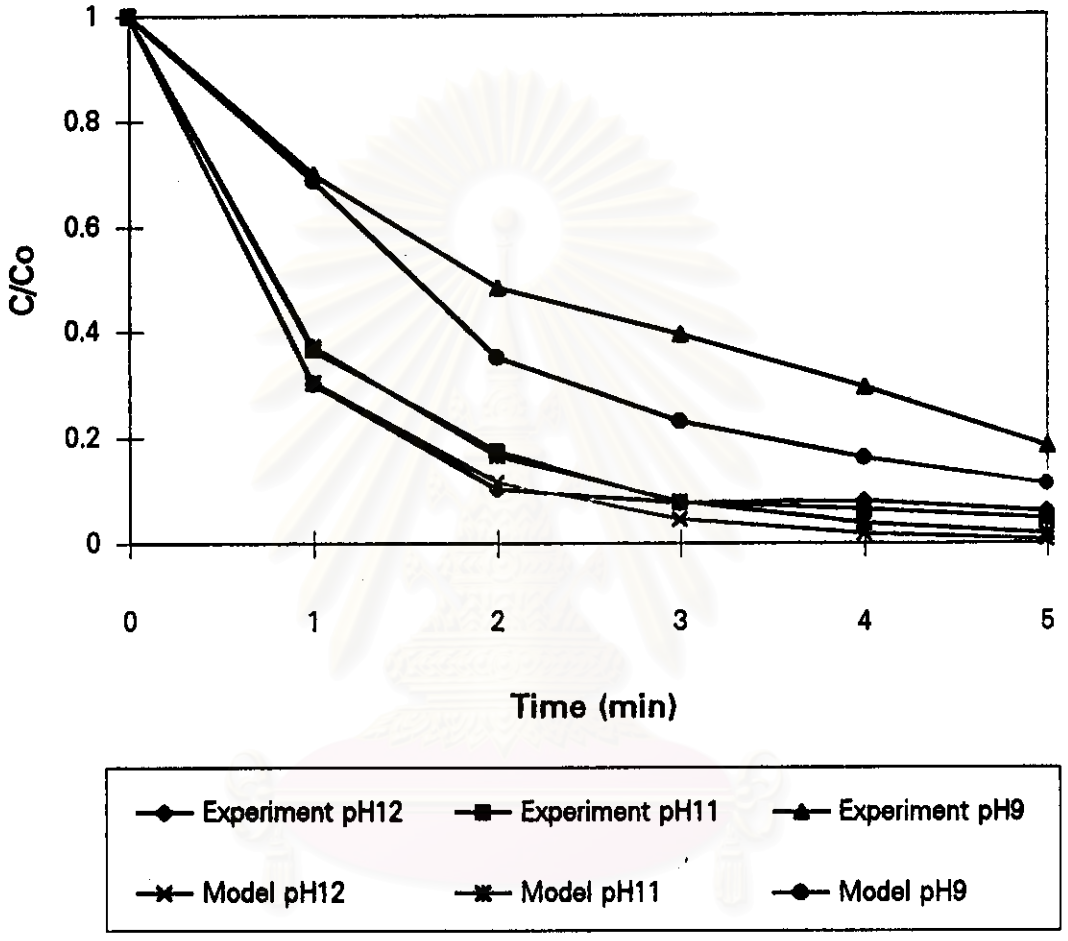

Figure 6.7 Variation in the Predicted Concentration-Time Profile as a Function of Mass Transfer and Diffusion Coefficients ($k = 7.4359*10^{-4}$ cm/s and $D = 2.0781*10^{-5}$ cm^2/s)