Mathematical Modeling of Carrier Mediated Mass Transfer through Liquid Membrane Systems

by

Keng Chao Wang

Dissertation Submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial
fulfillment of the requirements for the degree of
Doctor of Engineering Science
1984

APPROVAL SHEET

Title of Thesis:

Mathematical Modeling of Carrier Mediated
Mass Transfer
through
Liquid Membrane Systems

Name of Candiate:

Keng Chao Wang
Doctor of Engineering Science, 1984

Thesis and Abstract Approved:

Dr. Ching-Rong Huang
Professor & Assistant Chairman
Department of Chemical Engineering

Date

Date

Date

Date

VITA

Name: Keng Chao Wang

Degree and date to be conferred: D. Eng. Sci., October, 1984.

Secondary education: First Taichuang High School
Taichuang, Taiwan

Collegiate Institutions attended	Dates	Degree	Date of Degree
National Taiwan University	63/67	BS ChE	6/67
State University of New york at Buffalo	68/71	MS ChE	2/71
New Jersey Institute of Technology	82/84	D. Eng. Sci.	10/84

Major field: Chemical Engineering

Publications

MS Thesis: "Temperature Profiles for Pulsating Laminar Flow in a Rigid Tube,"(1971).

"Mathematical Modeling of Phenol Removal with Dispersed Liquid Membranes,"-in preparation for publication.

Position Held

1980-1982 Senior Process Engr, The Lummus Co., Bloomfield, NJ.

1979-1980 Process Engineer, Wilputte Corp., Murray Hill, NJ.

1977-1979 Process Engineer, Polychrome Corp., Murray Hill, NJ.

1974-1977 Project Engineer, Pfaudler Co., Rochester, NY.

Professional

New York State Licensed Professional Engineer.

ABSTRACT

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Dr. Ching-Rong Huang
Professor & Assistant Chairman
Department of Chemical Engineering & Chemistry

Dispersed liquid membrane systems are double emulsion drops. Two immiscible phases are separated by a third phase which is immiscible with the other two phases. The liquid membrane systems were classified into three types: (1) carrier mediated mass transfer, (2) mass transfer with reaction in the receiving phase, (3) mass transfer without any reaction involved. Copper extraction, phenol removal and solvent extraction were used as typical examples for each type of the membrane systems in the derivation of their mathematical models. Models with or without the consideration of film resistances were developed and compared. The models developed in this study can predict the extraction rate through dispersed liquid membranes theoretically. All parameters required in the models can be determined before

an experimental extraction run.

Experimental data from this study (copper extraction) and from literature (phenol removal and solvent extraction) were used to test the models. The agreements between the theoretical predictions and the experiemental data were very good. The advantages of dispersed liquid membrane systems over traditional methods were discussed. The models developed in this research can be used directly for the design of dispersed liquid membrane systems. The results of this study represent a very significant step toward the practical applications of the dispersed liquid membrane technology.

DEDICATION

To My Mother

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my thesis advisor, Professor C. R. Huang, for all his time, ideas and interest. Professor Huang's aid has been invaluable in directing this research to a succesful conclusion.

I also wish to acknowledge my gratitute to Dr. J. E. McCormick, Dr. J. W. Bozzelli and Dr. D. S. Kristol of the department of Chemical Engineering and Chemistry, and Dr. Edward Sarian and Dr. James McHugh of the department of Computer and Information Science, for their interest and valuable suggestions.

I am also grateful to a lot of friends for their help in the drafting of the dissertation.

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CHAPTER I

INTRODUCTION

The field of liquid membrane technology is currently undergoing a rapid expansion of the areas of both research and industrial separation techniques. Liquid membranes can be manipulated to selectively separate a specific solute from a mixture, and even to extract a solute against its concentration gradient. Liquid membrane systems are comprised of three liquid phases. Two of these are miscible with each other but separated by a third phase (the membrane phase) which is immiscible with both. Mass is transferred from one of the miscible phase across the liquid membrane to the second miscible phase. In general, liquid membranes are either supported or unsupported. Supported liquid membranes can be held in a porous structure or bounded on either side by two thin polymeric films. Unsupported liquid membranes are usually in the form of double emulsion drops. For a water/oil/water (W/O/W) system, it is the immiscible oil phase, separating the two aqueous phases. For a O/W/O system, the liquid membrane is the immiscible water phase which separates the two oil phases. Fig. 1.1 shows possible configurations for unsupported and supported liquid membrane systems.

The effectiveness of the liquid membrane process can

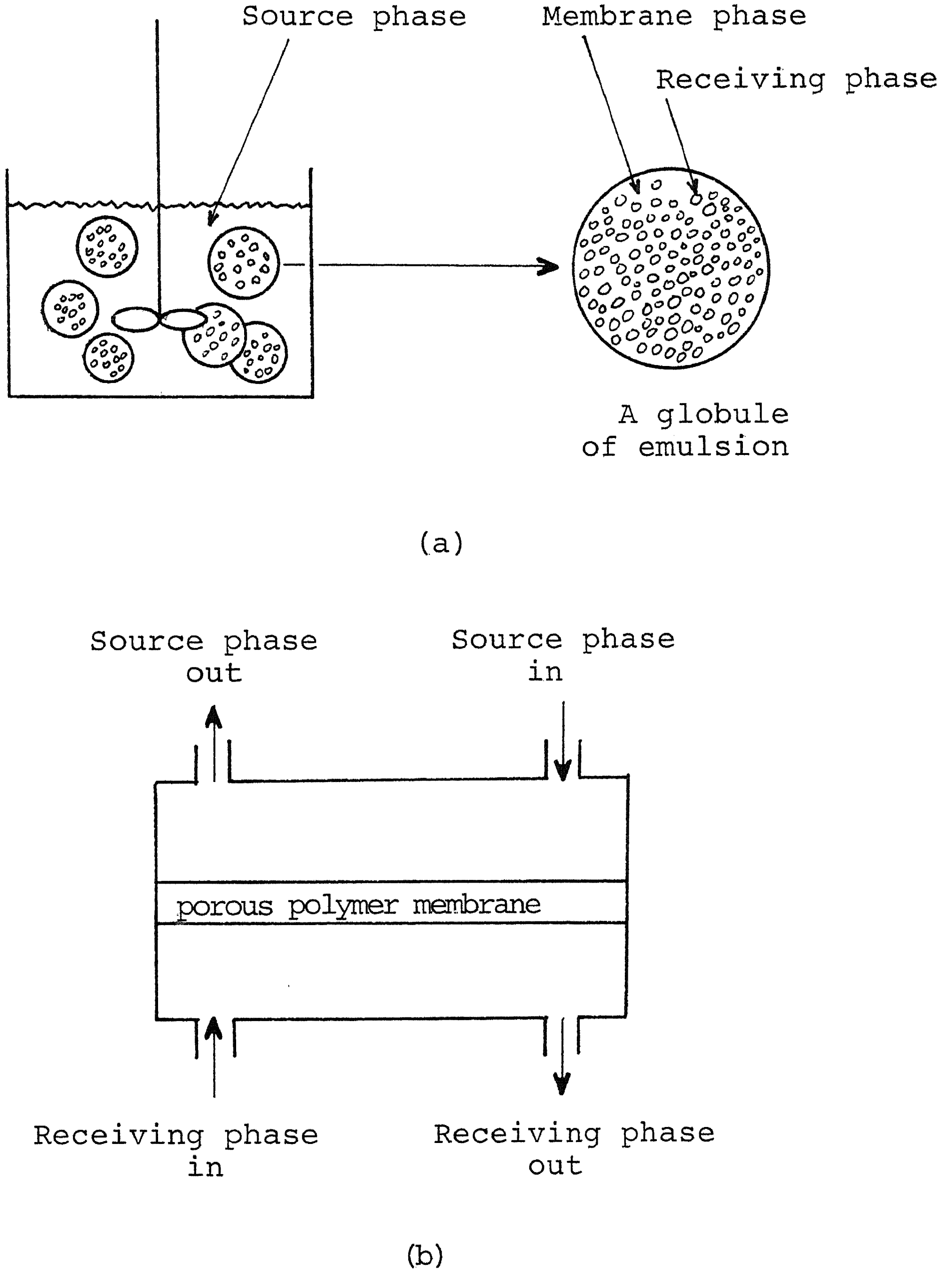


Fig. 1.1 Possible configurations for (a) unsupported (b) supported liquid membranes.

be enhanced by utilizing a facilited transport mechanism to maximize both the flux through the membrane phase, and the capacity of the receiving phase for the diffusing species. Matulevicius and Li (1975) and Li (1981) have identified two mechanisms which they call Type 1 and Type 2 facilitations, respectively. In facilitation of the first type, the concentration gradient of the membrane soluble permeate is maximized by irreversibly reacting the solute in the receiving phase, and thereby maintaining the permeate concentration effectively zero in this phase. it is desirable that the reaction product be incapable of diffusing back through the membrane. In Type 2 facilitation, an ion exchange reagent incorporated in the membrane phase "carriers" the diffusing species across the membrane to the receiving phase. This is commonly known as carrier mediated transport. In both cases, the diffusing species are eventually immobilized at the expense of some consumable reagent. For instance, phenol can be reacted with NaOH to form the oil insoluble sodium phenolate, whereas extraction of the cupric ion is ofen balanced by the counter transport of protons.

Facilitated transport through membranes probably takes place in life processes. Scholander (1960), Wittenberg (1959), and Wyman (1966) described the facilited diffusion of oxygen in systems containing proteins. Hlasky (1972) extended the theory to explain the transport of ions across liquid membranes. The experimental results from Ciani et al. (1975) supported the accepted view that complexation between ions and the macrocyclic antibitics occurs at the membrance surface.

This facilitated transport phenomena has attracted the attention of chemical engineers because of its highly selective characteristics. Schults et al. (1974) reviewed carrier mediated transport in biological membranes and liquid membrane systems in chemical industry. By appropriately adjusting cation and anion concentration on both sides of a membrane, liquid membranes containing carriers can transport or pump a specific cation against its concentration gradient. Table 1.1 lists some carrier mediated membrane systems from literature.

Polymer-supported membranes are made of three groups. The first is a solvent clamped between two highly permeable membranes, with the solute diffusion through one membrane, across the solvent, and then through the other membrane. The solvent layer between the two membranes should be as thin as possible to minimize the diffusing resistance, a difficult thing to accomplish. One method is to soak a glass fiber sheet in a solvent and mount it between two dialysis papers.

Table 1.1

Liquid Membrane systems

Form	Solvent	Carrier	Material Transferred	Feed/Stripping	Ref.
Liquid held between highly permeable membrane	Water	HCO_3^-	CO_2	Gas/Gas	Donaldson (1975)
Liquid in Porous Ploymer	Water	$CO_3^=$	H_2S	Gas/Gas	Matson(1977)
..	Octanol	LIX-64N LIX-65N	Cu^{++}, Ni^+	Aq/Aq	Lee(1978)
..	Aq. Buffer	Hemoglobin	O_2	Gas/Gas	Wittenberg (1966)
Dispersed Liquid Membranes	Toluene	Bsthocuproine	Cu^{++}	Aq/Aq	Ohki(1982)
..	Oil	Crown Ether	Pb^{++},Li^+,K^+	Aq/Aq	Biehl(1982)
..	Paraffinic Solvent	DEHPA	Uranium	Aq/Aq	Bock(1982)
..	Mineral Oil	LIX-64N	Cu^{++}	Aq/Aq	Lee(1978)

The second group consists of a porous polymer membrane with the solvent strongly adsorbed in the pores. Solutes diffuse through the pores of the membrane directly. In order to achieve a good membrane, two factors must be satisfied: the membrane must be strong enough to withstand an appreciable pressure difference between feed and stripping systems, and the membrane must hold sufficient solvent for an appreciable area for solute diffusion. However, to achieve a reasonable degree of mechanical strength, the polymer film may be slightly cross-linked to inhibit swelling and still be flexible.

The third class is that of membranes which sorb the immiscible solvent, swell in the process, and thus form a gel phase. A preferred type is the interpolymer membrane, one consisting of two kinds of polymer, one which swells strongly in the solvent phase, and the second which is insoluble in the solvent phase and, as opposed to the first, is a film-forming polymer of high mechanical strength in the solvent.

Unsupported liquid membranes (dispersed liquid membranes) were first proposed by Li (1968) over a decade ago. The advantages of dispersed liquid membrane systems as compared to supported liquid membrane systems are the ratio of surface areas to volume can be made very large by using smaller drops, and also dispersed liquid membranes are easy to prepare and operate. Since their discovery, dispersed liquid membrane systems have demonstrated considerable potential as effective tools for an increasingly wide variety of separations. The mechanisms of mass transfer in liquid membrane systems can generally be classified into three types. They are: (1) diffusion only without any reaction involved; (2) difussion with reaction in the receiving phase; (3) carrier mediated mass transfer. Typical applications of the first type are the separations of hydrocarbons (Li, 1971; Shah and Owens, 1972; Cahn and Li, 1976; Casamatta et al., 1978; Alessi et al., 1980; Halwachs et al., 1980; Kremesec, 1981; Kremesec and Slattery, 1982). Typical applications of the second type are the removal and/or recovery of various compounds from liquid streams, such as phenol (Li and Shrier, 1972; Cahn and Li, 1974; Terry et al., 1981; Ho et al., 1982; Teramoto et al., 1983; Kim et al., 1983), ammonia and amines (Kitagawa et al., 1977; Teramoto et al., 1981; Hatton et al., 1983). Typical applications of the third type are the recovery and enrichment of heavy metal ions (Schiffer et al., 1974; Hochauser and Cussler, 1975; Matulevicius and Li, 1975; Martin and Davies, 1976/1977; Frankenfeld and Li, 1977; Lee et al., 1978; Volkel et al., 1980; Strzelbicki and Charewicz, 1980; Frankfel et al., 1981; Hayworth et al., 1983; Ohki et al., 1982; Biehl et al., 1982; Bock and Vallnt, Jr., 1982; Teramoto et al., 1983) and oxygen enriched air (

Parkinson, 1983).

Fig. 1.2 shows a sequence of events in the preparation and operation for a W/O/W dispersed liquid membrane system. The dispersed systems are usually prepared by first forming an emulsion between two immiscible phases by vigorously stirring at 2,000 rpm or larger of mixing speed. Then disperse this emulsion in a third continuous phase (external phase) by low speed agitation. The liquid membrane phase is that which separates the encapsulated droplets in the emulsion form the external continuous phase. In general, the internal phase droplets are very small, having diameters of 1-10 μm, whereas the emulsion globules are usually about 0.1-2 mm in diameter. Surfactants and additives are normally included in the membrane phase formulation to control the stability, permeability and selectivity of the membrane. At the end of an extraction run, the emulsion and external phases can be separated, and the reacted internal reagent phase can be recovered, if desired, by breaking the emulsion.

While a number of investigators have experimentally demonstrated that dispersed liquid membrane systems are useful for separating various materials, such as hydrocarbons, phenol and heavy metals, physical interpretations of the results in term of existing mathematical models have not been satisfactory. Cahn and Li (1974) presented a very simplified

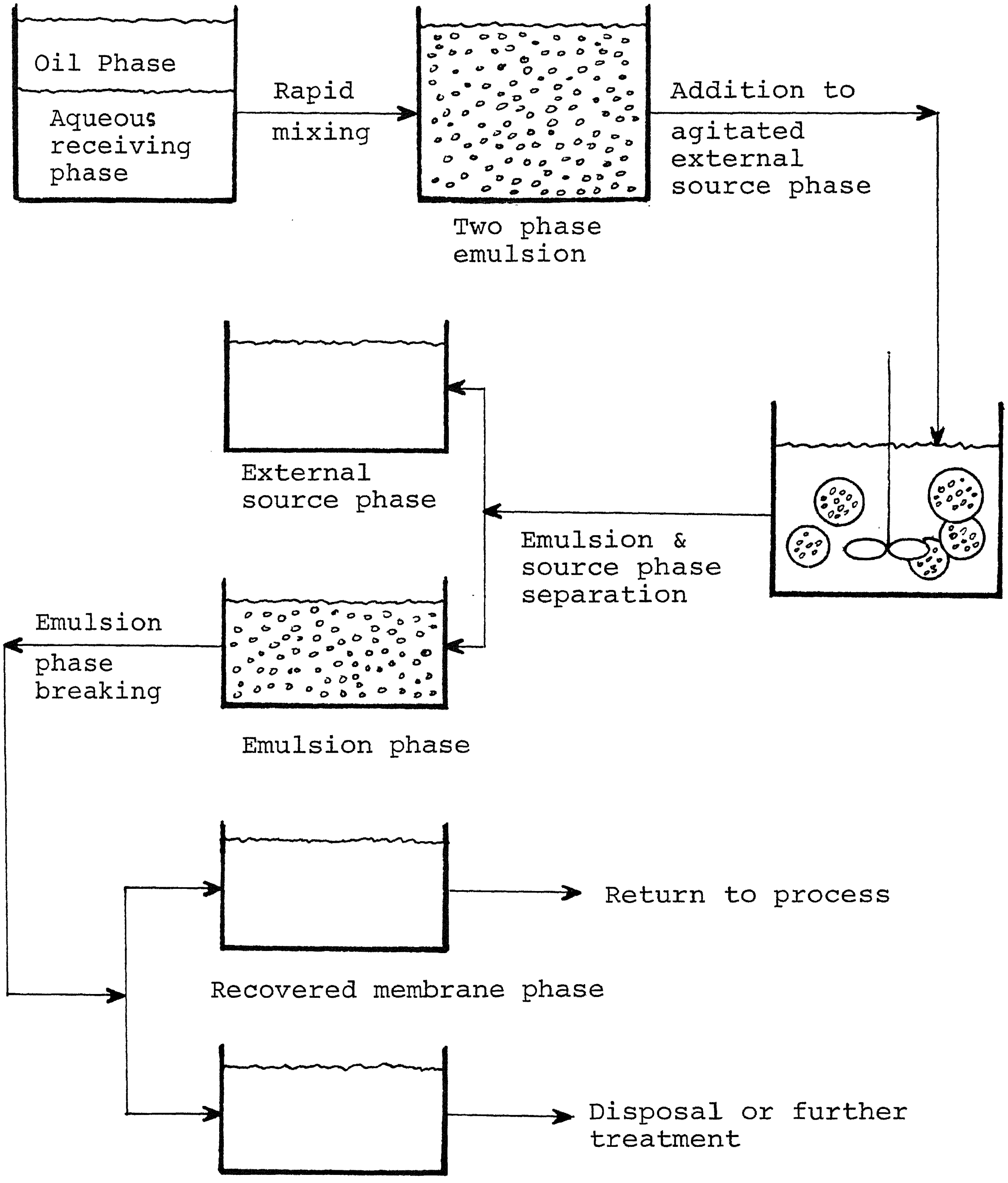


Fig. 1.2 A sequence of events for a W/O/W liquid membrane system.

model for the extraction of phenol which assumed that the extraction rate is proportional to the solute concentration difference between two aqueous phases. Later, Matulevicius and Li (1975), Volkel et al. (1980), and Kremesec (1981) proposed a model in which mass transfer resistance is localized in the peripheral oil or water layer of the emulsion drop, and the complete mixing inside the drop is assumed. It is evident, however, that this model cannot be applied to the case where the internal mass transfer resistance is controlling. Casamatta et al. (1978) analyzed the permeation rate of hydrocarbons through water membranes in an O/W/O emulsion system by taking mass transfer resistances both inside and outside of emulsion globules into account and found that the diffusion through the peripheral water layer of the emulsion globules is rate controlling because of very low solubility of hydrocarbons in water phase. A serious drawback of this model is that they do not require that the species balanced in and all across of the phases be satisfied. Marr et al. (1980) proposed a shrinking core model for the extraction of copper using LIX-64N as carriers. Ho et al. (1982) also proposed a shrinking core model for the extraction of phenol. However in the shrinking core model, the mass transfer resistance between the membrane and internal phase might also be important too was neglected. Furthermore, because chemical equilibrium in the internal aqueous phase containing NaOH and phenol was not considered, this model cannot predict the concentration of phenol attained when three phases, i.e., the internal and external aqueous phases and the oil membrane phase, are in equilibrium. Hatton et al. (1983) applied this model to design an internal recycle mixing device for the extraction of ammonia from waste water. Kim et al. (1983) proposed a similar shrinking core model to predict the extraction rate of phenol. Recently, Masaaki Teramato et al. (1982, 1983) presented models to explain experimental data for the extraction of copper and phenol by dispersed liquid membrane systems. Their models requires some parameters to be determined by curve fitting method. Their parameter values are varied with experimental conditions, and this is beyond practical applications.

Clearly, a model which can predict the extraction rate more accurately without experimental run and is easy to apply is necessary for the dispersed liquid membrane technology to be more practical.

In this research, we have developed a more detailed description of the transport phenomena in dispersed liquid membrane systems. The models developed from this research were tested by experimental data. The models are easy to apply, and enable the prediction of batch extraction rates without the need of any experimental extraction data, requiring only a knowledge of the partition coefficient for the solute between membrane and aqueous phase, average globule diameter and average droplet size and some physical properties. This is a significant improvement over existing models which rely to some degree on parameters which can not estimated independently of the extraction runs themselves. The models developed in this research can also be easily modified for continuous flow situations.

Models for the following three types of dispersed liquid membrane systems are presented in the subsequent chapters.

(1) Carrier mediated mass transfer through liquid membranes.
(2) Mass transfer through liquid membranes with reaction in the receiving phase.
(3) Solvent extraction by liquid membrane systems.

CHAPTER II

CARRIER MEDIATED MASS TRANSFER THROUGH LIQUID MEMBRANES

Liquid membrane systems with carrier have been tested experimentally and are succesfully in the removal of heavy metal ions from waste water and/or extracting mineral values from aqueous process streams. Generally, different carriers will be used to mediate the transport of different metal ions. For example, Macrocyclic Crown Ether (dicyclohexano-18-crown-6) was used to mediate the transport of Pb^{++}, Li^{+} and K^{+} (M. P. Biehl et al., 1982), Di-2-ethyhexyl phosphoric acis was used to extract uranium from wet process phosphoric acid (H. C. Hayworth et al., 1983), and Aliphatic α-hydroxy-oxime and β-hydroxybenzo-phenone oxime were used widely to extract copper from aqueous streams (Iaso Komasawa, 1983).

In carrier mediated mass transfer,the chemistry and membrane composition may be different for different applications of dispersed liquid membrane systems, but their mechanisms are all very similar. In this research, copper extraction process is used as a typical example in deriving the mathematical models of carrier mediated mass transfer through liquid membranes. Fig. 2.1 shows the mechanism of copper extraction through dispersed liquid membranes. The models derived from copper extraction can be applied to

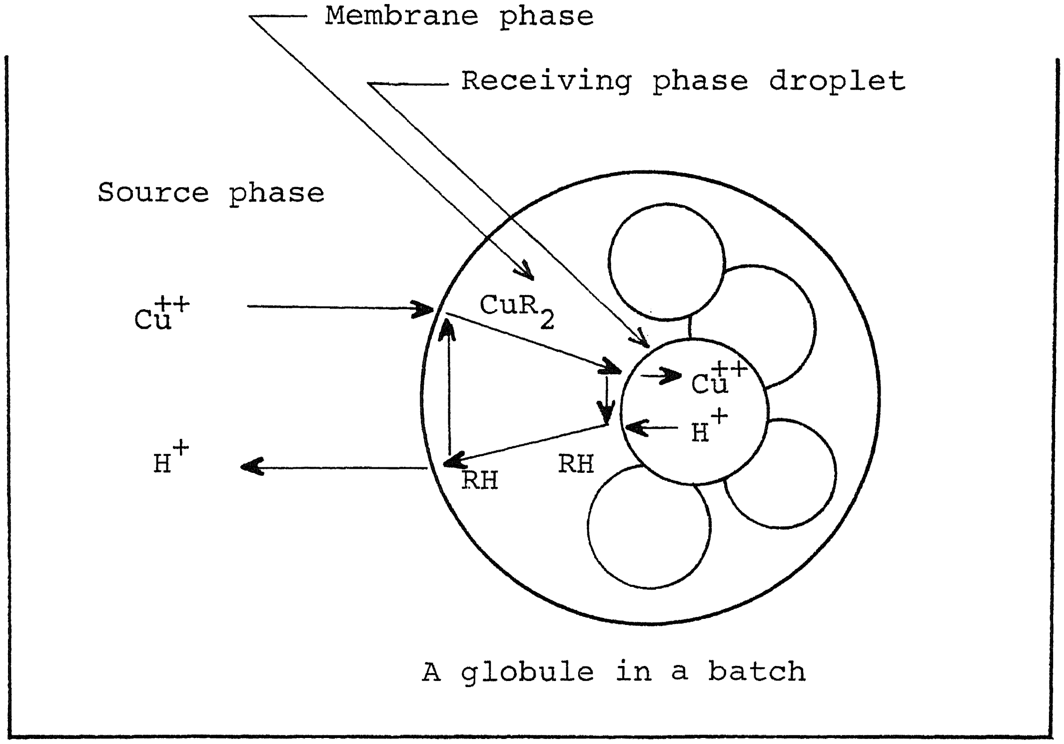


Fig. 2.1 Mechanism of carrier mediated copper extraction through dispersed liquid membranes.

other similar systems.

In this research LIX-64N (a mixture of aliphatic α-hydroxyoxime and β-hydroxybenzo phenone oxime) is used as carrier to mediate the copper extraction. The membrane phase consists of 2%W LIX-64N (abbrivated as RH), 5%V surfactant Span 80 and the rest is n-heptane. LIX-64N is a water insoluble liquid ion exchange material of the oxime kind, one which forms a strong and selective complex with copper. The copper ions are insoluble in the membrane phase but the complexes are soluble in the menbrane phase. These complexes diffuse through the membrane and react with the strong acid in the internal receiving phase. The copper ions are trapped and concentrated in the receiving phase. This concentrated copper ion solution is then easier for recovery or disposal. After the reaction of the complexex and the strong acid, the carriers are reformed and diffuse back to the membrane external interphase. By properly controlling the pH values on both sides of the membrane, copper can be extracted from the low concentration external phase to the high concentration internal phase.

An overall extraction equilibrium formulation for copper and LIX-64N is expressed as follows:

$$Cu^{++} + 2\overline{RH} \rightleftharpoons \overline{CuR_2} + 2H^{+}$$

where a bar on the top means the molecule exists only in the membrane phase. An equilibrium constant can be expressed as follows:

$$K_{eq} = \frac{[\overline{CuR_2}]\,[H^+]^2}{[Cu^{++}]\,[\overline{RH}]^2}$$

$[\overline{CuR_2}]$ and $[\overline{RH}]$ are concentrations of CuR_2 and RH in the membrane phase. $[Cu^{++}]$ and $[H^+]$ are concentrations of copper ion and hydrogen ion in the external or internal aqueous phase.

In order to model this very complicated batch extraction process, we make the following assumptions:

(1) Uniform globule sizes (Sauter mean diameter is used).
(2) No internal circulation in globules.
(3) No coalescense and redistribution of globules.
(4) Mass transfer by diffusion only.
(5) The membrane phase contains only diffusion species. Diffusion by itself without carrier is negligible.
(6) The chemical reactions at both the membrane external and internal interfaces take place very rapidly as compared to diffusion rate.
(7) Tank is well mixed. The concentration in the external phase is uniform.
(8) Diffusion coefficients are constant.

(9) The internal receiving phase droplets are so small, that their concentrations are assumed uniform.

(10) No volume change for each phase.

(11) Leakage through membrane rupture is negligible.

Three cases are considered for the carrier mediated copper extraction through dispersed liquid membranes in a batch. They are:

(1) Both the membrane external and internal film mass transfer resistances are neglected.

(2) Only the membrane external film mass transfer resistance is considered.

(3) Both the membrane external and internal film mass transfer resistance are considered.

A. BOTH THE MEMBRANE EXTERNAL AND INTERNAL FILM MASS TRANSFER RESISTANCES ARE NEGLECTED.

In this case both the membrane external interphase mass transfer resistance and the membrane internal interphase mass transfer resistance are neglected. Fig. 2.2 shows a single globule in a copper extraction batch. From the principal of material balance the governing equations that describe the concentrations of copper, carrier and complex in each phases are (Bird et al., 1960):

Membrane phase:

$$(1-\varepsilon)\frac{\partial C_x}{\partial t} = D_{ex}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{C_x}{r}\right)\right) - R_x \qquad (2.2)$$

$t=0 \quad C_x=0 \quad$ for all r

$r=0 \quad C_x=$finite

$r=R \quad C_x=C_x^*$

where $D_{ex}=(1-\varepsilon)D_x$

C_x: concentration of CuR_2 in the membrane phase.

D_{ex}: effective diffusion coefficient of CuR_2 in the emulsion phase.

D_x: diffusion coefficient of CuR_2 in the membrane.

ε: volume fraction of internal phase in emulsion phase.

R_x: the rate of disaperance of CuR_2 per unit volume of the emulsion phase.

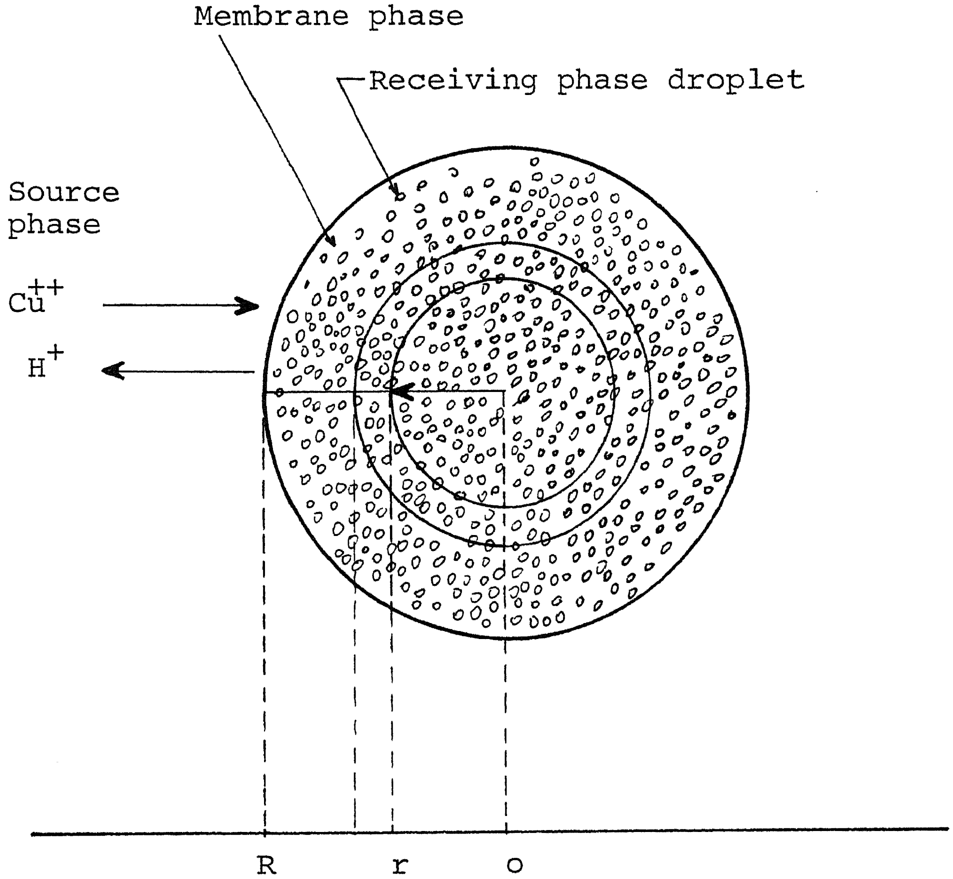


Fig. 2.2 A single globule in a copper extraction batch.

R: Sauter mean radius of globules.

C_x^*: concentration of CuR_2 at membrane external interface.

$$(1-\varepsilon)\frac{\partial C_{RH}}{\partial t} = D_{eRH}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{RH}}{\partial r}\right)\right) - 2R_x \qquad (2.3)$$

$t=0 \quad C_{RH}=C_{RHO} \quad$ for all r

$r=0 \quad C_{RH}=$finite

$r=R \quad C_{RH}=C_{RH}^*$

where $D_{eRH}=(1-\varepsilon)D_{RH}$

C_{RH}: concentration of RH in the membrane phase.

D_{eRH}: effective diffusion coefficient of RH in the emulsion phase.

D_{RH}: diffusion coefficient of RH in the membrane.

C_{RHO}: initial concentration of RH in the membrane.

C_{RH}^*: concentration of RH at the membrane external interphase.

External source phase:

$$V_t(1-\phi')\frac{dCu}{dt} = N(4\pi R^2)D_{ex}\left(\frac{\partial C_x}{\partial r}\right)_{r=R} \qquad (2.4)$$

$t=0 \quad Cu=Cuo$

where V_t: total liquid volume in a batch.

ϕ': volume fraction of emulsion phase in a batch.

Cu: concentration of copper ion in the external phase.

N: the total number of globules in a batch.

Cuo: initial concentration of copper ion in the external phase.

Internal receiving phase:

$$\varepsilon\frac{\partial Cui}{\partial t} = R_x \tag{2.5}$$

$$t=0 \quad Cui=0$$

where Cui: concentration of copper ion in the internal phase.

Since the total moles of carrier is constant, a constrain is needed:

$$(1-\varepsilon)\int_0^R 4\pi r^2(2C_x)dr + \int_0^R 4\pi r^2 C_{RH}dr = \frac{4}{3}(1-\varepsilon)\pi R^3 C_{RHO}$$

or

$$\int_0^R (2C_x + C_{RH})r^2 dr = \frac{1}{3}R^2 C_{RHO} \tag{2.6}$$

The above governing equations can be simplified through the assumptions. Fig. 2.3 shows the concentrations of different species at the membrane external interface. The equilibrium relations of different species have the following form:

$$K_{eq} = \frac{C_x^* \cdot C_H^{*2}}{Cu^* \cdot C_{RH}^{*2}} \tag{2.7}$$

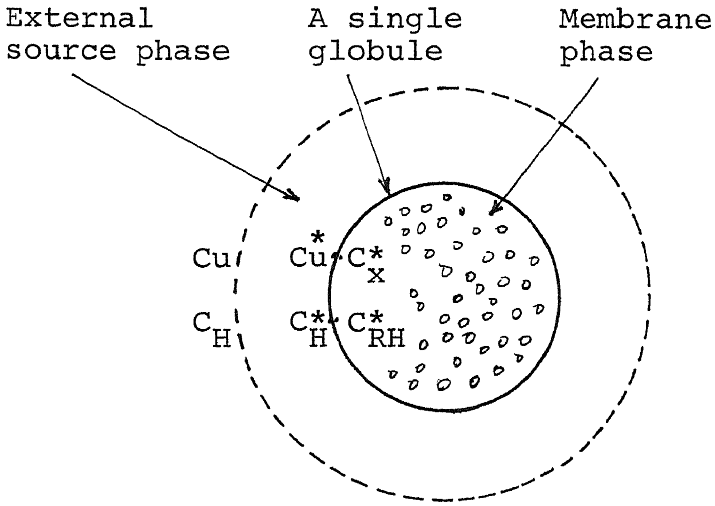


Fig. 2.3 Concentrations of different species at membrane external interface.

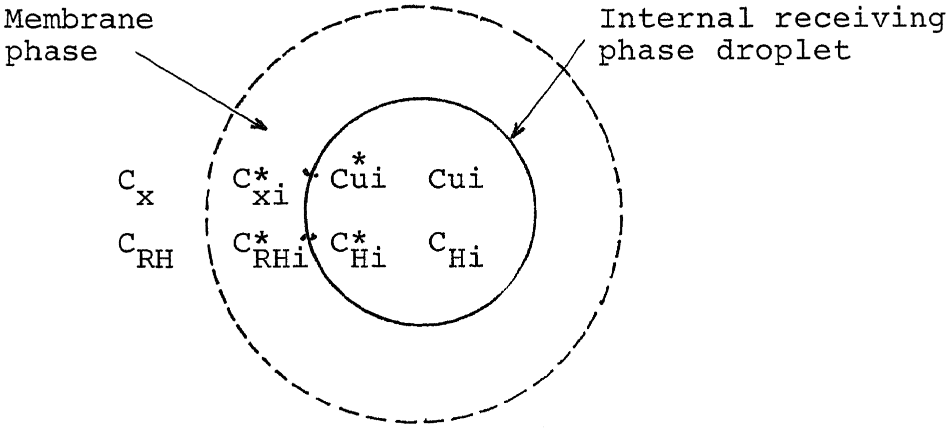


Fig. 2.4 Concentrations of different species at membrane internal interface.

By the assumptions of no external film resistance and well mixed tank, we have the following relations:

$$Cu^{*} = Cu, \quad C_{H}^{*} = C_{H} \tag{2.8}$$

where Cu*: concentration of copper ion at the membrane external interface.

C_H: hydrogen ion concentration in the external phase.

C_H^*: hydrogen ion concentration at the membrane external interface.

Substitute eqn. (2.8) into eqn. (2.7), we obtain:

$$C_{x}^{*} = \left(\frac{K_{eq}\cdot C_{RH}^{*}{}^{2}}{C_{H}{}^{2}}\right) Cu \tag{2.9}$$

Similarly, Fig. 2.4 shows the concentrations of various species around a receiving phase droplet. The equilibrium relations of the various species around the droplet have the following form:

$$K_{eq} = \frac{C_{xi}^{*}\cdot C_{Hi}^{*}{}^{2}}{Cui^{*}\cdot C_{RHi}{}^{2}} \tag{2.10}$$

By the assumptions of no internal film resistance and uniform concentration in the droplets, we have:

$$C_{xi}^{*} = C_{x}, \quad C_{RHi}^{*} = C_{RH} \tag{2.11}$$
$$Cui^{*} = Cui, \quad C_{Hi}^{*} = C_{Hi}$$

where Cui*: copper ion concentration on the droplet surface.

C_{Hi}: hydrogen ion concentration in the receiving phase.

C^*_{Hi}: hydrogen ion concentration on the droplet surface.

Substitute eqn. (2.11) into eqn. (2.10), we obtain:

$$Cui = \left(\frac{C_{Hi}{}^2}{K_{eq}\cdot C_{RH}{}^2}\right)C_x \qquad (2.12)$$

In practical applications, the source phase copper concentration is usually very low and is about 150 ppm and initial carrier concentration is usually about 2-4% by weight. We can expect the CuR_2 concentration in the membrane phase is very low as compared to the carrier concentration. The initial nitric acid is about 1.5% by weight and is very high as compared to copper concentration. Based on these facts, we can make the following approximations:

$$C^*_{RH} \simeq C_{RH} \simeq C_{RHO} \qquad (2.13)$$

$$C_{Hi} \simeq C_{HOi}$$

$$C_H \simeq C_{HO}$$

where C_{HOi}: initial concentration of hydrogen ion in the receiving phase.

Having the above relations, eqns. (2.9) and (2.12) can then be expressed in the following forms:

$$C_x^* = mCu \qquad (2.14a)$$

$$Cui = qC_x \qquad (2.14b)$$

where $$m = \left(\frac{K_{eq} \cdot C_{RH}^{*2}}{C_H^2}\right) \simeq \left(\frac{K_{eq} \cdot C_{RHO}^2}{C_{HO}^2}\right) = \text{constant} \qquad (2.15a)$$

$$q = \left(\frac{C_{Hi}^2}{K_{eq} \cdot C_{RH}^2}\right) \simeq \left(\frac{C_{Hi}^2}{K_{eq} \cdot C_{RHO}^2}\right) = \text{constant} \qquad (2.15b)$$

Through the above simplifications, the copper extraction process can be described by the following set of equations:

$$(1-\varepsilon)\frac{\partial C_x}{\partial t} = D_{ex}\left(\frac{1}{r^2}\frac{\partial}{r}\left(r^2\frac{\partial C_x}{\partial r}\right)\right) - R_x \qquad (2.16)$$

$t=0 \quad C_x=0$ for all r

$r=0 \quad C_x=\text{finite}$

$r=R \quad C_x=C_x^*$

$$-V_t(1-\phi')\frac{dCu}{dt} = N(4\pi R^2)D_{ex}\left(\frac{\partial C_x}{\partial r}\right)_{r=R} \qquad (2.17)$$

$t=0 \quad Cu=Cuo$

$$\frac{\partial Cui}{\partial t} = R_x \qquad (2.18)$$

$t=0 \quad Cui=0$

$$C_x^* = mCu \qquad (2.19)$$

$$Cui = qC_x \qquad (2.20)$$

Combine eqns. (2.20), (2.18) and (2.16), we obtain:

$$(1-\varepsilon+q\varepsilon)\frac{\partial C_x}{\partial t} = D_{ex}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_x}{\partial r}\right)\right) \tag{2.21}$$

Introduce the following relations and dimensionless variables,

$$\begin{aligned} y &= \frac{r}{R} \\ \tau &= \frac{D_{ex}}{R^2}t \\ N &= \frac{V_t\phi'}{(4/3)\pi R^3} \\ b &= (1-\varepsilon+q\varepsilon) \\ \phi &= \frac{3\phi'}{1-\phi'} \end{aligned} \tag{2.22}$$

eqns. (2.21) and (2.17) become:

$$b\,\frac{\partial C_x}{\partial \tau} = \frac{1}{y^2}\frac{\partial}{\partial y}\left(y^2\frac{\partial C_x}{\partial y}\right) \tag{2.23}$$

$$\begin{aligned} &\tau=0 \quad C_x=0 \\ &y=0 \quad C_x=\text{finite} \\ &y=1 \quad C_x=C_x^* \end{aligned}$$

$$-\frac{dCu}{d\tau} = \left(\frac{\partial C_x}{\partial y}\right)_{y=1} \tag{2.24}$$

$$\tau=0 \quad Cu=Cuo$$

Eqns. (2.23) and (2.24) have to be solved together. Take Laplace transform on both equations, we obtain:

$$bs\bar{C}_x = \frac{1}{y^2}\frac{d}{dy}(y^2\frac{d\bar{C}_x}{dy}) \qquad (2.25)$$

$$y=0 \qquad \bar{C}_x=\text{finite} \qquad (2.25a)$$

$$y=1 \qquad \bar{C}_x=\bar{C}_x^*$$

$$(s\bar{C}u - Cuo) = -\phi(\frac{d\bar{C}_x}{dy})_{y=1} \qquad (2.26)$$

Let $\bar{z}=y\bar{C}_x$ and substitute it into eqn. (2.25),

$$bs\bar{C}_x = \frac{1}{y^2}\frac{d}{dy}(y^2\frac{d}{dy}(\frac{\bar{z}}{y})) = \frac{1}{y^2}\frac{d}{dy}(y^2\,\frac{y\bar{z}'-z}{y^2}) = \frac{\bar{z}''}{y}$$

and we obtain a very simple equation:

$$bs\bar{z} = \frac{d^2\bar{z}}{dy^2} \qquad (2.27)$$

The general solution of eqn. (2.27) is:

$$\bar{z} = C_1\sinh\sqrt{bs}y + C_2\cosh\sqrt{bs}y$$

or
$$\bar{C}_x = \frac{C_1\sinh\sqrt{bs}y}{y} + \frac{C_2\cosh\sqrt{bs}y}{y} \qquad (2.28)$$

By the boundary condition of eqn. (2.25a), at y=0, C_x is finite and since cosh(0) =1, C_2 must be equal to 0, so

$$\bar{C}_x = \frac{C_1\sinh\sqrt{bs}y}{y} \qquad (2.29)$$

By the boundary condition of eqn. (2.25b), we can find the constant C_1, it is:

$$C_1 = \frac{\bar{C}_x^*}{\sinh\sqrt{bs}}$$

Substitute it into eqn. (2.29), we obtain:

$$\bar{C}_x = \frac{\bar{C}_x^* \sinh\sqrt{bs}y}{y \sinh\sqrt{bs}} \tag{2.30}$$

and $$\left(\frac{d\bar{C}_x}{dy}\right)_{y=1} = \frac{\bar{C}_x^*}{\sinh\sqrt{bs}}\left[\frac{d}{dy}\left(\frac{\sinh\sqrt{bs}y}{y}\right)\right]_{y=1}$$

$$= \frac{\bar{C}_x^*}{\sinh\sqrt{bs}}\left[\frac{y\sqrt{bs}\cdot\cosh\sqrt{bs} - \sinh\sqrt{bs}}{y^2}\right]_{y=1}$$

$$= \frac{\bar{C}_x^*(\sqrt{bs}\cosh\sqrt{bs} - \sinh\sqrt{bs})}{\sinh\sqrt{bs}} \tag{2.31}$$

From eqn. (2.19), $\bar{C}_x^* = m\bar{C}u$, substitute this into eqn. (2.31), we obtain:

$$\left(\frac{d\bar{C}_x}{dy}\right)_{y=1} = \frac{m\bar{C}u(\sqrt{bs}\cosh\sqrt{bs} - \sinh\sqrt{bs})}{\sinh\sqrt{bs}} \tag{2.32}$$

Substitute the above eqn. into eqn. (2.26), we get:

$$(s\bar{C}u - Cuo) = \frac{-m\phi\bar{C}u(\sqrt{bs}\cosh\sqrt{bs} - \sinh\sqrt{bs})}{\sinh\sqrt{bs}}$$

Solve the above eqn. for $\bar{C}u$, we obtain:

$$\frac{\bar{C}u}{Cuo} = \frac{\sinh\sqrt{bs}}{s\cdot\sinh\sqrt{bs} + m\phi\sqrt{bs}\cosh\sqrt{bs} - m\phi\sinh\sqrt{bs}} \tag{2.33}$$

The external source phase copper concentration is the inverse Laplace transform of eqn. (2.33).

$$\frac{Cu}{Cuo} = L^{-1}\left\{\frac{\sinh\sqrt{bs}}{s\cdot\sinh\sqrt{bs} + m\phi\sqrt{bs}\cosh\sqrt{bs} - m\phi\sinh\sqrt{bs}}\right\}$$

$$= L^{-1}\left\{F_1(s)\right\} \qquad (2.33a)$$

The theoretical background for the inverse Laplace transform can be referred to the book by Churchill (1972) or the book by Spiegel (1965). The inverse Laplace transform is equal to the sum of all the residues of the function $F_1(s)$. To find the residues of $F_1(s)$, we have to find its poles first. Because of $\sqrt{s}$, it would appear that s = 0 is a branch point. That this is not so, it can be seen by the series expansion of $F_1(s)$.

$$F_1(s) = \frac{\sinh\sqrt{bs}}{s\cdot\sinh\sqrt{bs} + m\phi\sqrt{bs}\cosh\sqrt{bs} - m\phi\sinh\sqrt{bs}}$$

$$= \frac{\sqrt{bs}+\frac{1}{3!}(\sqrt{bs})^3+\frac{1}{5!}(\sqrt{bs})^5+\ldots}{s\left[\sqrt{bs}+\frac{1}{3!}(\sqrt{bs})^3+\ldots\right]+m\phi\left[\sqrt{bs}\,(1+\frac{1}{2!}(\sqrt{bs})^2+..)-(\sqrt{bs}+\frac{1}{3!}(\sqrt{bs})^3+..)\right]}$$

$$= \frac{1+\frac{1}{3!}(bs)+\frac{1}{5!}+\ldots\ldots}{s\left[1+\frac{1}{3!}(bs)+\frac{1}{5!}(bs)^2+..\right]+m\phi\left[\frac{1}{3}(bs)+(\frac{1}{4!}-\frac{1}{5!})(bs)^2+..\right]} \qquad (2.34)$$

From which it is evident that there is no branch point at s=0. However, there is a simple pole at s=0.

The function $F_1(s)$ also has infinitely many poles given

given by the roots of the following equation.

$$s \cdot \sinh\sqrt{bs} + m\phi(\sqrt{bs}\cosh\sqrt{bs} - \sinh\sqrt{bs}) = 0 \qquad (2.35)$$

After rearrangement, the above equation becomes:

$$\tanh\sqrt{bs} = \frac{m\phi\sqrt{bs}}{m - s} \qquad (2.36)$$

Let $$\sqrt{bs} = x + i\beta \qquad (2.37)$$

Since we are interested only in the real part of s, s has to be either positive or negative, so either β or x have to be zero. If $\beta=0$, then $s=x^2/b$. Substitute this into eqn. (2.36), we have:

$$\tanh x = \frac{m\phi x}{m\phi-(x^2/b)} \qquad (2.38)$$

From the curves shown in Fig. 2.5, it can be seen that there is no solution to the eqn. (2.38), except x=0. So in eqn. (2.37), x is 0, and we can write:

$$\sqrt{bs} = i\beta \quad \text{or} \quad s = -\frac{\beta^2}{b} \qquad (2.39)$$

Substitute eqn. (2.39) into eqn. (2.36), we have:

$$\tanh(i\beta) = \frac{m\phi(i\beta)}{m\phi+(\beta^2/b)} = i\tan(\beta)$$

or $$\tan(\beta) = \frac{m\phi b\beta}{m\phi b + \beta^2} \qquad (2.40)$$

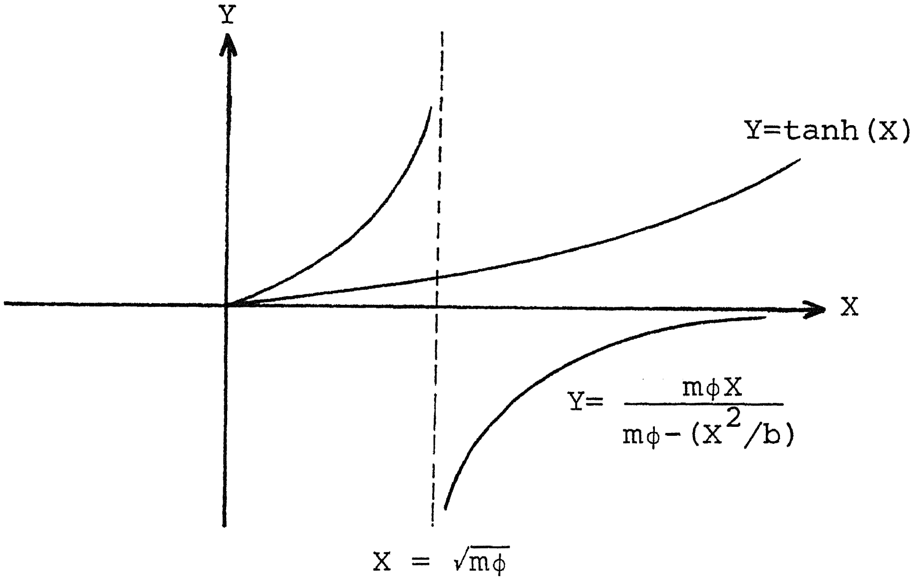


Fig. 2.5 Curves for $\tanh(X) = \frac{m\phi X}{m\phi-(X^2/b)}$

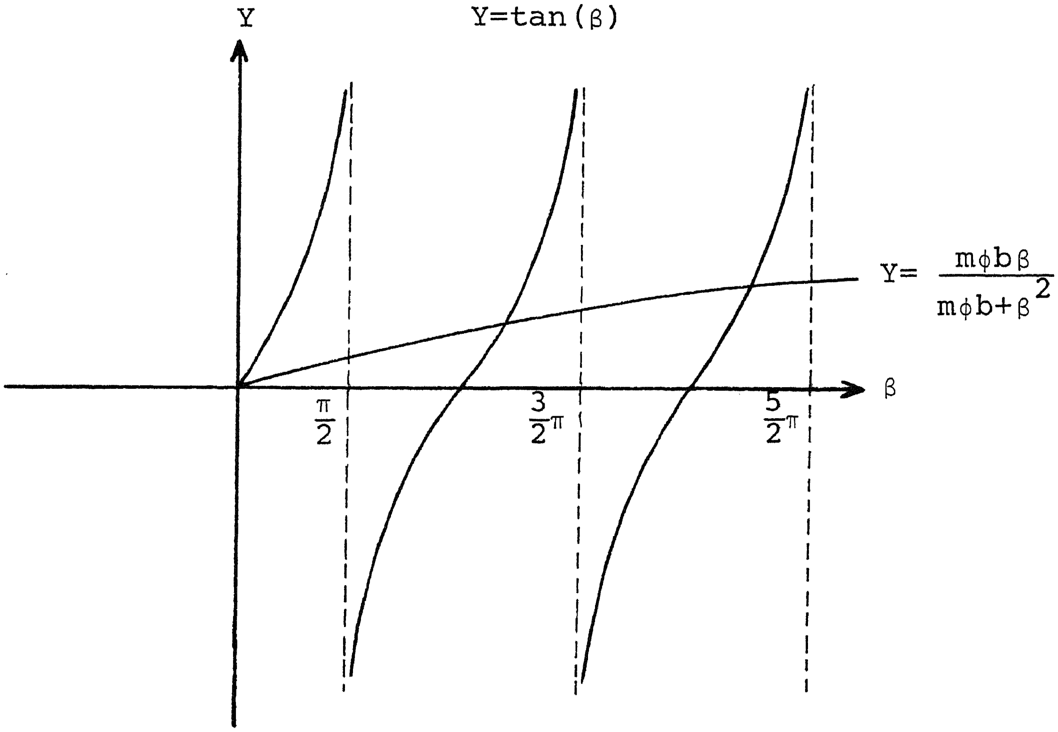


Fig. 2.6 Curves for $\tan(\beta) = \frac{m\phi b\beta}{m\phi b+\beta^2}$

Let β_n represent all eigenvalues of eqn. (2.40). The pole for each eigen value is a simple pole. This can be seen from the graphic solution of eqn. (2.40) as shown in Fig. 2.6. Fig. 2.6 shows that there is no double root solution of eqn. (2.40). Thus we conclude that the function $F_1(s)$ has no multiple pole and all the simples are at $s=0$ and $s=-\beta^2/b$.

Now we are going to find the residues for each pole.

Residue at $s=0$,

$$\mathrm{Res}(0) = \lim_{s\to 0}\left[sF_1(s)e^{s\tau}\right]$$

$$=\lim_{s\to 0}\left\{se^{s\tau}\frac{1+\frac{1}{3!}(bs)+\frac{1}{5!}(bs)^2+....}{s\left[1+\frac{1}{3!}(bs)+\frac{1}{5!}(bs)^2+...\right]+m\phi\left[\frac{1}{3}(bs)+(\frac{1}{4!}-\frac{1}{5!})(bs)^2+...\right]}\right\}$$

$$= \frac{3}{3+m\phi b} \tag{2.41}$$

Residues at $s=s_n= -\beta_n^2/b$,

$$\mathrm{Res}(s_n)= \lim_{s\to s_n}\left\{(s-s_n)\ \frac{\sinh\sqrt{bs}\ e^{s\tau}}{s\cdot\sinh\sqrt{bs}+m\phi(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})}\right\}$$

$$= \lim_{s\to s_n}\left\{\frac{s-s_n}{s\cdot\sinh\sqrt{bs}+m\phi(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})}\right\}, *$$

$$* \lim_{s\to s_n}\left\{\sinh\sqrt{bs}\cdot e^{s\tau}\right\}$$

$$= \lim_{s\to s_n}\left\{\frac{1}{\frac{d}{ds}\left[s\cdot\sinh\sqrt{bs}+m\phi(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})\right]}\right\}\cdot(\sinh\sqrt{bs}\cdot e^{s_n\tau}) \tag{2.42}$$

where $\frac{d}{ds}[s\cdot\sinh\sqrt{bs} + m\phi(\sqrt{bs}\cosh\sqrt{bs} - \sinh\sqrt{bs})]$

$$= (1 + \frac{m\phi b}{2})\sinh\sqrt{bs} + \frac{1}{2}\sqrt{bs}\cosh\sqrt{bs} \qquad (2.43)$$

Substitute eqn. (2.43) into eqn. (2.42), we obtain:

$$\text{Res}(s_n) = \lim_{s\to s_n} \frac{1}{(1+\frac{m\phi b}{2})\sinh\sqrt{bs}+\frac{1}{2}\sqrt{bs}\cosh\sqrt{bs}} \quad \sinh\sqrt{bs}_n \; e^{s_n\tau}$$

$$= \frac{\sinh\sqrt{bs_n}}{(1+\frac{m\phi b}{2})\sinh\sqrt{bs_n} + \frac{1}{2}\sqrt{bs_n}\cosh\sqrt{bs_n})} e^{s_n\tau} \qquad (2.44)$$

Substitute in $s_n = -\beta_n^2/b$, we obtain:

$$\text{Res}(-\beta_n^2/b) = \frac{\sinh(i\beta_n)}{(1+\frac{m\phi b}{2})\sinh(i\beta_n)+\frac{1}{2}(i\beta_n)\cosh(i\beta_n)} e^{-\frac{\beta_n^2}{b}\tau}$$

$$= \frac{\tanh(i\beta_n)}{(1+\frac{m\phi b}{2})\tanh(i\beta_n)+\frac{1}{2}(i\beta_n)} e^{-\frac{\beta_n^2}{b}\tau}$$

$$= \frac{\tan(\beta_n)}{(1+\frac{m\phi b}{2})\tan(\beta_n)+\frac{1}{2}\beta_n} e^{-(\beta_n^2/b)\tau} \qquad (2.45)$$

The inverse Laplace transform of $F_1(s)$ is the sum of all residues. The source phase copper concentration can then be expressed as follows:

$$\frac{Cu}{Cuo} = \frac{3}{3+m\phi b} + \sum_{n=1}^{\infty} \frac{\tan(\beta_n)}{(1+\frac{m\phi b}{2})\tan(\beta_n)+\frac{1}{2}\beta_n} e^{-\frac{\beta_n^2}{b}\tau} \qquad (2.46)$$

where

$$b = 1-\varepsilon+q\varepsilon$$

$$\tau = \frac{D_{ex}}{R^2}t$$

$$\phi = \frac{3\phi'}{1-\phi'}$$

$$m = \frac{K_{eq} \cdot C_{RHO}^2}{C_{HO}^2}$$

$$q = \frac{C_{HOi}^2}{K_{eq} \cdot C_{RHO}^2}$$

β_n are eigen values of $\tan(\beta) = \frac{m\phi b\beta}{m\phi b+\beta^2}$

B. ONLY THE MEMBRANE EXTERNAL FILM MASS TRANSFER RESISTANCE IS CONSIDERED.

In this case, the membrane external interphase mass transfer resistance is considered while the membrane internal interphase mass transfer resistance is neglected. The governing equations for the copper extraction process are:

Membrane phase:

$$(1-\varepsilon)\frac{\partial C_x}{\partial t} = D_{ex}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_x}{\partial r}\right)\right) - R_x \tag{2.47}$$

$t=0 \quad C_x=0 \quad$ for all r

$r=0 \quad C_x=\text{finite}$

$r=R \quad C_x=C_x^*$

$$(1-\varepsilon)\frac{\partial C_{RH}}{\partial t} = D_{eRH}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{RH}}{\partial r}\right)\right) - 2R_x \tag{2.48}$$

$t=0 \quad C_{RH}=C_{RHO} \quad$ for all r

$r=0 \quad C_{RH}=\text{finite}$

$r=R \quad C_{RH}=C_{RH}^*$

External source phase

$$-V_t(1-\phi')\frac{dCu}{dt} = N(4\pi R^2)k_o(Cu - Cu^*) \tag{2.49}$$

$t=0 \quad Cu=Cuo$

$$N(4\pi R^2)k_o(Cu - Cu^*) = N(4\pi R^2)D_{ex}\left(\frac{\partial C_x}{\partial r}\right)_{r=R} \qquad (2.50)$$

where k_o: film mass transfer coefficient at membrane external interphase.

Internal receiving phase:

$$\varepsilon\frac{\partial Cui}{\partial t} = R_x \qquad (2.51)$$

$$t=0 \quad Cui=0$$

Constrain:

$$\int_0^R (2C_x + C_{RH})r^2dr = \frac{1}{3}R^2C_{RHO} \qquad (2.52)$$

Refer to Fig. 2.3 and Fig. 2.4 and similar approximations as shown in section A, we have the following equilibrium relations:

$$C_x^* = mCu^* \qquad (2.53)$$

$$Cui = qC_x \qquad (2.54)$$

where m and q are defined by eqns. (2.15a) and (2.15b). Also similar to section A, the governing equations can be reduced to the following set of equations:

$$(1-\varepsilon)\frac{\partial C_x}{\partial t} = D_{ex}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_x}{\partial r}\right)\right) - R_x \qquad (2.55)$$

$$t=0 \quad C_x=0 \quad \text{for all } r$$

$$r=0 \quad C_x=\text{finite}$$

$$r=R \quad C_x=C_x^*$$

$$-V_t(1-\phi')\frac{dCu}{dt} = N(4\pi R^2)k_o(Cu - Cuo) \tag{2.56}$$

$$t=0 \quad Cu=Cuo$$

$$N(4\pi R^2)k_o(Cu-Cu^*)=N(4\pi R^2)D_{ex}\left(\frac{\partial C_x}{\partial r}\right)_{r=R} \tag{2.57}$$

$$\varepsilon\frac{\partial Cui}{\partial t} = R_x \tag{2.58}$$

$$t=0 \quad Cui=0$$

$$C_x^* = mCu^* \tag{2.59}$$

$$Cui = qC_x \tag{2.60}$$

Combine eqns. (2.60), (2.58) and (2.55) and introduce the following relations and dimensionless variables:

$$b=1-\varepsilon+q\varepsilon \tag{2.61}$$

$$N= \frac{V_t\phi'}{(4/3)\pi R^2}$$

$$\phi= \frac{3\phi'}{1-\phi'}$$

$$y= \frac{r}{R}$$

$$\tau= \frac{D_{ex}}{R^2}\,t$$

$$K_o= \frac{D_{ex}}{Rk_o}$$

The governing equations become:

$$b\frac{\partial C_x}{\partial \tau} = \frac{1}{y^2}\frac{\partial}{\partial y}(y^2\frac{\partial C_x}{\partial y}) \tag{2.62}$$

$\tau=0 \quad C_x=0$

$y=0 \quad C_x=\text{finite}$

$y=1 \quad C_x=C_x^*$

$$\frac{dCu}{d\tau} = -\frac{\phi}{K_o}(Cu - Cu^*) \tag{2.63}$$

$\tau=0 \quad Cu=Cuo$

$$\frac{1}{K_o}(Cu - Cu^*) = (\frac{\partial C_x}{\partial y})_{y=1} \tag{2.64}$$

$$C_x^* = mCu^* \tag{2.64a}$$

$$Cui = qC_x \tag{2.64b}$$

The Laplace transforms of the above governing eqns. are:

$$bs\bar{C}_x = \frac{1}{y^2}\frac{d}{dy}(y^2\frac{d\bar{C}_x}{dy}) \tag{2.65}$$

$y=0 \quad C_x=\text{finite}$

$y=1 \quad \bar{C}_x=\bar{C}_x^*$

$$(s\bar{C}u-\bar{C}u^*) =- \frac{\phi}{K_o}(\bar{C}u - \bar{C}u^*) \tag{2.66}$$

$$\frac{1}{K_o}(\bar{C}u-\bar{C}u^*) = (\frac{d\bar{C}_x}{dy})_{y=1} \tag{2.67}$$

Follow the same procedures as described in section A of this chapter, we have:

$$\left(\frac{d\bar{C}_x}{dy}\right)_{y=1} = \frac{m\bar{C}u^*(\sqrt{bs}\cosh\sqrt{bs} - \sinh\sqrt{bs})}{\sinh\sqrt{bs}} \tag{2.68}$$

Substitute the above eqn. into eqn. (2.67) and solve it for $\bar{C}u^*$, we have:

$$\bar{C}u^* = \frac{\sinh\sqrt{bs}}{\sinh\sqrt{bs}+mK_o(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})}\bar{C}u \tag{2.69}$$

Substitute the above eqn. into eqn. (2.66) and solve it for $\bar{C}u$, we have:

$$\frac{\bar{C}u}{Cuo} = \frac{\sinh\sqrt{bs} + mK_o(\sqrt{bs}\cosh\sqrt{bs} - \sinh\sqrt{bs})}{s\cdot\sinh\sqrt{bs} + (smK_o + m\phi)(\sqrt{bs}\cosh\sqrt{bs} - \sinh\sqrt{bs})} = F_2(s) \tag{2.70}$$

The external source phase copper concentration is the inverse Laplace transform of eqn. (2.70).

$$\frac{Cu}{Cuo} = L^{-1}\left\{\frac{\sinh\sqrt{bs}+mK_o(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})}{s\cdot\sinh\sqrt{bs}+(smK_o+m\phi)(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})}\right\}$$

$$= L^{-1}\left\{F_2(s)\right\} \tag{2.71}$$

The inverse Laplace transform of $F_2(s)$ is equal to the sum of the residues of $F_2(s)$. Similar to eqn. (2.34), we can express $F_2(s)$ in series form and show that s=0 is not a branch point and is a simple pole. Other poles are given by the roots of the following equation.

$$s\cdot\sinh\sqrt{bs}+(smK_o+m\phi)(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})=0 \tag{2.72}$$

After rearrangement, the above equation becomes:

$$\tanh\sqrt{bs} = \frac{\sqrt{bs}(smK_o + m\phi)}{(mK_o - 1)s + m\phi} \tag{2.73}$$

Let $\sqrt{bs} = i\beta$ or $s= -\beta^2/b$ (2.73a)

Substitute the above relation into eqn. (2.72), we obtain:

$$\tanh(i\beta)= \frac{(i\beta)(-\beta^2 mK_o/b + m\phi)}{(mK_o-1)(-\beta^2/b)+m\phi}$$

or

$$\tan(\beta)= \frac{(m\phi b - mK_o\beta^2)}{(1 - mK_o)\beta^2 + m\phi b} \tag{2.74}$$

Let β_n represent all eigenvalues of eqn. (2.74). By similar method as described in section A in this chapter, all eigenvalues are distinctive and $F_2(s)$ has no multiple pole. All simples are at s=0 and $s= -\beta_n{}^2/b$.

Now we are going to find all the residues of $F_2(s)$.

Residue at s=0,

$$\mathrm{Res}(0) = \lim_{s\to 0}\left[sF_2(s)\cdot e^{s\tau}\right]$$

$$=\lim_{s\to 0}\left\{se^{s\tau}\frac{1+\frac{1}{3!}(bs)+\frac{1}{5!}(bs)^2+\ldots+mK_o\left[\frac{1}{3}(bs)+(\frac{1}{4!}-\frac{1}{5!}(bs)^2+..\right]}{s\left[1+\frac{1}{3!}(bs)+\frac{1}{5!}(bs)^2+\ldots\right]+(smK_o+m\phi)\left[\frac{1}{3}(bs)+(\frac{1}{4!}-\frac{1}{5!})(bs)^2+..\right]}\right\}$$

$$= \frac{3}{3+m\phi b} \tag{2.75}$$

Residue at $s=s_n=-\beta_n^2/b$,

$$\mathrm{Res}(s_n)=\lim_{s\to s_n}\left\{(s-s_n)\frac{\sinh\sqrt{bs}+mK_o(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})}{s.\sinh\sqrt{bs}+(smK_o+m_\phi)(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})}\,e^{s\tau}\right\}$$

$$=\lim_{s\to s_n}\left\{\frac{s-s_n}{s\cdot\sinh\sqrt{bs}+(smK_o+m_\phi)(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})}\right\}\cdot *$$

$$*\lim_{s\to s_n}\left\{\sinh\sqrt{bs}+mK_o(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs}).e^{s\tau}\right\}\quad(2.76)$$

where $$\lim_{s\to s_n}\left\{\frac{s-s_n}{s\cdot\sinh\sqrt{bs}+(smK_o+m_\phi)(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})}\right\}$$

$$=\lim_{s\to s_n}\left\{\frac{1}{\frac{d}{ds}[s\cdot\sinh\sqrt{bs}+(smK_o+m_\phi)(\sqrt{bs}\cosh\sqrt{bs}-\sinh\sqrt{bs})]}\right\}$$

$$=\lim_{s\to s_n}\left\{\frac{1}{(1-mK_o+\frac{1}{2}smK_o+\frac{m_\phi b}{2})\sinh\sqrt{bs}+(\frac{1}{2}+mK_o)\sqrt{bs}\cosh\sqrt{bs}}\right\}$$

(2.76a)

Substitute eqn. (2.76a) into eqn. (2.76), we obtain:

$$\mathrm{Res}(s_n)=\frac{(1-mK_o)\tanh\sqrt{bs}+mK_o\sqrt{bs}}{(1-mK_o+\frac{1}{2}smK_ob+\frac{m_\phi b}{2})\tanh\sqrt{bs}+(\frac{1}{2}+mK_o)\sqrt{bs}}\,e^{s\tau}\Bigg|_{s=-\beta_n^2/b}$$

$$=\frac{(1-mK_o)\tanh(i\beta_n)+mK_o(i\beta)}{(1-mK_o-\frac{1}{2}mK_o\beta_n^2+\frac{1}{2}m_\phi b)\tanh(i\beta_n)+(\frac{1}{2}+mK_o)(i\beta_n)}\,e^{-\frac{\beta_n^2}{b}\tau}$$

$$=\frac{(1-mK_o)\tan(\beta_n)+mK_o\beta_n}{(1-mK_o-\frac{1}{2}mK_o\beta_n^2+\frac{1}{2}m_\phi b)\tan(\beta_n)+(\frac{1}{2}+mK_o)\beta_n}\,e^{-\frac{\beta_n^2}{b}\tau}\quad(2.76b)$$

The source phase copper concentration is the sum of all residues of $F_2(s)$ and is as follows:

$$\frac{cu}{Cuo} = \frac{3}{3+m\phi b} + \sum_{n=1}^{\infty} \frac{(1-mK_o)\tan(\beta_n)+mK_o\beta_n}{(1-mK_o-\frac{1}{2}mK_o\beta_n^2+\frac{1}{2}m\phi b)\tan(\beta_n)+(\frac{1}{2}+mK_o)\beta_n} e^{-\frac{\beta_n^2}{b}\tau} \tag{2.77}$$

where

$$b = 1-\varepsilon+q\varepsilon$$

$$\tau = \frac{D_{ex}}{R^2}t \tag{2.78}$$

$$\phi = \frac{3\phi'}{1-\phi'}$$

$$m = \frac{K_{eq}\cdot C_{RHO}^2}{C_{HO}^2}$$

$$q = \frac{C_{HOi}^2}{K_{eq}\cdot C_{RHO}^2}$$

$$K_o = \frac{D_{ex}}{Rk_o}$$

β_n are eigenvalues of

$$\tan(\beta) = \frac{(m\phi b - mK_o\beta^2)\beta}{(1-mK_o)\beta^2+m\phi b}$$

C. BOTH THE MEMBRANE EXTERNAL AND INTERNAL FILM MASS TRANSFER RESISTANCES ARE CONSIDERED.

In this case both the membrane external interphase mass transfer resistance and the membrane internal interphase mass transfer resistance are considered. The governing eqns. for the copper extraction process are:

Membrane phase:

$$(1-\varepsilon)\frac{\partial C_x}{\partial t} = D_{ex}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_x}{\partial r}\right)\right)-k_i a(C_x-C^*_{xi}) \qquad (2.79)$$

$t=0 \quad C_x=0 \quad$ for all r

$r=0 \quad C_x=\text{finite}$

$r=R \quad C_x=C^*_x$

$$(1-\varepsilon)\frac{\partial C_{RH}}{\partial t} = D_{eRH}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{RH}}{\partial r}\right)\right)-2k_i a(C_x-C^*_{xi}) \qquad (2.80)$$

$t=0 \quad C_{RH}=C_{RHO} \quad$ for all r

$r=0 \quad C_{RH}=\text{finite}$

$r=1 \quad C_{RH}=C^*_{RH}$

External source phase:

$$-V_t(1-\phi')\frac{dCu}{dt} = N(4\pi R^2)k_o(Cu-Cu^*) \qquad (2.81)$$

$t=0 \quad Cu=Cuo$

$$N(4\pi R^2)k_o(Cu-Cu^*) = N(4\pi R^2)D_{ex}\left(\frac{\partial C_x}{\partial r}\right)_{r=R} \qquad (2.82)$$

where k_i: film mass transfer coefficient at membrane internal interface.

a: membrane internal interphase area per unit volume of emulsion.

Internal receiving phase:

$$\varepsilon\frac{\partial Cui}{\partial t} = k_i a(C_x - C^*_{xi}) \qquad (2.82)$$

$$t=0 \quad Cui=0$$

Constrain:

$$\int_0^R (2C_x + C_{RH}) r^2 dr = \frac{1}{3}R^3 C_{RHO} \qquad (2.83)$$

Refer to Fig. 2.3 and Fig. 2.4 and similar approximations as shown in section A of this chapter, we have the following equilibrium relations:

$$C^*_x = mCu^* \qquad (2.84a)$$

$$Cui = qC^*_{xi} \qquad (2.84b)$$

where m and q are defined by eqns. (2.15a) and (2.15b). Also similar to section A of this chapter, the governing equations can be reduced to the following set of equations:

$$(1-\varepsilon)\frac{\partial C_x}{\partial t} = D_{ex}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_x}{\partial r}\right)\right) - k_i a(C_x - C^*_{xi}) \qquad (2.85)$$

$t=0 \quad C_x=0$ for all r

$r=0 \quad C_x=\text{finite}$

$r=R \quad C_x=C_x^*$

$$-V_t(1-\phi')\frac{dCu}{dt} = N(4\pi R^2)k_o(Cu-Cu^*) \qquad (2.86)$$

$t=0 \quad Cu=Cuo$

$$N(4\pi R^2)k_o(Cu-Cu^*) = N(4\pi R^2)D_{ex}\left(\frac{\partial C_x}{\partial r}\right)_{r=R} \qquad (2.87)$$

$$\varepsilon\frac{\partial Cui}{\partial t} = k_i a(C_x-C_{xi}^*) \qquad (2.88)$$

$t=0 \quad Cui=0$

$$C_x^* = mCu^* \qquad (2.89)$$

$$Cui = qC_{xi}^* \qquad (2.90)$$

Introduce the following relations and dimensionless variables:

$$b=1-\varepsilon+q\varepsilon \qquad (2.91)$$

$$N= \frac{V_t\phi'}{\frac{4}{3}\pi R^3}$$

$$\tau= \frac{D_{ex}}{R^2} t$$

$$y= \frac{r}{R}$$

$$\phi= \frac{3\phi'}{1-\phi'}$$

$$K_o= \frac{D_{ex}}{Rk_o}$$

$$K_i = \frac{D_{ex}}{R^2 k_i a}$$

$$a = \frac{3\varepsilon}{d_r}$$

where d_r: average receiving phase droplet diameter.

The governing equations become:

$$(1-\varepsilon)\frac{\partial C_x}{\partial \tau} = \frac{1}{y^2}\frac{\partial}{\partial y}(y^2 \frac{\partial C_x}{\partial y}) - \frac{1}{K_i}(C_x - C^*_{xi}) \tag{2.92}$$

$\tau=0 \quad C_x=0 \quad$ for all y

$y=0 \quad C_x=\text{finite}$

$y=0 \quad C_x=C^*_x$

$$\frac{dCu}{d\tau} = -\frac{\phi}{K_o}(Cu-Cu^*) \tag{2.93}$$

$\tau=0 \quad Cu=Cuo$

$$\frac{1}{K_o}(Cu-Cu^*) = (\frac{\partial C_x}{\partial y})_{y=1} \tag{2.94}$$

$$\varepsilon\frac{\partial Cui}{\partial \tau} = \frac{1}{K_i}(C_x - C^*_{ci}) \tag{2.95}$$

$\tau=0 \quad Cui=0$

$$C^*_x = mCu^* \tag{2.95a}$$

$$Cui = qC^*_{xi} \tag{2.95b}$$

The Laplace transforms of the above governing equations are:

$$(1-\varepsilon)s\bar{C}_x = \frac{1}{y^2}\frac{d}{dy}\left(y^2\frac{d\bar{C}_x}{dy}\right) - \frac{1}{K_i}(\bar{C}_x - \bar{C}^*_{xi}) \qquad (2.96)$$

$$y=0 \qquad \bar{C}_x = \text{finite}$$

$$y=1 \qquad \bar{C}_x = \bar{C}^*_x$$

$$(s\bar{C}u - Cuo) = -\frac{\phi}{K_o}(\bar{C}u - \bar{C}u^*) \qquad (2.97)$$

$$\frac{1}{K_o}(\bar{C}u - \bar{C}u^*) = \left(\frac{d\bar{C}_x}{dy}\right)_{y=1} \qquad (2.98)$$

$$\varepsilon s\bar{C}ui = -\frac{1}{K_i}(\bar{C}_x - \bar{C}^*_x) \qquad (2.99)$$

$$\bar{C}^*_x = m\bar{C}u^* \qquad (2.100)$$

$$\bar{C}ui = q\bar{C}^*_{xi} \qquad (2.101)$$

Eliminate $\bar{C}ui$ and $\bar{C}_{xi}$ from eqns. (2.101), (2.99) and (2.96) we obtain:

$$(1-\varepsilon)s\bar{C}_x = \frac{1}{y^2}\frac{d}{dy}\left(y^2\frac{d\bar{C}_x}{dy}\right) - \frac{1}{K_i}\left(\bar{C}_x - \frac{1}{q\varepsilon K_i s+1}\bar{C}_x\right) \qquad (2.102)$$

or

$$\frac{(1-\varepsilon)q\varepsilon K_i s^2 + (1-\varepsilon+q\varepsilon)s}{q\varepsilon K_i s+1}\bar{C}_x = \frac{1}{y^2}\frac{d}{dy}\left(y^2\frac{d\bar{C}_x}{dy}\right) \qquad (2.103)$$

Let

$$p(s) = \frac{(1-\varepsilon)q\varepsilon K_i s^2 + (1-\varepsilon+q\varepsilon)s}{q\varepsilon K_i s+1} = \frac{(1-\varepsilon)q\varepsilon K_i s^2 + bs}{q\varepsilon K_i s+1} \qquad (2.104)$$

By the above relation, eqn. (2.103) becomes:

$$p(s)\bar{C}_x = \frac{1}{y^2}\frac{d}{dy}\left(y^2 \frac{d\bar{C}_x}{dy}\right) \tag{2.105}$$

$$y=0 \quad \bar{C}_x=\text{finite}$$

$$y=1 \quad \bar{C}_x=\bar{C}_x^*$$

Follow the same procedures as in section A of this chapter, the solution to the above equation is:

$$\bar{C}_x = \frac{\bar{C}_x^* \sinh\sqrt{p(s)}\,y}{y\sinh\sqrt{p(s)}} = \frac{m\bar{C}u^*\ \sinh\sqrt{p(s)}\,y}{y\cdot\sinh\sqrt{p(s)}} \tag{2.106}$$

and $$\left(\frac{d\bar{C}_x}{dy}\right)_{y=1} = \frac{m\bar{C}u^*(\sqrt{p(s)}\cosh\sqrt{p(s)} - \sinh\sqrt{p(s)})}{\sinh\sqrt{p(s)}} \tag{2.107}$$

Substitute eqn. (2.107) into eqn. (2.98) and solve it for $\bar{C}u^*$, we obtain:

$$\bar{C}u^* = \frac{\sinh\sqrt{p(s)}}{\sinh\sqrt{p(s)}+mK_o(\sqrt{p(s)}\cosh\sqrt{p(s)}-\sinh\sqrt{p(s)})}\ \bar{C}u \tag{2.108}$$

Substitute the above eqn. into eqn. (2.97) and solve it for $\bar{C}u$, we obtain:

$$\frac{\bar{C}u}{Cuo} = \frac{\sinh\sqrt{p(s)}+mK_o(\sqrt{p(s)}\cosh\sqrt{p(s)}-\sinh\sqrt{p(s)})}{s\cdot\sinh\sqrt{p(s)}+(smK_o+m\phi)(\sqrt{p(s)}\cosh\sqrt{p(s)}-\sinh\sqrt{p(s)})} = F_3(s) \tag{2.109}$$

The source phase copper concentration is equal to the sum of all residues of the function $F_3(s)$ and is as follows:

$$\frac{Cu}{Cuo} = L^{-1}\left\{F_3(s)\right\} \tag{2.110}$$

The inverse Laplace transform of $F_3(s)$ is equal to the sum of all the residues of $F_3(s)$. Similar to eqn. (2.34), we can express $F_3(s)$ in series form and can prove that s=0 is not a branch point and is a simple pole. At $s=s'= -\frac{1}{q\varepsilon K_i}$, $q\varepsilon K_i s+1=0$, but s' is not a pole as proved below:

$$\lim_{s\to s'}\left\{F_3(s)\right\}=\lim_{s\to s'}\left\{\frac{\tanh\sqrt{p(s)}+mK_o(\sqrt{p(s)}-\tanh\sqrt{p(s)})}{s\cdot\tanh\sqrt{p(s)}+(smK_o+m\phi)(\sqrt{p(s)}-\tanh\sqrt{p(s)})}\right\}$$

$$=\lim_{s\to s'}\left\{\frac{1+mK_o(\sqrt{p(s)}-1)}{s+(smK_o+m\phi)(\sqrt{p(s)}-1)}\right\}$$

$$= \frac{mK_o}{(-\frac{1}{q\varepsilon K_i}mK_o+m\phi)} = \text{constant} \tag{2.111}$$

The above shows that as s approaches s', $F_3(s)$ approaches a constant. So s=s' is not a pole. Other poles are given by the roots of the following equation.

$$s\cdot\sinh\sqrt{p(s)}+(msK_o+m\phi)(\sqrt{p(s)}\cosh\sqrt{p(s)}-\sinh\sqrt{p(s)})=0 \tag{2.112}$$

After rearrangement, the above equation becomes:

$$\tanh\sqrt{p(s)} =\frac{(smK_o+m\phi)\sqrt{p(s)}}{m\phi-(1-mK_o)s} \tag{2.113}$$

To find the eigenvalues of eqn. (2.113), we let:

$$\sqrt{p(s)} = ih \tag{2.114}$$

or $$p(s) = \frac{(1-\varepsilon)q\varepsilon K_i s+b\ s}{q\varepsilon K_i s+1} = -h^2 \tag{2.115}$$

Solve the above equation for s, we obtain two roots, they are:

$$s^{+} = -\beta = \frac{-(b+q\varepsilon K_i h^2)+\sqrt{(b+q\varepsilon K_i h^2)^2-4(1-\varepsilon)q\varepsilon K_i h^2}}{2(1-\varepsilon)q\varepsilon K_i} \tag{2.116}$$

$$s^{-} = -\gamma = \frac{-(b+q\varepsilon K_i h^2)-\sqrt{(b+q\varepsilon K_i h^2)^2-4(1-\varepsilon)q\varepsilon K_i h^2}}{2(1-\varepsilon)q\varepsilon K_i} \tag{2.117}$$

The value of h can be found by substituting eqn. (2.116) and eqn. (2.117) and solve the equations for h. Substitute eqns. (2.116) and (2.117), we obtain two eqns:

$$\tan(h) = \frac{(-\beta m K_o+m\phi)h}{m\phi+(1-mK_o)\beta} \tag{2.118}$$

$$\tan(h) = \frac{(-\gamma m K_o+m\phi)h}{m\phi+(1-mK_o)\gamma} \tag{2.119}$$

Let h_n and h_j represent all eigen values of h of eqn. (2.118) and eqn. (2.119) respectively. Substitue h_n and h_j into eqn. (2.116) and eqn. (2.117) respectively. Let us denote them as $s_n^{+} = -\beta_n$ and $s_j^{-} = -\gamma_j$ respectively. s_n and s_j are poles of the function $F_3(s)$ and they are all simple poles. The simple poles statement will be proved later.

Now we are going to find all the residues of $F_3(s)$.

Residue at s=0,

$$\mathrm{Res}(0) = \lim_{s\to 0}\left[sF_3(s)e^{s\tau}\right]$$

$$=\lim_{s\to 0}\left[se^{s\tau}\,\frac{1+\frac{1}{3!}p+\frac{1}{5!}p^2+\ldots+mK_o(\frac{1}{3}p+(\frac{1}{4!}-\frac{1}{5!})p^2+\ldots}{s(1+\frac{1}{3!}p+\frac{1}{5!}p^2+\ldots)+(smK_o+m\phi)(\frac{1}{3}p+(\frac{1}{4!}-\frac{1}{5!})p^2+..)}\right]$$

$$= \frac{3}{3+m\phi b} \qquad (2.120)$$

Residue at s= $s_n = -\beta_n$, and $h=h_n$ of eqn. (2.118).

$$\mathrm{Res}(s_n) = \lim_{s\to s_n}\left[(s-s_n)F_3(s)e^{s\tau}\right]$$

$$= \lim_{s\to s_n}\left[\frac{s-s_n}{s\cdot\sinh\sqrt{p(s)}+(smK_o+m\phi)(\sqrt{p(s)}\cosh\sqrt{p(s)}-\sinh\sqrt{p(s)})}\right]$$

$$*\cdot\lim_{s\to s_n}\left[\left[\sinh\sqrt{p(s)}+mK_o(\sqrt{p(s)}\cosh\sqrt{p(s)}-\sinh\sqrt{p(s)})\right]e^{s\tau}\right]$$

(2.121)

Where $$\lim_{s\to s_n}\left[\frac{s-s_n}{s\cdot\sinh\sqrt{p(s)}+(smK_o+m\phi)(\sqrt{p(s)}\cosh\sqrt{p(s)}-\sinh\sqrt{p(s)})}\right]$$

$$= \lim_{s\to s_n}\left[\frac{1}{\frac{d}{ds}\left[s\cdot\sinh\sqrt{p(s)}+(smK_o+m\phi)(\sqrt{p(s)}\cosh\sqrt{p(s)}-\sinh\sqrt{p(s)})\right]}\right],$$

(2.121a)

$$= \lim_{s\to s_n}\left[\frac{1}{\left[1-mK_o+\frac{1}{2}(smK_o+m\phi)\left(\frac{p(s)}{s}-Q(s)\right)\right]\sinh\sqrt{p(s)}}\right. *$$

$$\left. *\frac{}{+\left[\frac{s}{2p(s)}\left(\frac{p(s)}{s}-Q(s)\right)+mK_o\sqrt{p(s)}\right]\cosh\sqrt{p(s)}}\right] \qquad (2.122)$$

where

$$Q(s) = \frac{q^2\varepsilon^2 K_i s}{(q\varepsilon K_i s+1)^2} \qquad (2.123)$$

Substitute eqn. (2.122) into eqn. (2.121), we obtain:

$$\mathrm{Res}(s_n) = \lim_{s\to s_n}\left[\frac{\sinh\sqrt{p(s)}+mK_o\left(\sqrt{p(s)}\cosh\sqrt{p(s)}-\sinh\sqrt{p(s)}\right)\ e^{s\tau}}{\left[1-mK_o+\frac{1}{2}(smK_o+m\phi)\left(\frac{p(s)}{s}-Q(s)\right)\right]\sinh\sqrt{p(s)}}\right. *$$

$$\left. *\frac{}{+\left[\frac{s}{2\sqrt{p(s)}}\left(\frac{p(s)}{s}-Q(s)\right)+mK_o\sqrt{p(s)}\right]\cosh\sqrt{p(s)}}\right]$$

$$= \lim_{s\to s_n}\left[\frac{\left[(1-mK_o)\tanh\sqrt{p(s)}+mK_o\ p(s)\right]e^{s\tau}}{\left[1-mK_o+\frac{1}{2}(smK_o+m\phi)\left(\frac{p(s)}{s}-Q(s)\right)\right]\tanh\sqrt{p(s)}+\left[\frac{s}{2\sqrt{p(s)}}\left(\frac{p(s)}{s}\right.\right.}\right. *$$

$$\left. *\frac{}{\left.\left.-Q(s)\right)+mK_o\right]\sqrt{p(s)}}\right]$$

$$= \frac{\left[(1-mK_o)\tan(h_n)+mK_o h_n\right]e^{-\beta_n\tau}}{\left[1-mK_o+\frac{1}{2}(m\phi-\beta_n mK_o)\left(h_n^2/\beta_n-Q(-\beta_n)\right)\right]\tan(h_n)+\left(\frac{1}{2}-\frac{\beta_n}{2h_n^2}Q(-\beta_n)+mK_o\right)h_n} \qquad (2.124)$$

Since, $\lim_{s\to s_n}\left[(s-s_n)F_3(s)e^{s\tau}\right]$ appears to be a constant, so $s=s_n$ is a simple pole of $F_3(s)$.

Similarly, the residue for $s=s_j=-\gamma_n$, $h=h_j$ of eqn. (2.119).

$$\mathrm{Res}(s_j)=\lim_{s\to s_j}\left[(s-s_j)F_3(s)e^{s\tau}\right]$$

$$=\frac{\left[(1-mK_o)\tan(h_j)+mK_oh_j\right]e^{-\gamma_j\tau}}{\left[1-mK_o+\frac{1}{2}(m\phi-\gamma_jmK_o)(h_j^2/\gamma_j-Q(-\gamma_j))\right]\tan(h_j)+(\frac{1}{2}-\frac{\gamma_j}{2h_j^2}Q(-\gamma_j)+mK_o)h_j}$$

(2.125)

The external source phase copper concentration is equal to the sum of all residues of $F_3(s)$ and is as the follows:

$$\frac{Cu}{Cuo}=\frac{3}{3+m\phi b}$$

$$+\sum_{n=1}^{\infty}\frac{\left[(1-mK_o)\tan(h_n)+mK_oh_n\right]e^{-\beta_n\tau}}{\left[1-mK_o+\frac{1}{2}(m\phi-\beta_nmK_o)(\frac{h_n^2}{\beta_n}-Q(-\beta_n))\right]\tan(h_n)+(\frac{1}{2}-\frac{\beta_n}{2h_n^2}Q(-\beta_n)+mK_o)h_n}$$

$$+\sum_{j=1}^{\infty}\frac{\left[(1-mK_o)\tan(h_j)+mK_oh_j\right]e^{-\gamma_n\tau}}{\left[1-mK_o+\frac{1}{2}(m\phi-\gamma_jmK_o)(\frac{h_j^2}{\gamma_j}-Q(-\gamma_j))\right]\tan(h_j)+(\frac{1}{2}-\frac{\gamma_j}{2h_j^2}Q(-\gamma_j)+mK_o)h_j}$$

(2.126)

where

$$b = 1-\varepsilon+q\varepsilon \tag{2.117}$$

$$\tau = \frac{D_{ex}}{R^2} t$$

$$y = \frac{r}{R}$$

$$\phi = \frac{3\phi'}{1-\phi'}$$

$$K_o = \frac{D_{ex}}{Rk_o}$$

$$K_i = \frac{D_{ex}}{R^2 k_i a}$$

$$a = \frac{3\varepsilon}{d_r}$$

$$m = \frac{K_{eq} \cdot C_{RHO}^2}{C_{HO}^2}$$

$$q = \frac{C_{HOi}^2}{K_{eq} \cdot C_{RHO}^2}$$

$$Q(s) = \frac{q^2 \varepsilon^2 K_i s}{(q\varepsilon K_i s+1)^2}$$

β_n and γ_j are defined by eqn. (2.116) and eqn. (2.117).

h_n and h_j are eigenvalues of eqn. (2.118) and eqn. (2.119) respectively.

CHAPTER III

MASS TRANSFER THROUGH LIQUID MEMBRANES WITH REACTION IN RECEIVING PHASE

In Chapter II, we have discussed one type of liquid membrane system, where metal ions can not diffuse themself through the membrane. Carriers have to be added to the membrane phase to mediate the transport of metal ions. In this chapter, we present the type of liquid membrane system, where substrate is soluble in the membrane phase and can diffuse itself through the membrane phase. A reaction in the receiving phase will reduce the substrate concentration to a very low level and this will provide the necessary potential for continuous diffusion of the substrate until the final equilibrium is reached.

The removal of phenol from waste water is used as an example in deriving the mathematical models of dispersed liquid membranes with reaction in the internal receiving phase. Fig. 3.1 shows the mechanism of phenol removal through dispersed liquid membranes. Phenol is oil soluble, will permeate readily from the outside water phase through the oil membrane phase into the internal receiving phase droplets which are caustic. In the receiving phase the phenol will be neutralized by the caustic solution and tied up as sodium phenolate which is insoluble in oil

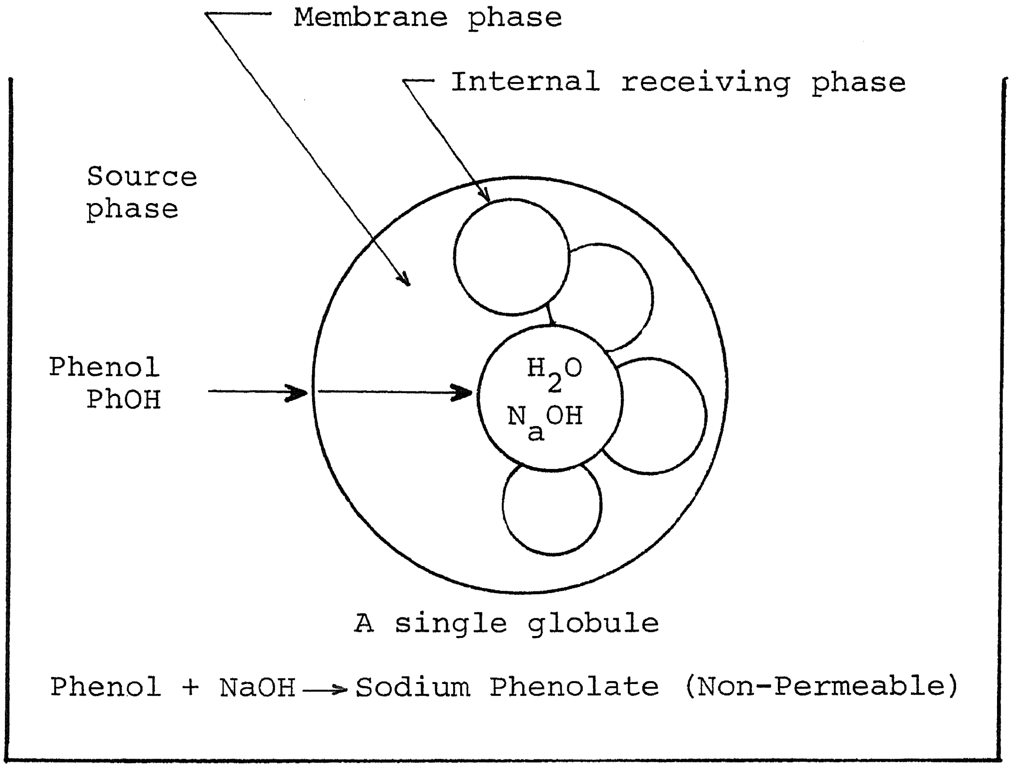


Fig. 3.1 Mechnism of phenol removal with dispersed liquid membranes.

phase, and consequently, can not diffuse back out again. Other waste water constituents that can be removed by this type of liquid membrane system are H_2S, HCN, acetic acid, NH_3, amines and other organic acids etc. The models derived for phenol removal can easily be applied to other constituents without or with little modifications. In the phenol removal case, the membrane is Kerosene containing 5%V of Span 80 and the receiving phase is NaOH solution.

Dissociation equilibria of phenol and water are expressed by eqn. (3.1) and eqn. (3.2) respectively.

$$\frac{[PhO^-][H^+]}{[PhOH]} = Ka \qquad (3.1)$$

$$[H^+][OH^-] = Kw \qquad (3.2)$$

Where Ka and Kw are the acid dissociation constant of phenol and the ion product of water. At 25°C, Ka is 1.28×10^{-10} and Kw is equal to 10^{-14}. With this information we can construct an equilibrium relation for phenol between dissociated and undissociated form. For the caustic receiving phase, electrical neutrality requires that, disregarding the H^+ concentration, we must have:

$$[Na^+] = [OH^-] + [PhO^-] = M$$

or
$$[OH^-] = M - [PhO^-] \qquad (3.3)$$

which can be substituted into the water equilibrium eqn. (3.2) to give:

$$[H^+] = \frac{Kw}{M - [PhO^-]} \tag{3.4}$$

When this expression is used to replace the $[H^+]$ in the phenol dissociation equilibrium eqn. (3.1), we obtain the following expression for the undissociated phenol in the caustic receiving phase:

$$[PhOH] = \frac{[PhO^-]\cdot Kw}{(M - [PhO^-])\,Ka} \tag{3.5}$$

Substitute in the values of Kw and Ka at 25°C, we have:

$$[PhOH] = \frac{[PhO^-]}{M-[PhO^-]}\cdot\frac{1}{1.28}x10^{-4} \tag{3.5a}$$

When the sodium ion concentration is high as compared to the total phenol concentration, from eqn. (3.5a), we know the undissociated form of phenol [PhOH]is very low, and we can say that in caustic phase the phenol is essentially completely dissociated. When the total phenol concentration is very low as compared to the sodium io concentration M, we can use the following approximation:

$$[Total\ PhOH] = [PhO^-] + [PhOH] \simeq [PhO^-] \tag{3.6}$$

From eqn. (3.5), we also have the following approximation in caustic solution:

$$[\mathrm{PhOH}] \simeq \frac{Kw}{M \cdot Ka} [\mathrm{PhO}^{-}] \qquad (3.7)$$

In the external phase, the pH value is approximately equal to 7. From eqn. (3.1), we can calculate the ratio of dissociated form of phenol to undissociated form of phenol. The ratio is so small, we can say practically all of the phenol in the source phase is presented in the undissociated form. That is, in the source phase we have the following approximation:

$$[\text{Total PhOH}] \fallingdotseq [\mathrm{PhOH}] \qquad (3.8)$$

In order to model this complicated phenol removal process, we make the following assumptions:

(1) Uniform globule sizes (Sauter mean diameter is used).
(2) No internal circulation in globules.
(3) No coalescense and redistribution of globules.
(4) Mass transfer by diffusion only.
(5) Diffusion coefficient is constant.
(6) Well mixed tank.
(7) Chemical equilibrium exists at the membrane external and internal interphases.

(8) The internal receiving phase droplets are so small, that their concentrations are assumed uniform.

(9) No volume change for each phase.

(10) Leakage through membrane rupture is negligible.

Three cases are considered for the phenol removal through dispersed liquid membrane in batch. They are:

(1) Both the membrane external and internal film mass transfer resistances are neglected.

(2) Only the membrane external film mass transfer resistance is considered.

(3) Both the membrane external and internal film mass transfer resistance are considered.

A. BOTH THE MEMBRANE EXTERNAL AND INTERNAL FILM MASS TRANSFER RESISTANCES ARE CONSIDERED.

In this case both the membrane external interphase mass transfer resistance and the membrane internal interphase mass transfer resistance are neglected. From the principal of material balance, the governing equations that describe the phenol concentration in each phase are:

Membrane phase:

$$(1-\varepsilon)\frac{\partial Cm}{\partial t} = D_{ep}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial Cm}{\partial r}\right)\right) - R_p \qquad (3.9)$$

$t=0$ $Cm=0$ for all r

$r=0$ $Cm=\text{finite}$

$r=R$ $Cm=Cm^*$

where $D_{ep}= (1-\varepsilon)D_p$

Cm: concentration of phenol in the membrane phase.

ε: volume fraction of internal phase in emulsion phase.

D_{ep}: effective diffusion coefficient of phenol in the emulsion phase.

D_p: phenol diffusivity in the membrane phase.

R: the sauter mean radius of globules.

R_p: Rate of phenol reacted per unit volume of emulsion phase.

Cm*: phenol concentration at the membrane external interphase.

External source phase:

$$-V_t(1-\phi')\frac{dCe}{dt} = N(4\pi R^2)D_{ep}(\frac{\partial Cm}{\partial r})_{r=R} \qquad (3.10)$$

$$t=0 \quad Ce=Ceo$$

where Ce: concentration of phenol in the external phase.

V_t: total liquid volume in a batch.

N: total numver of globules in a batch.

Ceo: initial concentration of phenol in the source phase.

ϕ': volume fraction of emulsion phase in a batch.

Internal receiving phase:

$$\varepsilon\frac{\partial Crt}{\partial t} = R_p \qquad (3.11)$$

$$t=0 \quad Crt=0$$

where Crt: Total Phenol concentration in the receiving phase.

Fig. 3.2 shows the phenol concentrations at a globule surface. By the assumptions, we have the following equilibrium relationship at the membrane external interphase:

$$Cm^* = \alpha Ce^* \qquad (3.12)$$

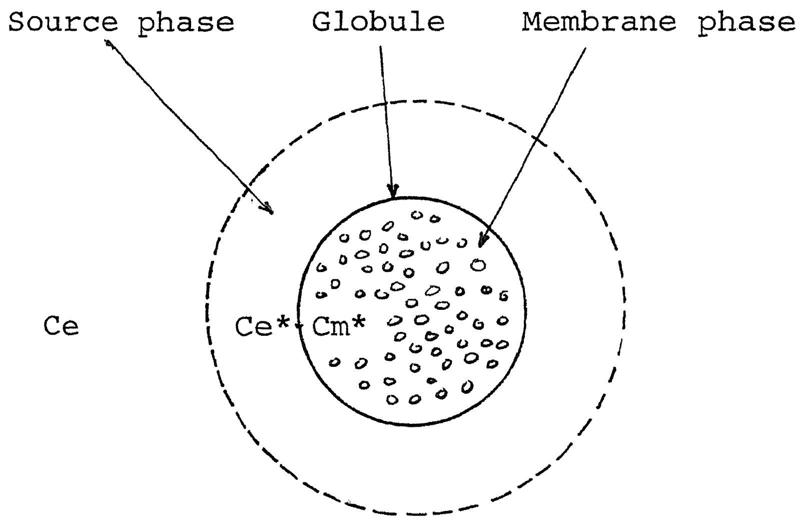


Fig. 3.2 Phenol concentrations at membrane external interphase.

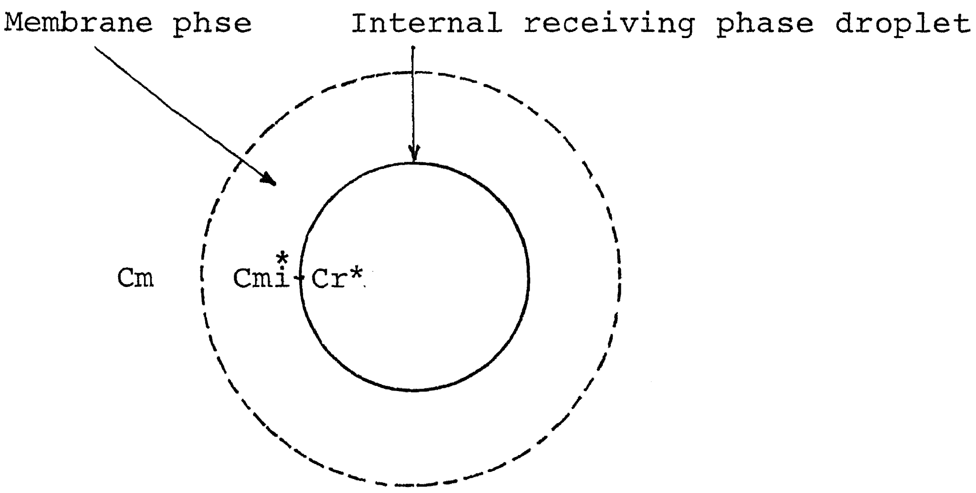


Fig. 3.3 Concentrations of phenol at membrane internal interphase.

Also by the assumptions of no external film resistance and well mixed tank, we have $Ce = Ce^*$, and eqn. (3.12) becomes:

$$Cm^* = \alpha Ce \tag{3.13}$$

where α: the partition coeficient of phenol in aqueous and membrane solutions.

Ce^*: source phase phenol concentration at the membrane external interphase.

Fig. 3.3 shows the phenol concentrations around a receiving phase droplet. The equilibrium relation at the membrane internal interphase is:

$$Cmi^* = \alpha Cr^* \tag{3.14}$$

By the assumptions of no internal film resistance and uniform concentations in the droplets, we have:

$$Cmi^* = Cm \quad \text{and} \quad Cr^* = Cr \tag{3.15}$$

where Cr: phenol concentration in the internal phase.

Cr^*: receiving phase phenol concentration at the membrane internal interphase.

Cmi^*: phenol concentration at the membrane internal interphase.

Substitute eqn. (3.15) into eqn. (3.14), we obtain:

$$Cmi^* = \alpha Cr \tag{3.16}$$

Since in practical applications, the phenol concentration in the source phase is usually very low and is less than 500 ppm, and the NaOH concentration in the caustic receiving phase is about 1.5% by wieght or higher, eqns. (3.6) and (3.7) can be used for the receiving phase caustic solution. We then have:

$$Cr = \frac{[PhO^-]\cdot Kw}{M\cdot Ka} \tag{3.17}$$

$$Crt = [PhO^-] + [PhOH] \simeq [PhO^-] \tag{3.18}$$

Substitute eqn. (3.18) into eqn. (3.17), we obtain:

$$Cr = \left(\frac{Kw}{M\cdot Ka}\right) Crt \tag{3.19}$$

Eliminate Cr from eqn. (3.16) and eqn. (3.19), we obtain:

$$Crt = gCmi^* \tag{3.20}$$

where $g = \frac{M\cdot Ka}{\alpha Kw} = \text{constant}$ (3.20a)

For the no internal film resistance case, Cmi*=Cm, eqn.(3.20) becomes:

$$Crt = gCm \tag{3.20b}$$

Substitute eqn. (3.20b) into eqn. (3.11), we get:

$$g\varepsilon\frac{\partial Cm}{\partial t} = R_p \tag{3.21}$$

Eliminate R_p from eqns. (3.21) and (3.9) and by the following relations and dimensionless variables:

$$N = \frac{V_t\phi'}{\frac{4}{3}\pi R^3} \tag{3.22}$$

$$b = 1-\varepsilon+g\varepsilon$$

$$\phi = \frac{3\phi'}{1-\phi'}$$

$$y = \frac{r}{R}$$

$$\tau = \frac{D_{ep}}{R^2}\,t$$

The governing equations become:

$$b\,\frac{\partial Cm}{\partial \tau} = \frac{1}{y^2}\frac{\partial}{\partial y}\left(y^2\,\frac{\partial Cm}{\partial y}\right) \tag{3.23}$$

$\tau=0$ $Cm=o$

$y=0$ $Cm=\text{finite}$

$y=1$ $Cm=Cm^*$

$$\frac{\partial Ce}{\partial \tau} = -\phi\left(\frac{\partial Cm}{\partial y}\right)_{y=1} \tag{3.24}$$

$\tau=0$ $Ce=Ceo$

These equations are completely the same as eqns. (2.23) and (2.24) in Chapter II. Follow the same procedures, the phenol concentration in the external source phase can be expressed as follows:

$$\frac{Ce}{Ceo} = \frac{3}{3+\alpha\phi b} + \sum_{n=1}^{\infty} \frac{\tan(\beta_n)}{(1+\frac{\alpha\phi b}{2})\tan(\beta_n)+\frac{1}{2}\beta_n} e^{-\frac{\beta_n^2}{b}\tau} \qquad (3.25)$$

where β_n are eigenvalues of:

$$\tan(\beta) = \frac{\alpha\phi b\beta}{\alpha\phi b+\beta^2} \qquad (3.26)$$

B. ONLY THE MEMBRANE EXTERNAL FILM MASS TRANSFER RESISTANCE IS CONSIDERED.

In this case the membrane external interphase mass transfer resistance is considered while the membrane internal interphase mass transfer resistance is neglected. For this case, the governing equations are:

Membrane phase:

$$(1-\varepsilon)\frac{\partial Cm}{\partial t} = D_{ep}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\ \frac{\partial Cm}{\partial r}\right)\right)-R_p \qquad (3.27)$$

t=0 Cm=0 for all r

r=0 Cm=finite

r=R Cm=Cm*

External source phase:

$$-V_t(1-\phi')\frac{dCe}{dt} = N(4\pi R^2)k_o(C_e-Ce^*) \qquad (3.28)$$

t=0 Ce=Ceo

$$N(4\pi R^2)k_o(Ce-Ce^*)=N(4\pi R^2)D_{ep}\left(\frac{\partial Cm}{\partial t}\right)_{r=R} \qquad (3.29)$$

Internal receiving phase:

$$\varepsilon\frac{\partial Crt}{\partial t} = R_p \qquad (3.30)$$

t=0 Crt=0

For the no internal film resistance case, from eqn. (3.20b), we have:

$$Crt = gCm \tag{3.31}$$

Combine eqns. (3.31), (3.30) and (3.27) and by the following relations and dimensionless variables:

$$N = \frac{V_t\phi'}{(4/3)\pi R^3} \tag{3.32}$$

$$\phi = \frac{3\phi'}{1-\phi'}$$

$$b = 1-\varepsilon+g\varepsilon$$

$$y = \frac{r}{R}$$

$$\tau = \frac{D_{ep}}{R^2}\,t$$

$$K_o = \frac{D_{ep}}{Rk_o}$$

the governing equations become:

$$b\frac{\partial Cm}{\partial \tau} = \frac{1}{y^2}\,\frac{\partial}{\partial y}(y^2\,\frac{\partial Cm}{\partial y}) \tag{3.33}$$

$\tau=0$ $Cm=0$

$y=0$ $Cm=\text{finite}$

$r=1$ $Cm=Cm^*$

$$\frac{dCe}{d\tau} = -\,\frac{\phi}{K_o}(Ce-Ce^*) \tag{3.34}$$

$\tau=0$ $Ce=0$

$$\frac{1}{K_o}\,(Ce-Ce^*)=(\frac{\partial Cm}{\partial y})_{y=1} \tag{3.35}$$

The above equations are similar to eqns. (2.62), (2.63) and (2.64) in section B of chapter II. Follow the same procedures, the phenol concentration in the external source phase can be expressed as follows:

$$\frac{Ce}{Ceo} = \frac{3}{3+\alpha\phi b} + \sum_{n=1}^{\infty} \frac{(1-\alpha K_o)\tan(\beta_n)+\alpha K_o\beta_n}{(1-\alpha K_o-\frac{1}{2}\alpha K_o\beta_n^2+\frac{1}{2}\alpha\phi b)\tan(\beta_n)+(\frac{1}{2}+\alpha K_o)\beta_n}\, e^{-\frac{\beta_n^2}{b}\tau} \qquad (3.36)$$

where β_n are eigenvalues of the following equation:

$$\tan(\beta) = \frac{(\alpha\phi b-\alpha K_o\beta^2)\beta}{(1-\alpha K_o)\beta^2+\alpha\phi b} \qquad (3.37)$$

C. BOTH THE MEMBRANE EXTERNAL AND INTERNAL FILM MASS MASS TRANSFER RESISTANCE ARE CONSIDERED.

In this case both the membrane external interphase mass transfer resistance and the membrane internal interphase mass transfer resistance are considered. The governing equations for this case are:

Membrane phase:

$$(1-\varepsilon)\frac{\partial Cm}{\partial t} = D_{ep}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\ \frac{\partial Cm}{\partial r}\right)\right)-k_i a(Cm-Cmi^*) \qquad (3.38)$$

t=0 Cm=0 for all r

r=0 Cm=finite

r=R Cm=Cm*

External source phase:

$$-V_t(1-\phi')\frac{dCe}{dt} = N(4\pi R^2)k_o(Ce-Ce^*) \qquad (3.39)$$

t=0 Ce=Ce0

$$N(4\pi R^2)k_o(Ce-Ce^*)=N(4\pi R^2)D_{ep}\left(\frac{\partial Cm}{\partial r}\right)_{r=R} \qquad (3.40)$$

Internal receiving phase:

$$\varepsilon\frac{\partial Crt}{\partial t} = k_i a(Cm-Cmi^*) \qquad (3.41)$$

t=0 Crt=0

From eqn. (3.12) and eqn. (3.20), we have the following equilibrium relations:

$$Cm^* = \alpha Ce^* \tag{3.42}$$

$$Crt = gCmi^* \tag{3.43}$$

where g is defined by eqn. (3.20a).

Introduce the following relations and dimensionless variables:

$$N = \frac{V_t \phi'}{(4/3)\pi R^3} \tag{3.44}$$

$$\phi = \frac{3\phi'}{1-\phi'}$$

$$b = 1-\varepsilon+g\varepsilon$$

$$y = \frac{r}{R}$$

$$\tau = \frac{D_{ep}}{R^2} t$$

$$K_o = \frac{D_{ep}}{Rk_o}$$

$$K_i = \frac{D_{ep}}{R^2 k_i a}$$

$$a = \frac{3\varepsilon}{d_r}$$

the governing equations become:

$$(1-\varepsilon)\frac{\partial Cm}{\partial \tau} = \frac{1}{y^2}\frac{\partial}{\partial y}\left(y^2 \frac{\partial Cm}{\partial y}\right) - \frac{1}{K_i}(cm-Cmi^*) \qquad (3.45)$$

$\tau=0 \quad Cm=0$

$y=0 \quad Cm=\text{finite}$

$y=1 \quad Cm=Cm^*$

$$\frac{dCe}{d\tau} = -\frac{\phi}{K_o}(Ce-Ce^*) \qquad (3.46)$$

$\tau=0 \quad Ce=Ceo$

$$\frac{1}{K_o}(Ce-Ce^*) = \left(\frac{\partial Cm}{\partial y}\right)_{y=1} \qquad (3.47)$$

$$\varepsilon\frac{\partial Crt}{\partial \tau} = \frac{1}{K_i}(Cm-Cm^*) \qquad (3.48)$$

$\tau=0 \quad Crt=0$

$$Cm^* = \alpha Ce^* \qquad (3.49)$$

$$Crt = gCmi^* \qquad (3.50)$$

The above equations are similar to eqns. (2.92) - (2.95) in section C of chapter II. Follow the same procedures, the phenol concentration in the external source phase can be expressed as follows:

$$\frac{Ce}{Ceo} = \frac{3}{3+\alpha\phi b} + \sum_{n=1}^{\infty} \frac{[(1-\alpha K_o)\tan(h_n)+\alpha K_o h_n]e^{-\beta_n\tau}}{[1-\alpha K_o+\frac{1}{2}(\alpha\phi-\beta_n\alpha K_o)(\frac{h_n^2}{\beta_n}-Q(-\beta_n))]\tan(h_n)+[\frac{1}{2}-\frac{\beta_n}{2h_n^2}Q(-\beta_n)+\alpha K_o]h_n}$$

$$+\sum_{j=1}^{\infty} \frac{[(1-\alpha K_o)\tan(h_j)+ K_o h_j]e^{-\gamma_j \tau}}{[1-\alpha K_o+\frac{1}{2}(\alpha\phi-\gamma_n \alpha K_o)(\frac{h_j^2}{\gamma_j} -Q(-\gamma_j))]\tan(h_j)+[\frac{1}{2} -\frac{\gamma_j}{2h_j^2}Q(-\gamma_j)+ K_o]h_j} \tag{3.51}$$

where

$$Q(s) = \frac{g^2\varepsilon^2 K_i s}{(g\varepsilon K_i s+1)^2} \tag{3.52}$$

$$\beta_n= \frac{(b+g\varepsilon K_i h_n^2)-\sqrt{(b+g\varepsilon K_i h_n^2)^2-4(1-\varepsilon)g\varepsilon K_i h_n^2}}{2(1-\varepsilon)g\varepsilon K_i} \tag{3.53}$$

$$\gamma_j= \frac{(b+g\varepsilon K_i h_j^2)+\sqrt{(b+g\varepsilon K_i h_j^2)^2-4(1-\varepsilon)g\varepsilon K_i h_j^2}}{2(1-\varepsilon)g\varepsilon K_i} \tag{3.54}$$

h_n are eigenvalues of:

$$\tan(h)= \frac{(-\beta\alpha K_o+\alpha\phi)h}{\alpha\phi+(1-\alpha K_o)\beta} \tag{3.55}$$

h_j are eigenvalues of:

$$\tan(h)= \frac{(-\gamma\alpha K_o+\alpha\phi)h}{\alpha\phi+(1-\alpha K_o)\gamma} \tag{3.56}$$

CHAPTER IV

SOLVENT EXTRACTION BY LIQUID MEMBRANE SYSTEMS

In Chapter II and III we have discussed the types of liquid membrane systems where chemical reactions are involved. There is another type of liquid membrane, where no chemical reaction is involved. This type of liquid membrane is usually in O/W/O form and it can be used for solvent extraction. The work of Li (1971) on extraction from emulsified hydrocarbon mixtures constituted a valuable contribution to the development of low cost separation techniques for solvent separation. The idea is to interpose a water membrane stabilized by emulsification between a mixture of the hydrocarbon to be separated and a standard organic solvent. The permeation of the various hydrocarbon species through the emulsion water membrane, under rate controlled conditions, then proceeds in a selective maner due to the different solubulities of the hydrocarbon in water.

The O/W/O liquid membrane systems can represent also an interesting alternative when the conventional methods are not easily applicable, for example in the case of mixtures difficult or costly to separate. Possible applications are the separation of isomeric mixtures, azeotropes, thermally unstable compounds, mixtures of compounds having similar constitution and identical boiling points and the recovery of components from dilute streams.

Casamatta et al. (1978) have attempted to model the O/W/O type dispersed liquid membrane systems. Their model identified the outer membrane of an emulsion drop as the controlling mass transfer resistance for the conditions usually employed in the selective extraction of an hydrocarbon component from a given emulsified organic mixtures. Calculation of the transfer rate relies on the evalution of the thickness of the outer layer of an emulsion drop. Some serious drawbacks about the model are that they do not consider the effect of one component concentration by another diffusion component and that the shrinking volume of hydrocarbon phase is not considered. V. Kremesec et al. (1982) used an integral balance approach to model the O/W/O system. Their models are not affected by the intensity of mixing is unrealistic, and their models can not predict the extraction of different operating conditions.

The operating sequence of an O/W/O is similar to that as shown in Fig. 1.1. A schematic mechanism for the solvent extraction with dispersed liquid membranes is shown in Fig. 4.1. Two hydrocarbons are considered here only in the modeling of solvent extraction by a dispersed liquid membrane system. But the results can be applied to N component hydrocarbon system.

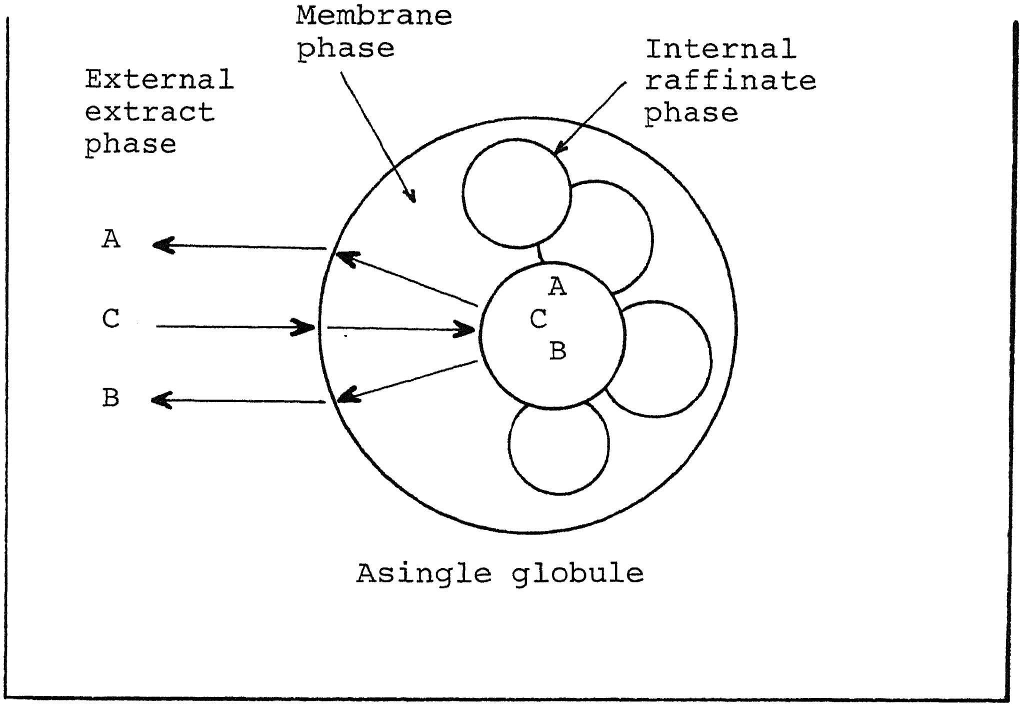


Fig. 4.1 Mechanism of solvent extraction with dispersed liquid membranes.

To model the complicated batch process of solvent extraction by dispersed liquid membranes, we make the following assumptions:

(1) Uniform globule sizes (Sauter mean diameter is used)
(2) No internal circulation in globules.
(3) No coalescense and redistribution of globules.
(4) Mass transfer by diffusion only.
(5) Diffusion coefficients are constant.
(6) Well mixed tank.
(7) Internal raffinate phase droplets are very small, their concentrations are uniform.
(8) No chemical reaction occurs.
(9) Phase equilibrium exists at each interphase.
(10) The total mass of membrane phase is independent of time.
(11) Leakage through membrane rupture is negligible.

Since the extraction rates of hydrocarbon A and B are very slow, for a short time period, variables such as volume fraction of internal phase in emulsion can be considered as constant for that short time period. After that short time period, these variables can then be calculated and readjusted and used for the next short time period. We can continue this process to a desired time. Also, because of the slow extraction process, the membrane external and internal film resistances are neglected.

The governing equations for hydrocarbon A and B, and extract solvent C in each phase are as follows:

Membrane phase:

$$(1-\varepsilon)\frac{\partial C_A}{\partial t} = D_{eA}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_A}{\partial r}\right)+R_A\right. \qquad (4.1)$$

$t=t_o \qquad C_A=C_{AO}$

$r=0 \qquad C_A=\text{finite}$

$r=R \qquad C_A=C_A^*$

$$(1-\varepsilon)\frac{\partial C_B}{\partial t} = D_{eB}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_B}{\partial r}\right)\right)+R_B \qquad (4.2)$$

$t=t_o \qquad C_B=C_{BO}$

$r=0 \qquad C_B=\text{finite}$

$r=1 \qquad C_B=C_B^*$

$$(1-\varepsilon)\frac{\partial C_C}{\partial t} = D_{eC}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_C}{\partial r}\right)-R_C\right. \qquad (4.3)$$

$t=t_o \qquad C_C=C_{CO}$

$r=0 \qquad C_C=\text{finite}$

$r=1 \qquad C_C=C_C^*$

where $D_{eA}=(1-\varepsilon)D_A$

$D_{eB}=(1-\varepsilon)D_B$

$D_{eC}=(1-\varepsilon)D_C$

ε: volume fraction of internal raffinate phase in emulsion phase at time t_o.

R: Sauter mean radius of globules at t_o.

C_A, C_B, C_C: concentration of A,B,C in the membrane phase.

C_A^*, C_B^*, C_C^*: concentration of A,B,C at the membrane external interphase.

D_A, D_B, D_C: diffusion coefficient of A,B,C in the membrane phase.

D_{eA}, D_{eB}, D_{eC}: effective diffusivity of A,B,C in emulsion phase.

R_A, R_B: rate of A,B transfered from receiving phase to membrane phase per unit volume of emulsion phase.

R_C: rate of C transfered from membrane phase to receiving phase per unit volume of emulsion phase.

C_{AO}, C_{BO}, C_{CO}: average concentration of A,B,C at time t_o.

External extract phase:

$$\frac{dA}{dt} = -N(4\pi R^2) D_{eA} \left(\frac{\partial C_A}{\partial r}\right)_{r=R} \qquad (4.4)$$

$$t=t_o \qquad A=A_o$$

$$\frac{dB}{dt} = -N(4\pi R^2) D_{eB} \left(\frac{\partial C_B}{\partial r}\right)_{r=R} \qquad (4.5)$$

$$t=t_o \qquad B=B_o$$

$$\frac{dC}{dt} = -N(4\pi R^2) D_{eC} \left(\frac{\partial C_C}{\partial r}\right)_{r=R} \qquad (4.6)$$

$$t=t_o \qquad C=C_o$$

$$N = \frac{V_{EO}}{(4/3)\pi R_o^3} \tag{4.7}$$

where N: total number of globules in a batch.

V_{EO}: initial volume of emulsion phase.

R_o: initial Sauter mean radius.

A,B,C: moles of A,B,C in the external extracr phase.

A_o,B_o,C_o: moles of A,B,C in the extract phase at t_o.

Internal raffinate phase:

$$\varepsilon M_R \frac{X_A}{t} = -R_A \tag{4.8}$$

$$t=t_o \quad X_A=X_{AO}$$

$$\varepsilon M_R \frac{X_B}{t} = -R_B \tag{4.9}$$

$$t=t_o \quad X_B=X_{BO}$$

$$\varepsilon M_R \frac{X_C}{t} = R_C \tag{4.10}$$

$$t=t_o \quad X_C=X_{CO}$$

where M_R: total number of moles per unit volume of internal raffinate phase.

X_A,X_B,X_C: mole fraction of A,B,C in the raffinate phase.

X_{AO},X_{BO},X_{CO}: mole fraction of A,B,C in the raffinate phase at time t_o.

By the equilibrium relations, we have:

$$\frac{C_A}{M_m} = m_A X_A \tag{4.11}$$

$$\frac{C_B}{M_m} = m_B X_B \tag{4.12}$$

$$\frac{C_C}{M_m} = m_C X_C \tag{4.13}$$

where M_m: total number of moles per unit volume of membrane phase.

m_A, m_B, m_C: distribution coefficient of A,B,C.

Substitute eqns. (4.11)-(4.13) into eqns. (4.1)-(4.3), we obtain:

$$(1-\varepsilon+\frac{\varepsilon M_R}{m_A M_m})\frac{\partial C_A}{\partial t} = D_{eA}(\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 \frac{\partial C_A}{\partial r})) \tag{4.14}$$

$t=t_o \quad C_A=C_{AO}$

$r=0 \quad C_C=\text{finite}$

$r=1 \quad C_A=C_A^*$

$$(1-\varepsilon+\frac{\varepsilon M_R}{m_B M_m})\frac{\partial C_B}{\partial t} = D_{eB}(\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 \frac{\partial C_B}{\partial r})) \tag{4.15}$$

$t=t_o \quad C_B=C_{BO}$

$r=0 \quad C_B=\text{finite}$

$r=1 \quad C_B=C_B^*$

$$(1-\varepsilon+\frac{\varepsilon M_R}{m_C M_m})\frac{\partial C_C}{\partial t} = D_{eC}(\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 \frac{\partial C_C}{\partial r})) \tag{4.16}$$

$t=t_o \quad C_C=C_{CO}$

$r=0 \quad C_C=\text{finite}$

$r=1 \quad C_C=C_C^*$

Introduce the following relations and dimensionless variables:

$$y = \frac{r}{R}$$

$$a_A = 1-\varepsilon+ \frac{\varepsilon M_R}{m_A M_m} \qquad (4.17)$$

$$a_B = 1-\varepsilon+ \frac{\varepsilon M_R}{m_B M_m}$$

$$a_C = 1-\varepsilon+ \frac{\varepsilon M_R}{m_C M_m}$$

$$\tau_A = \frac{D_{eA}}{R^2}\, t$$

$$\tau_B = \frac{D_{eB}}{R^2}\, t$$

$$\tau_C = \frac{D_{eC}}{R^2}$$

$$d = 3V_{EO}\left(\frac{R}{R_o}\right)^3$$

the governing equations become:

$$a_A\frac{\partial C_A}{\partial \tau_A} = \frac{1}{y^2}\frac{\partial}{\partial y}\left(y^2\frac{\partial C_A}{\partial y}\right) \qquad (4.18)$$

$\tau_A=\tau_{AO}$ $\quad C_A=C_{AO}$

$y=0$ $\quad C_A=\text{finite}$

$y=1$ $\quad C_A=C_A^*$

$$a_B\frac{\partial C_B}{\partial \tau_B} = \frac{1}{y^2}\frac{\partial}{\partial y}\left(y^2\frac{\partial C_B}{\partial y}\right) \qquad (4.19)$$

$\tau_B=\tau_{BO}$ $\quad C_B=C_{BO}$

$y=0$ $\quad C_B=\text{finite}$

$y=1$ $\quad C_B=C_B^*$

$$a_C\frac{\partial C_C}{\partial \tau_C} = \frac{1}{y^2}\frac{\partial}{\partial y}(y^2\frac{\partial C_C}{\partial y}) \tag{4.20}$$

$\tau_C=\tau_{CO}$ $\quad C_A=C_{AO}$

$y=0$ $\quad C_C=\text{finite}$

$y=1$ $\quad C_C=C_A^*$

$$\frac{dA}{d\tau_A} = -d(\frac{\partial C_A}{\partial y})_{y=1} \tag{4.21}$$

$\tau_A=\tau_{AO}$ $\quad A=A_o$

$$\frac{dB}{d\tau_B} = -d(\frac{\partial C_B}{\partial y})_{y=1} \tag{4.22}$$

$\tau_B=\tau_{BO}$ $\quad B=B_o$

$$\frac{dC}{d\tau_C} = -(\frac{\partial C_C}{\partial y})_{y=1} \tag{4.23}$$

$\tau_C=\tau_{CO}$ $\quad C=C_o$

As memtioned before, for avery short time period, we can assume R, a_A, a_B, a_C, M_R and d are all constant. Let $t'=t-t_o$, with this substitution, the governing equations for for component A become:

$$a_A\frac{\partial C_A}{\partial \tau_A'} = \frac{1}{y^2}\frac{\partial}{\partial y}(y^2\frac{\partial C_A}{\partial y}) \tag{4.24}$$

$\tau_A'=0$ $\quad C_A=C_{AO}$

$y=0$ $\quad C_A=\text{finite}$

$y=1$ $\quad C_A=C_A^*$

$$\frac{dA}{d\tau_A'} = -d(\frac{\partial C_A}{\partial y})_{y=1} \tag{4.25}$$

$\tau_A'=0$ $\quad A=A_o$

The Laplace transforms of eqns. (4.24) and (4.25) are:

$$a_A(s\overline{C}_A - C_{AO}) = \frac{1}{y^2}\frac{d}{dy}(y^2\frac{d\overline{C}_A}{dy}) \qquad (4.26)$$

$$y=0 \qquad \overline{C}_A=\text{finite}$$

$$y=1 \qquad \overline{C}_A=C_A^*$$

$$s\overline{A} - A_o = -d(\frac{d\overline{C}_A}{dy})_{y=1} \qquad (4.27)$$

The general solution to eqn. (4.26) is:

$$\overline{C}_A = C_1\frac{\sinh\sqrt{a_A s}\,y}{y} + C_2\frac{\cosh\sqrt{a_A s}\,y}{y} + \frac{C_{AO}}{s} \qquad (4.28)$$

From the boundary conditions of eqn. (4.26), we have:

$$C_1 = \frac{1}{\sinh\sqrt{a_A s}}(\overline{C}_A^* - \frac{C_{AO}}{s}) \qquad (4.29)$$

$$C_2 = 0$$

Substitute the above constants into eqn. (4.28), the solution of eqn. (4.26) becomes:

$$\overline{C}_A = \frac{C_{AO}}{s} + (\overline{C}_A^* - \frac{C_{AO}}{s})\frac{\sinh\sqrt{a_A s}\,y}{s\,\sinh\sqrt{a_A s}} \qquad (4.30)$$

and $$(\frac{d\overline{C}_A}{dy})_{y=1} = (\overline{C}_A^* - \frac{C_{AO}}{s})\frac{\sqrt{a_A s}\cosh\sqrt{a_A s} - \sinh\sqrt{a_A s}}{\sinh\sqrt{a_A s}} \qquad (4.31)$$

By the equilibrium relation at the membrane external interphase, we have:

$$\frac{\bar{C}^*_A}{M_m} = m_A \frac{\bar{A}}{A+B+C} = m_A \frac{\bar{A}}{M_t} \tag{4.32}$$

where

$M_t = A+B+C$ is the total number of moles in the external extract phase.

Substitute the above relation into eqn. (4.31), we have:

$$\left(\frac{d\bar{C}_A}{dy}\right)_{y=1} = \left(\frac{M_m m_A}{M_t}\bar{A} - \frac{C_{AO}}{s}\right)\frac{\sqrt{a_A s}\cosh\sqrt{a_A s}-\sinh\sqrt{a_A s}}{\sinh\sqrt{a_A s}} \tag{4.33}$$

Substitute eqn. (4.33) into eqn. (4.27) and solve it for $\bar{A}$, we obtain:

$$\bar{A} = \frac{A_o s\cdot\sinh\sqrt{a_A s}+dC_{AO}(\sqrt{a_A s}\cosh\sqrt{a_A s}-\sinh\sqrt{a_A s})}{s[s\cdot\sinh\sqrt{a_A s}+b_A(\sqrt{a_A s}\cosh\sqrt{a_A s}-\sinh\sqrt{a_A s})]} = G(s) \tag{4.34}$$

where $b_A = \frac{dM_m m_A}{M_t}$, $M_t = A+B+C$ (4.35)

The number of moles of A in the extract phase is equal to the inverse Laplace transform of G(s), and is expressed as:

$$A = L^{-1}\left[G(s)\right] \tag{4.36}$$

The inverse Laplace transform is equal to the sum of the residues of G(s). Similar to eqn. (2.34) in Chapter II, we can express G(s) in series form and prove that s=0 is a simple pole. Other poles are given by the roots of the following equation:

$$s\cdot\sinh\sqrt{a_A s}+b_A(\sqrt{a_A s}\cosh\sqrt{a_A s}-\sinh\sqrt{a_A s})=0 \tag{4.37}$$

After rearrangement, the above equation becomes:

$$\tanh\sqrt{a_A s} = \frac{b_A\sqrt{a_A s}}{b_A - s} \tag{4.38}$$

Let $\sqrt{a_A s} = i\beta$ (4.39)

or $s = -\beta^2/a_A$ (4.39a)

Substitute eqn. (4.39) and eqn. (4.39a) into eqn. (4.38), after simplifications, we have:

$$\tan(\beta) = \frac{a_A b_A \beta}{a_A b_A + \beta^2} \tag{4.40}$$

Let β_n represent all eigenvalues of eqn. (4.40), then $s=s_n= -\beta_n^2/a_A$ are poles of G(s) and as shown in section A of chapter II, they are all simples. Similar to section A of chapter II, the residues for each pole are as follows:

$$\mathrm{Res}(0)= \lim_{s\to 0}\left[sG(s)e^{s\tau'_A}\right] = \frac{3A_o+da_A C_{AO}}{3 + a_A b_A} \tag{4.41}$$

$$\mathrm{Res}(s_n)= \lim_{s\to s_n}\left[(s-s_n)G(s)e^{s\tau'_A}\right]$$
$$=\frac{(\beta_n^2 A_o+a_A dC_{AO})\tan(\beta_n)-dC_{AO}\beta_n a_A}{(1+\frac{1}{2}b_A a_A)\beta_n^2\tan(\beta_n)+\frac{1}{2}\beta_n^3}\,e^{-(\frac{\beta_n^2}{a_A})\tau'_A} \tag{4.42}$$

The number of moles of A in the external extract phase is equal to the sum of all residues of G(s) and is as follows:

$$A=\frac{da_A C_{AO}+3A}{a_A b_A+3}+\sum_{n=1}^{\infty}\frac{(\beta_n^2 A_o+a_A dC_{Ao})\tan(\beta_n)-dC_{AO}\beta_n a_A}{(1+\frac{1}{2}b_A a_A)\beta_n^2\tan(\beta_n)+\frac{1}{2}\beta_n^3}\,e^{-(\frac{\beta_n^2}{a_A})\tau'_A} \tag{4.43}$$

$$a_A=1-\varepsilon+\frac{\varepsilon M_R}{m_A M_m} \tag{4.43a}$$

$$b_A=\frac{dm_A M_m}{M_t}$$

$$d=3V_{EO}(\frac{R}{R_o})^3$$

β_n are eigenvalues of $\tan(\beta)=\frac{a_A b_A\beta}{a_A b_A+\beta^2}$

Similarly, the number of moles of B and C in the external extract phase:

$$B=\frac{da_B C_{BO}+3B_o}{a_A b_B+3}+\sum_{n=1}^{\infty}\frac{(\gamma_n^2 B_o+a_B dC_{BO})\tan(\gamma_n)-dC_{BO}\gamma_n a_B}{(1+\frac{1}{2}b_B a_B)\gamma_n^2\tan(\gamma_n)+\frac{1}{2}\gamma_n^3}\,e^{-(\frac{\gamma_n^2}{a_B})\gamma'_B} \tag{4.44}$$

$$a_B=1-\varepsilon+\frac{\varepsilon M_R}{m_A M_m} \tag{4.45}$$

$$b_B=\frac{dm_B M_m}{M_t}$$

$$d=3V_{EO}(\frac{R}{R_o})^3$$

γ_n are eigenvalues of $\tan(\gamma)=\frac{a_B b_B\gamma}{a_B b_B+\gamma^2}$

$$C=\frac{da_C C_{CO}+3C_o}{a_C b_C+3}+\sum_{n=1}^{\infty}\frac{(\lambda_n^2 C_o+a_C dC_{CO})\tan(\lambda_n)-dC_{CO}\lambda_n a_C}{(1+\frac{1}{2}b_C a_C)\lambda_n^2\tan(\lambda_n)+\frac{1}{2}\lambda_n^3}\,e^{-(\frac{\lambda_n^2}{a_C})\tau'_C} \tag{4.46}$$

$$a_C=1-\varepsilon+\frac{\varepsilon M_R}{m_C M_m}$$

To evaluate the effectiveness of the separation of hydrocarbons A and B, we define a separation factor SF as follows:

$$SF = \frac{\text{ratio of mole fraction of A to B in the extract phase}}{\text{ratio of mole fraction of A to B in the raffinate phase}}$$

$$= \frac{A/B}{(A_{Oi}-A)/(B_{Oi}-B)} \tag{4.48}$$

where A_{Oi}: initial number of moles of A in the internal raffinate phase.

B_{Oi}: initial number of moles of B in the internal raffinate phase.

To apply the models developed in this chapter, we start from time t=0 and let $t_0=0$. At time t=0, we can calculate the following parameters:

ε = (initial volume of raffinate phase)/(initial volume of emulsion phase)

$M_R = (A_{Oi}+B_{Oi})$/(initial volume of raffinate phase)

$M_t = C(t=0)$

$R = R_o$

$$C_{AO} = m_A M_m X_{AO} = m_A M_m \frac{A_{Oi}}{A_{Oi}+B_{Oi}} \tag{4.49}$$

$$C_{BO} = m_B M_m X_{BO} = m_B M_m \frac{B_{Oi}}{A_{Oi}+B_{Oi}}$$

$C_{CO}= m_A M_m X_{CO}=0$

Having the above parameter values, we can apply eqns. (4.43), (4.44) and (4.46) to calculate A, B and C at next short time $t=t_1$. When we have the moles of A, B and C at time t_1, we can adjuste the parameter values as follows:

$$\varepsilon = \frac{(A_{Oi}-A)V_A+(B_{Oi}-B)V_B+ CV_A}{V_{EO}-AV_A-BV_B+ CV_C} \tag{4.50}$$

$$M_R= \frac{A_{Oi}+B_{Oi}-A-B+C}{(A_{Oi}-A)V_A+(B_{Oi}-B)V_B+ CV_C}$$

$$M_t= A+B+C$$

$$R = \left[\frac{3}{4\pi N}(V_{EO}-AV_A-BV_B+ CV_C\right]^{\frac{1}{3}}$$

$$C_{AO}= m_A M_m X_A= m_A M_m \frac{A_{Oi}-A}{A_{Oi}+B_{Oi}-A-B+C}$$

$$C_{BO}= m_B M_m X_B= m_B M_m \frac{B_{Oi}-B}{A_{Oi}+B_{Oi}-A-B+C}$$

$$C_{CO}= m_C M_m X_C= m_C M_m \frac{C}{AOi+B_{Oi}-A-B+C}$$

where V_A, V_B, V_C: molar volume of A,B, C.

From the above parameters amd let $t'=t-t_1$, we can again apply eqns. (4.43), (4.44) and (4.46) to calculate the moles of A,B and C in the extract phase at a next short time $t=t_2$, and we can continue this procedures to the moles of A, B and in the extract phase at any desired time.

CHAPTER V

ESTIMATION OF DIFFUSIVITY AND MASS TRANSFER COEFFICIENT

The models developed in Chapter II, III and IV enable us to predict the extraction rate through dispersed liquid membranes without the need of experimental data. All parameters required for the prediction can be classified into three categories. They are: (1) physical and chemical properties, such as density, molar volume and equilibrium constant etc., which can be found from literature or can be determined by independent experiment. (2) parameters such as volume fraction of internal phase in emulsion phase, volume fraction of emulsion in a batch and the Sauter mean diameter of globules , which are determined by operating conditions and can be determined before extraction run. (3)diffusivity and mass transfer coefficient which are resulted from the relative movement of molecules, if they are not available in literature, the methods presented in this chapter can be used for the estimation.

Diffusivity

The correlation by Wilke-Chang (1955) is used to estimate the required diffusivities. The correlation for diffusion coefficient in water and in nonassociated solvents can be expressed by the following equation:

$$D = 7.4\text{x}10^{-8} \frac{(\eta M)^{1/2} T}{\mu V^{0.6}} \tag{5.1}$$

where T: temperature, °K.

M: molecular weight of solvent.

μ: viscosity of solvent, cp.

V: molar volume of solute at normal boiling point, cc/g mole.

η: association parameter.

η is the association parameter to define the effective molecular weight of the solvent with respect to the diffusion process. For non-associated solvent η=1 and for water η=2.6.

Membrane External Film Mass Transfer Coefficient

Mass transfer between a fluid and a small suspended particules is important in many industrial situations and there have been numerous studies of mass transfer to solid particles suspended in liquid in agitated vessels. The correlation method described by Sherwood et al. (1975) is modified to estimate the external and internal mass transfer coefficients of globules in a dispersed liquid membrane system.

Harriott (1962) used a modified Frossling equation to calculate mass transfer coefficient by taking the slip velocity as the terminal velocity of the particle falling under the influence of gravity and adopting this as the velocity to be used in the Reynolds No. to estimate the coefficient.

$$\frac{K_o d_g}{D_e} = 2 + 0.6Re^{1/2}Sc^{1/3} \tag{5.2}$$

Following the procedures outlined by Sherwood et al., the terminal velocity can be determined as follows:

1. Calculate the terminal velocity from Stokes's law,

$$U_{TS} = \frac{d_g^2 \; \rho_e - \rho_g \; g}{18\mu_e} \tag{5.3}$$

2. Calculate the Reynolds number using U_{TS},

$$Re_{TS} = \frac{d_g U_{TS} \rho_e}{\mu_e} \tag{5.4}$$

3. Obtain U_T/U_{TS}, from the following table or Fig. 5.1.

Re_{TS}	1	10	100	1,000	10,000	100,000
U_T/U_{TS}	0.9	0.5	0.37	0.17	0.07	0.023

4. Obtain the terminal velocity as:

$$U_T = U_{TS} x (U_T/U_{TS}) \tag{5.5}$$

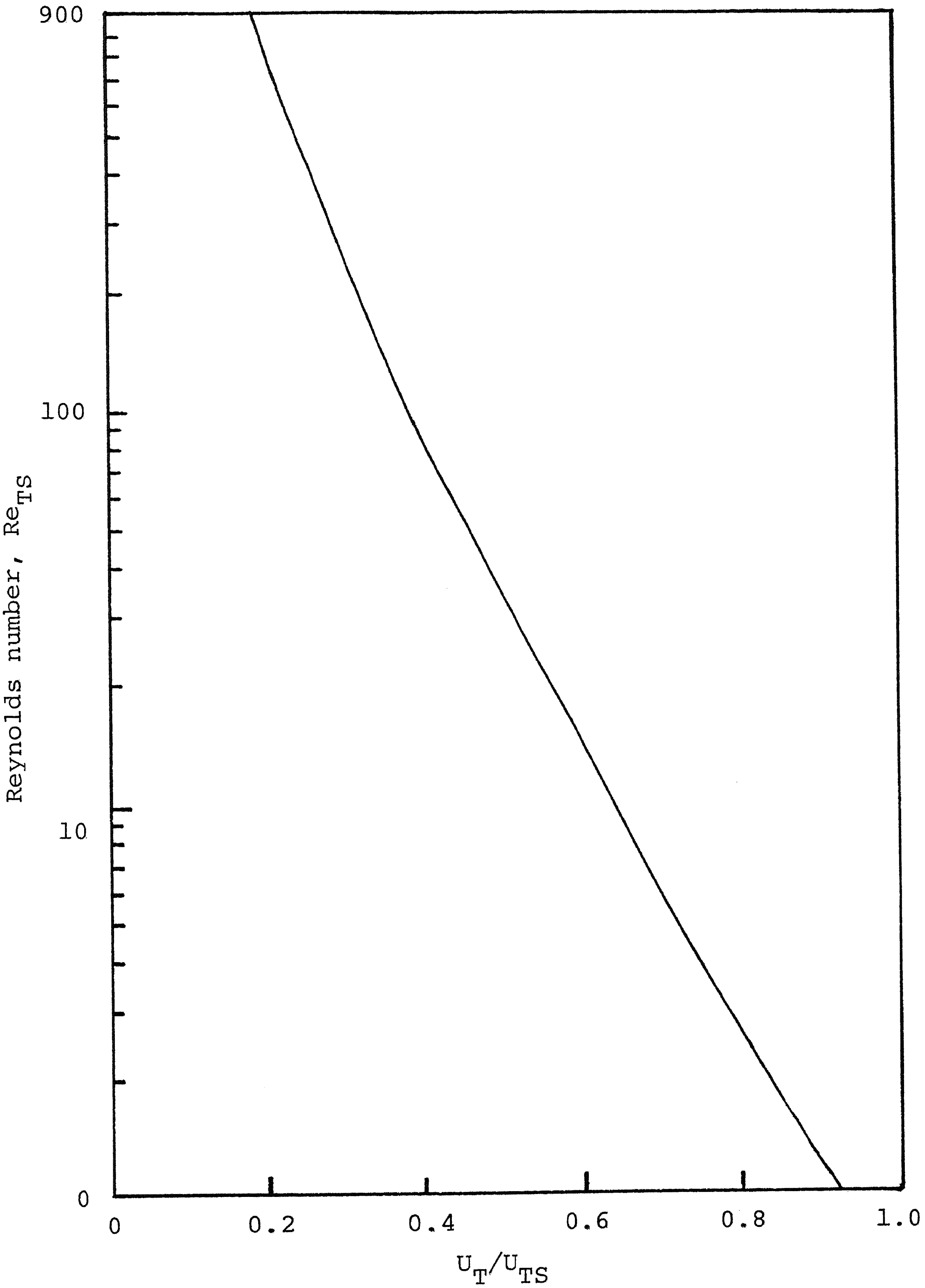


Fig. 5.1 Slipping velocity v.s. Reynolds number.

where d_g: the Sauter mean diameter of globules.

D_e: diffusivity of solute in external phase.

Re: Reynolds number, $\rho_e d_g U_T/\mu_e$.

Sc: Schmit number, $\mu/\rho_e D_e$

ρ_g: emulsion phase density (globules).

ρ_e: external phase density.

ρ_e: external phase viscosity.

Membrane Internal Film Mass Transfer Coefficient

For the internal film mass transfer coefficient k_i, the following correlation is used.

$$\frac{k_i d_r}{D_m} = 2 \tag{5.6}$$

where d_r: average diameter of internal phase droplets.

D_m: diffusivity of solute in membrane phase.

CHAPTER VI

EXPERIMENTAL

A. COPPER EXTRACTION THROUGH DISPERSED LIQUID MEMBRANES.

All salts and solvents were reagent grade and were used as received. The mobile carriers in the membrane phase were LIX-64N (a mixture of aliphatic α-hydroxyoxime and β-hydroxybenzo-phenone oxime from Henkel Co. Ltd). The membrane were n-heptane. Dispersed liquid membranes were stabilized with Span 80 (Sorbitan monoleate, from ICI America).

A membrane solution was prepared consisting of 2% by weight of LIX-64N and 5% by volume of Span 80 and the rest was n-heptan. A water-in-oil emulsion phase was made by adding 157.5 ml of the membrane solution and 150 ml of 1.5%W Nitric acid solution to a Waring commercial blender and stirred at 3000 rpm of mixing speed for about 10 minutes.

To make a diffusion experiment, 80 ml of the emulsion phase was added to an agitated vessel containing 340 ml deionized water under stirring at 290 rpm by a three vane marine type of mixing propeller in a 1000 ml beaker. In about 2 minutes 60 ml of 1000 ppm copper solution was poured into the vessel to start the extraction process. To monitor the diffusion of metal ions across the membranes, samples were taken from time to time. The copper concentrations of the samples were measured by a Varian Atomic Absorption Spectrphotometer.

The equilibrium constant or distribution coefficient of copper between aqueous and membrane phases was measured by shaking equal volumes (100 ml) of the membrane solution and 100 ppm copper solution. The final copper concentration in the aqueous solution was measured and the pH value of the aqueous solution was also measured. Equilibrium constant was then calculated.

The stability of the membranes were tested by using 1000 ppm copper solution as the internal phase in the membrane system. Followed the same procedures as in the experimental extraction run. Samples from the external phase were taken from time to time, to measure the leaked copper ions in the external phase. In the leakage experiment, various mixing speed were used. The emulsion phase was added to the stirring vessel either slowly or abruptly to test their effect on leakage rate.

Experimental data produced from this research are presented in the appendixes.

B. PHENOL REMOVAL BY DISPERSED LIQUID MEMBRANE SYSTEMS.

Experimental data by Teramoto et al. (1983) were used to test the mathematical models developed in Chapter III for the removal of phenol by dispersed liquid membrane systems. The detailed procedures of their experiments were described in their paper. Their procedures are briefly summarized as follows:

A mixture of 50 ml of kerosene containing 5% by volume of Span 80 and the same volume of aqueous solution of NaOH was agitated for 15 min by a vibromixer. Then the mixture was sonicated by ultrasonic homogenizer by either the direct or indirect method. The emulsion phase thus prepared was added to an agitated vessel containing 550 ml of deionized water under stirring at 188 rpm. The vessel was 9 cm in diameter, and equiped with a six-bladed turbine agitator. In about two min, phenol solution was poured into the vessel to start extraction. The total volume was 750 ml.

C. SOLVENT EXTRACTION BY DISPERSED LIQUID MEMBRANE SYSTEMS.

Experimental data by Kremesec, Jr. and Slattery (1982) were used to test the models developed in Chapter IV. In their procedures, a binary hydrocarbon mixture of toluene and n-heptane was separated by means of a glycerol-water membrane and o-xylene solvent. Glycerol (about 70% by weight) and Span 80 (about 1% by weight) were added to the water in order to obtain a stable emulsion. All hydrocarbons contained traces of water and other impurities that were ignored.

The hydrocarbons, glycerol, water and Span 80 were agitated in a blender at a low setting for one minute to form a stable emulsion with glycerol-water as the membrane phase and hydrocarbons as internal phase. This emulsion was added to a 1,500 ml beaker containing the o-xylene solvent and dispersed with a two inch propeller. The mass fraction of each species in the solvent was followed as a function of time with a gas chromatograph.

CHAPTER VII

RESULTS AND DISCUSSION

In this chapter, we compare the theoretical predictions against experimental data to see how good are the models developed in Chapter II for copper extraction, Chapter III for phenol removal and Chapter IV for solvent extraction.

Before we do so, we will examine some mathematical aspects of the models. In the copper extraction process and the phenol removal process, we have considered three cases: (1) both film resistances are neglected, (2) only external film resistance is considered, (3) both film resistances are considered. When the internal film resistance is negligible, the models for case 3 should be able reduced to the models for case 2, and when both film resistances are neglected, the models for case 2 should be able reduced to the models for case 1.

When the internal film resistance is negligible, the film resistance approaches to zero or K_i in the models for case 3 (eqn. 2.126 and eqn. 3.51) approaches to 0. When K_i approaches to 0, eqn. (2.126) and eqn. (3.51) should be reduced to eqn. (2.78) and eqn. (3.36) respectively which are the models for case 2.

From eqn. (2.126), when K_i approaches to 0, we have the following approximations:

$$\sqrt{(b+q\varepsilon K_i h^2)^2-4(1-\varepsilon)q\varepsilon K_i h^2} \simeq b+K_i\frac{[b-2(1-\varepsilon)]q\varepsilon h^2}{b}+O(K_i^{\,2})$$

$$\beta=\frac{(b+q\varepsilon K_i h^2)-\sqrt{(b+q\varepsilon K_i h^2)^2-4(1-\varepsilon)q\varepsilon K_i h^2}}{2(1-\varepsilon)q\varepsilon K_i} \simeq \frac{h^2}{b} \tag{7.1}$$

$$\gamma=\frac{(b+q\varepsilon K_i h^2)+\sqrt{(b+q\varepsilon K_i h^2)^2-4(1-\varepsilon)q\varepsilon K_i h^2}}{2(1-\varepsilon)q\ K_i} \tag{7.2}$$

$$\simeq \frac{1+\varepsilon K_i h^2}{(1-\varepsilon)K_i} \simeq \frac{1}{(1-\varepsilon)K_i} \simeq \infty \tag{7.3}$$

$$Q(-\beta)=\frac{q^2\varepsilon^2K_i(-\beta)}{(-q\varepsilon K_i\beta+1)^2} \simeq 0 \tag{7.4}$$

$$Q(-\gamma)=\frac{q^2\varepsilon^2K_i(-\gamma)}{(-q\varepsilon K_i\gamma+1)^2} \simeq \frac{q^2\varepsilon}{\left(\frac{q}{1-\varepsilon}+1\right)^2} = \text{constant} \tag{7.4a}$$

Substitute the above approximations and $K_i=0$, into eqn. (2.126), we have the following result:

$$\frac{Cu}{Cuo}=\lim_{K_i\to 0}\Bigg[\frac{3}{3+m\phi b}$$

$$+\sum_{n=1}^{\infty}\frac{[(1-mK_o)\tan(h_n)+mK_oh_n]e^{-\beta_n\tau}}{[1-mK_o+\frac{1}{2}(m\phi-\beta_n mK_o)(\frac{h_n}{\beta_n}-Q(-\beta_n))]\tan(h_n)+(\frac{1}{2}-\frac{n}{2h_n^2}Q(-\beta_n)+mK_o)h_n}$$

$$+\sum_{n=1}^{\infty} \frac{(1-mK_o)\tan(h_j)+mK_o h_j \; e^{-\gamma_j}}{1-mK_o+\frac{1}{2}(m\phi-\gamma_j mK_o)\left(\frac{h_j}{\gamma_j}-Q(-\gamma_j)\right) \tan(h_j)+\left(\frac{1}{2}-\frac{\gamma_j}{2h_j^2}Q(-\gamma_j)+mK_o\right) h_j} \Bigg]$$

$$= \frac{3}{3+m\phi b} + \sum_{n=1}^{\infty} \frac{(1-mK_o)\tan(h_n)+mK_o h_n}{(1-mK_o-\frac{1}{2}mK_o h_n^2+\frac{1}{2}m\ b)\tan(h_n)+(\frac{1}{2}+mK_o)h_n} e^{-\frac{h_n^2}{b}}$$

= Eqn. (2.78) by change h_n to β_n.

Similarly, we can show that when the internal film resistance is negligible, eqn. (3.51) can be reduced to eqn. (3.36).

Now we turn to look the other situation, when the external film resistance is negligible, or say K_o approaches to 0, the models for case 2 shoude be reduced to the models for case 1. This can be shown as follows: from eqn. (2.78),

$$\frac{Cu}{Cuo} = \lim_{K_o \to 0} \left[\frac{3}{3+m\phi b} + \sum_{n=1}^{\infty} \frac{(1-mK_o)\tan(\beta_n)+mK_o\beta_n}{(1-mK_o-\frac{1}{2}mK_o\beta_n^2+\frac{m\phi b}{2})\tan(\beta_n)+(\frac{1}{2}+mK_o)\beta_n} e^{-\frac{\beta_n^2}{b}} \right]$$

$$= \frac{3}{3+m\phi b} + \sum_{n=1}^{\infty} \frac{\tan(\beta_n)}{(1+\frac{1}{2}m\phi b)\tan(\beta_n)+\frac{1}{2}\beta_n} e^{-\frac{\beta_n^2}{b}}$$

= Eqn. (2.46)

Similarly, we can show that when the external film resistance is negligible, eqn. (3.36) can be reduced to eqn. (3.25).

A. COPPER EXTRACTION THROUGH DISPERSED LIQUID MEMBRANES.

Leakage rate

One of the problems which have to be considered in the practical applications of dispersed liquid membrane systems is the membrane rupture problem. We have run four experiments to measure the leakage rate. The leakage rate is a function of many variables, such as mixing speed, membrane composition, methods of adding emulsion phase to the external aqueous phase and types of propeller etc. In our tests, the membrane composition was the same as that for the copper extraction experiments and was unchanged for all the leakage experiments. The mixing speed was maintained at 260 - 280 rpm. The emulsion phase was added to the stirring aqueous phase either slowly or abruptly. All the experimental data are shown in Appendex A. From the data, we found that when the emulsion phase was added slowly and carefully, the leakage rate was below 1% and when the emulsion was added abruptly, the leakage rate was about 2%. From the data, it seems that most of the leakage came at the time when the emulsion phase was breaking into small globules. After that initial period the leakage seems very slow. I practical applications, the 1% leakage rate is tolerable and is negligible.

Equilibrium

The equilibrium constant was measured by shaking equal volumes of membrane phase and aqueous phase and measured the copper ion concentration in the aqueous phase before shaking and after equilibrium. As shown in Chapter II, the equilibrium relation is:

$$K_{eq} = \frac{[CuR_2][H^+]^2}{[Cu^{++}][RH]^2} \tag{7.5}$$

In our tests, the carrier concentration was 2% by weight of LIX-64N. Hydrogen ion concentration was calculated from its pH value as measured by a pH mater. Copper ion concentrations before and after shaking were measured by an AAS, and CuR_2 concentration was then calculated. Substitute all the values into eqn. (7.5), we then calculated the equilibrium constant. The experimental data are shown in Appedex A. The average value of $K_{eq}[\underline{RH}]^2$ is 1.27×10^{-5}, where RH is 2%W LIX-64N.

Comparison of predictions and experimental data

The mean diameter of globules and equilibrium constant were measured before copper extraction run. Diffusivities and mass transfer coefficients were estimated from the correlations in Chapter V. The experimental conditions and all parameter values are summarized in Table 7.1 and Table 7.2. Having all the parameter values, with the aid of computers, we can use the models in Chapter II to calculate the external

Table 7.1

Experimental conditions for copper extraction

	Run 1	Run 2
Vol. of membrane phase, ml	40	40
Vol. of receiving phase, ml	40	40
Vol. of Source phase, ml	460	460
Con. of Cu in source phase, ppm	130	174
Con. of HNO_3 in Rec. phase, %W	1.1	1.1
Mixing speed, rpm	280	280
pH value in Rec. phase	0.77	0.77
pH value in source phase	0.23	0.23

Table 7.2

Summarized parameter values for copper extraction

	Run 1	Run 2
ε	0.5	0.5
ϕ'	0.148	0.148
ϕ	0.522	0.522
q	2169	2169
m	0.402	0.402
D_x, cm^2/s	$7x10^{-7}$	$7x10^{-7}$
D_{Cu}(in water)	$3.5x10^{-6}$	$3.5x10^{-6}$
R, cm	0.045	0.045
d_r, cm	0.0004	0.0004
k_o, cm/s	0.0017	0.0017
k_i, cm/s	0.0035	0.0035

phase copper concentrations for different cases, and the results are shown in Figs. (7.1) and (7.2). The experimental data are shown in Appendex B and are plotted in Figs. (7.1) and (7.2). From the comparison of the predictions and the experimental data, we can see that the model with both resistances considered, curves C, and the model with only external resistance, curves B, are reasonable good in agreement with the experimental data, while the model without film resistance shows appreciable deviation from the data. We also note that curve B and curve C in both figures are so close that they are almost indistinguishable. Based on the observation, we can say that the external film resistance is very important and cannot be neglected, while the internal film resistance is negligible.

Effect of Internal Phase Droplet Sizes

The membrane internal mass transfer resistance as defined in Chapter II is:

$$K_i = \frac{D_{ex}}{R^2 k_i a} \quad ; \qquad a = \frac{3}{d_r} \tag{7.6}$$

The above equations show that the internal phase droplet sizes directly affect the internal film resistance. The droplet sizes are also functions of many variables. In the preparation of an emulsion phase, the composition is usually

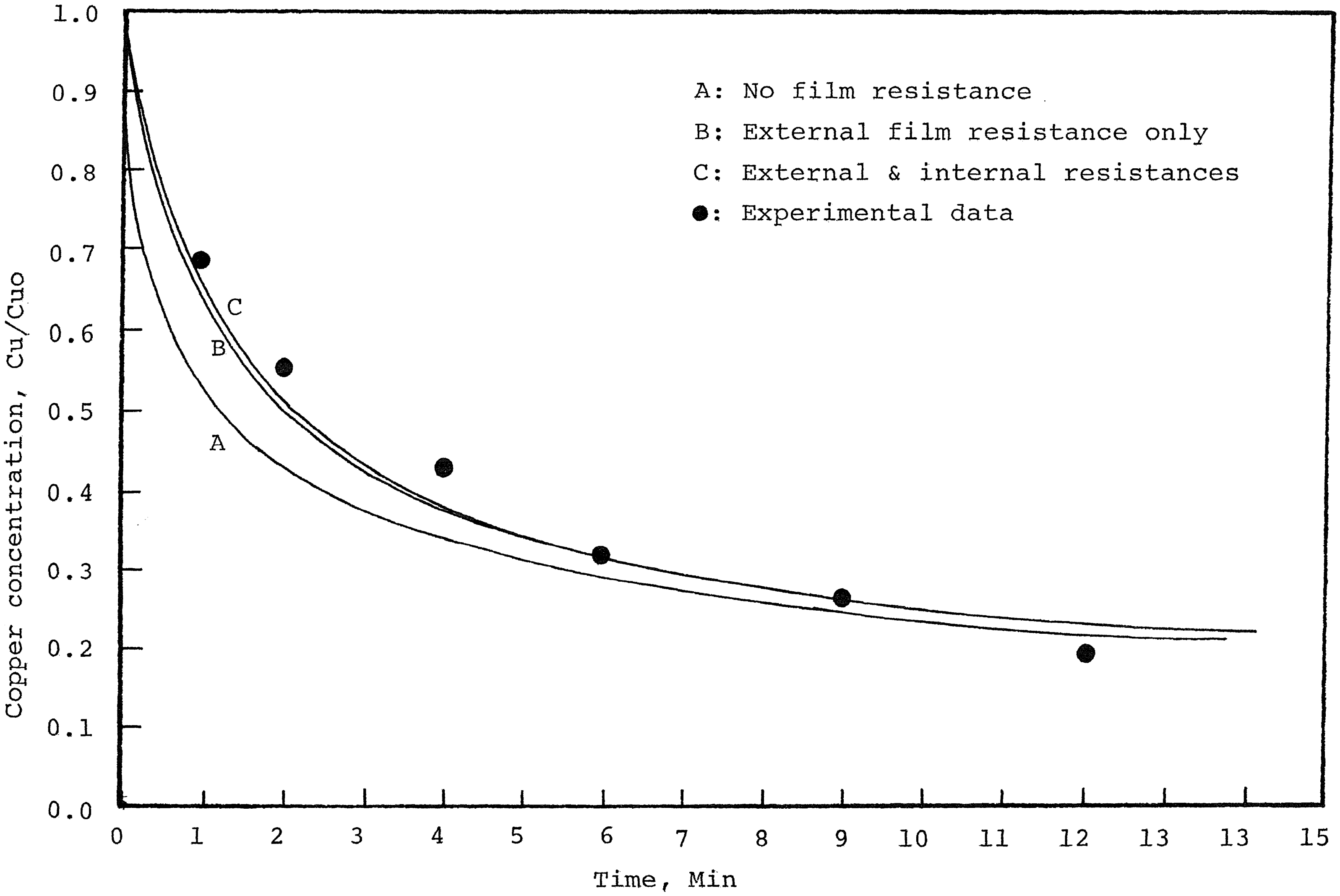


Fig. 7.1 Copper extraction - Run 1

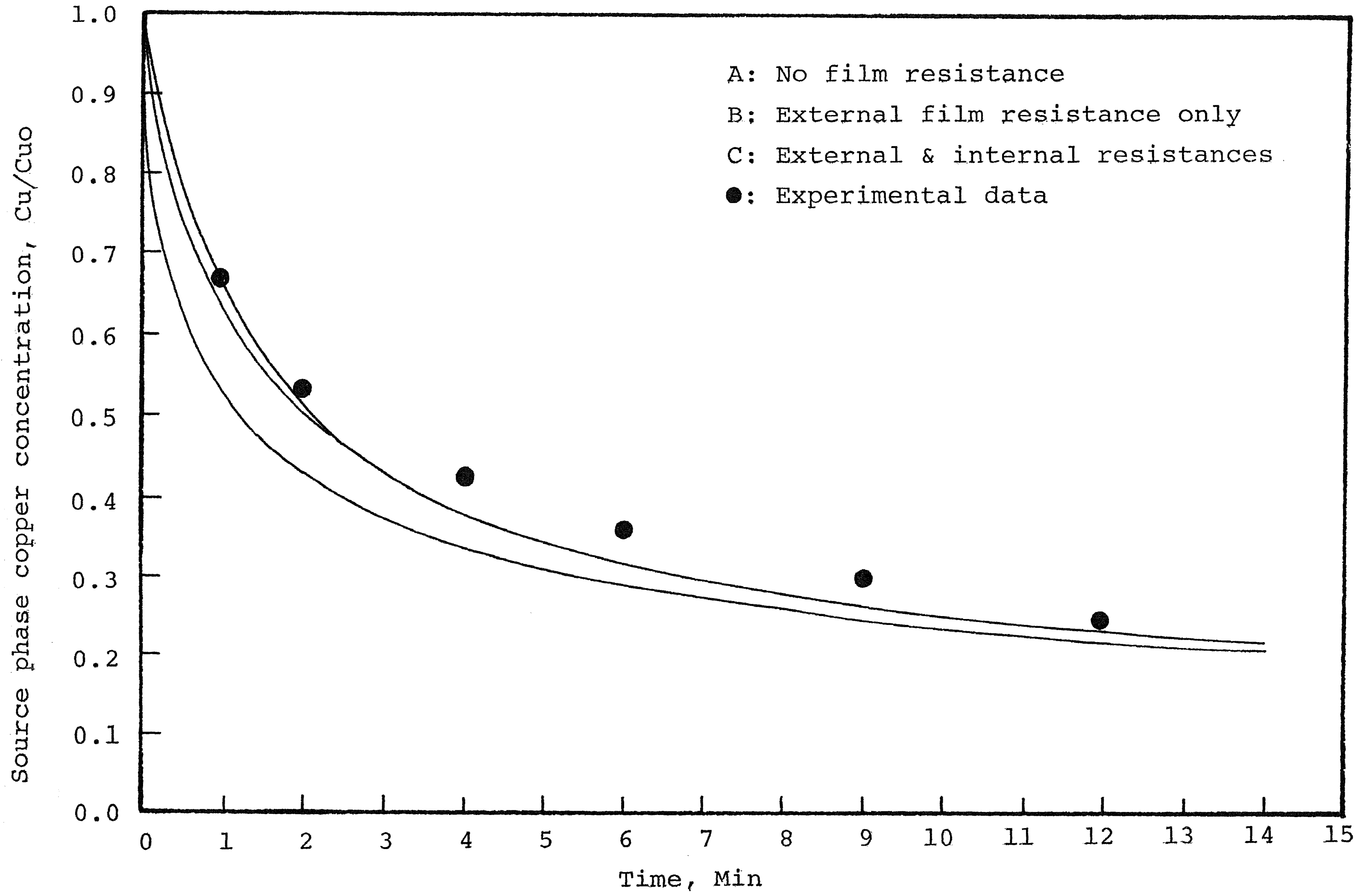


Fig. 7.2 Copper extraction - Run 2

decided by other factors and the intensity of agitation can be fixed, then the droplet sizes depend on the time of mixing or emulsification. The effect of the time factor on the droplet sizes in emulsions has been extensively investigated by several workers (Sherman, 1968), and the consensus of opinion among all the investigators is that prolonging the agitation beyond an optimum time interval does little to improve rhe quality of the emulsions. Under normal conditions of emulsification, the mean size of the particles decreases very rapidly in the first few seconds and then gradually attains the limiting value in 1-5 min. Therefore there is no appreciable reduction in size after that limiting value.

A semi-quantitative equation for the growth of the number of particles during emulsification were set by assuming that the decrease in the number N of the particles by coalescence is proportional to N^2 and that the increase is proportional to N, then (Sherman, 1968)

$$\frac{\partial Nt}{\partial t} = B'Nt - A'Nt^2 \tag{7.7}$$

Usually, the initial number of particles is small and in that case:

$$\frac{1}{Nt} = \frac{1}{N_\infty} + \left(\frac{1}{No} - \frac{1}{N_\infty}\right)e^{-B't} \; ; \; N_\infty = \frac{B'}{A'} \tag{7.8}$$

or, in terms of the volumes of the particles:

$$\upsilon_t=\upsilon_o-(\upsilon_o-\upsilon_\infty)(1-e^{-B't}) \qquad (7.9)$$

The volume of the particles shows an exponential type of decre decrease to the limiting value. The available experimental dara seem to follow this trend. Fig. 7.3 (Sherman, 1968) shows dependence of the particle size upon time of emulsification. In some cases, small changes in particle size or concentration are observed after prolonged agitation. As far as practical emulsiofication is concerned, there is an optimum of 1-5 min beyond which agitation produced no appreciable improvement of emulsion. The droplet sizes usually in the range of 1-10 μm after several min of agitation. In our experiments, the agitation time was about 10 min. The droplet sizes were very small. From eqn. (7.6), the internal mass transfer area per unit volume of emulsion phase were very large so that the internal film mass transfer resistance was negligible.

Effect of Carrier Concentration

Fig. 7.4 shows the effect of the carrier concentration on copper extraction rate. When the carrier concentration is low, RH is the monomeric species in a dilute and its concentration is related to the total concentration. At high concentration, oxime begin to dimerize (Komasawa and Otake, 1983). From Fig. 7.4. we can say that at low carrier

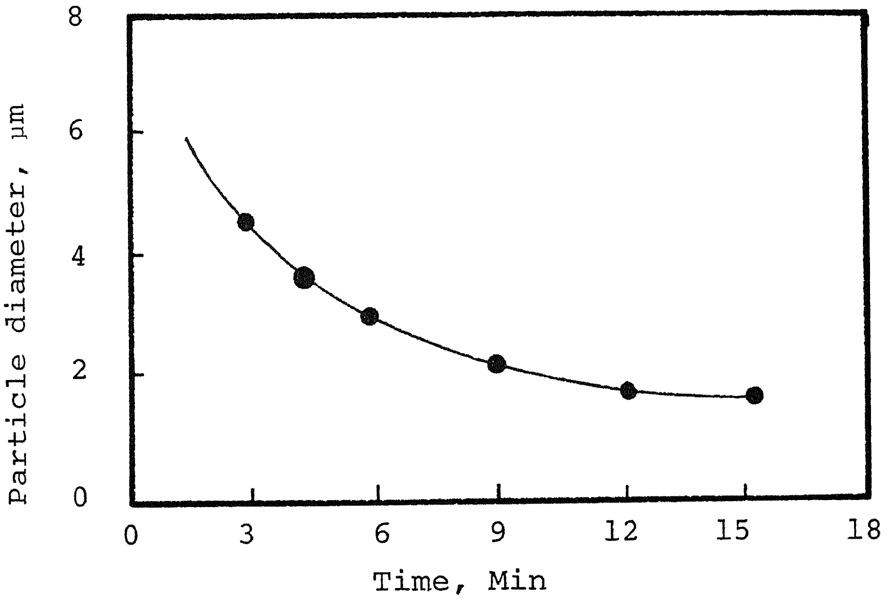


Fig. 7.3 Dependence of particle size upon time of emulsification.

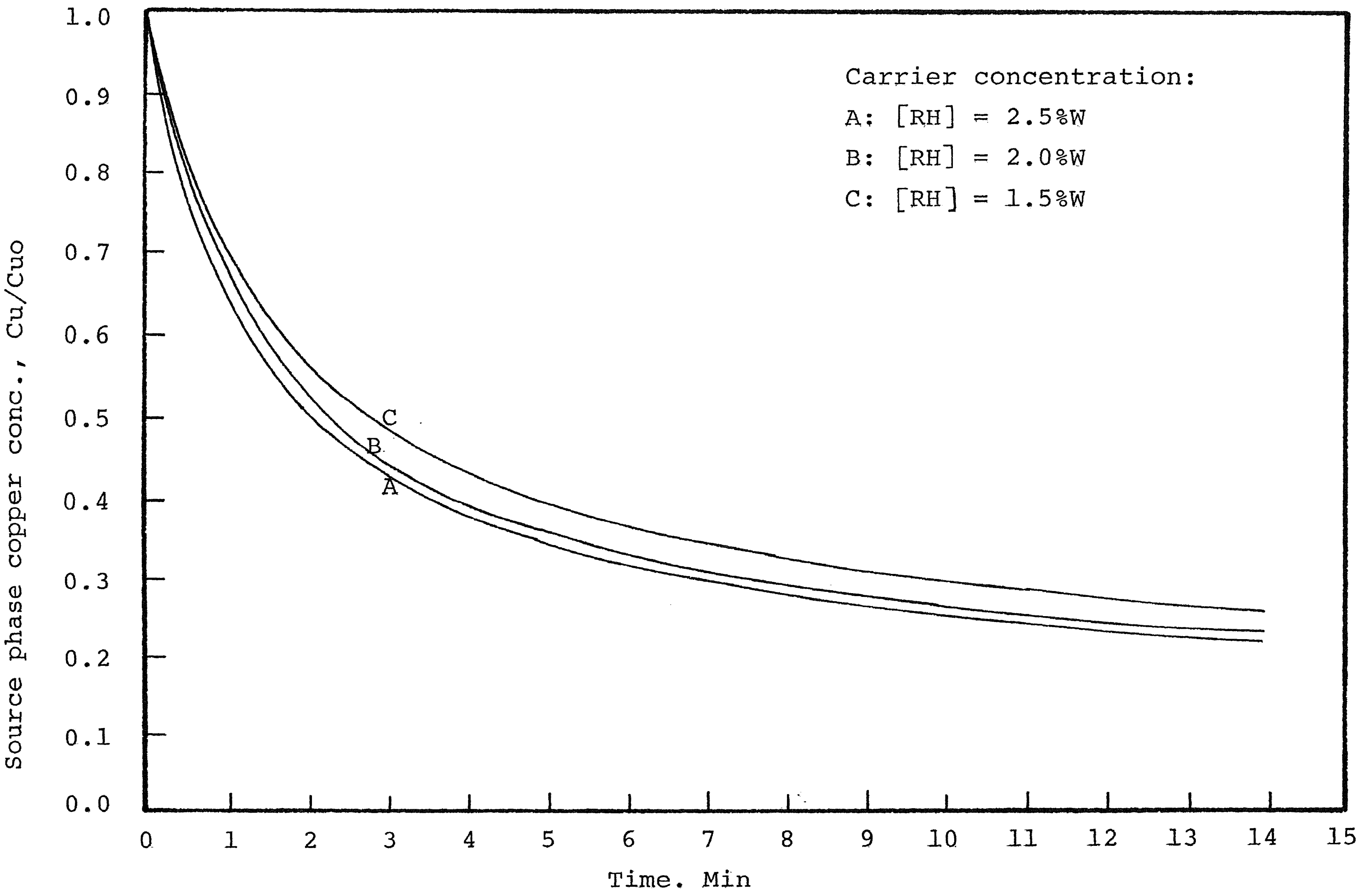


Fig. 7.4 Effect of carrier concentration on copper extraction rate

concentration, the increase of carrier concentration will increase the extraction rate. Because of the dimerization of oxime at high concentration, after certain optimum concentration, the increase of carrier concentration will have less effect on the copper extraction rate.

Effect of Receiving Phase Nitric Acid Concentration

Fig. (7.5) shows the effect of receiving phase nitric acid concentration on copper extraction rate. If the nitric acid concentration is high, then the driving force between the membrane and the receiving phase will also be high, and so the extraction rate will be increased. But since the membrane rupture problem exists, the nitric acid concentration cannot be too high. Too much acid in the external aqueous solution will reduce the effectiveness of the liquid membrane systems.

The above discussions are for the copper extraction process. But the results are similar to other metal ion extractions by the same liquid membrane system. One of the most important industrial applications of the liquid membrane systems and is currently under intensive research is the extraction of Uranium from wet process phosphoric acid. In Chapter VIII, Uranium extraction is used to show the cost advantage of dispersed liquid membrane systems to traditional processes.

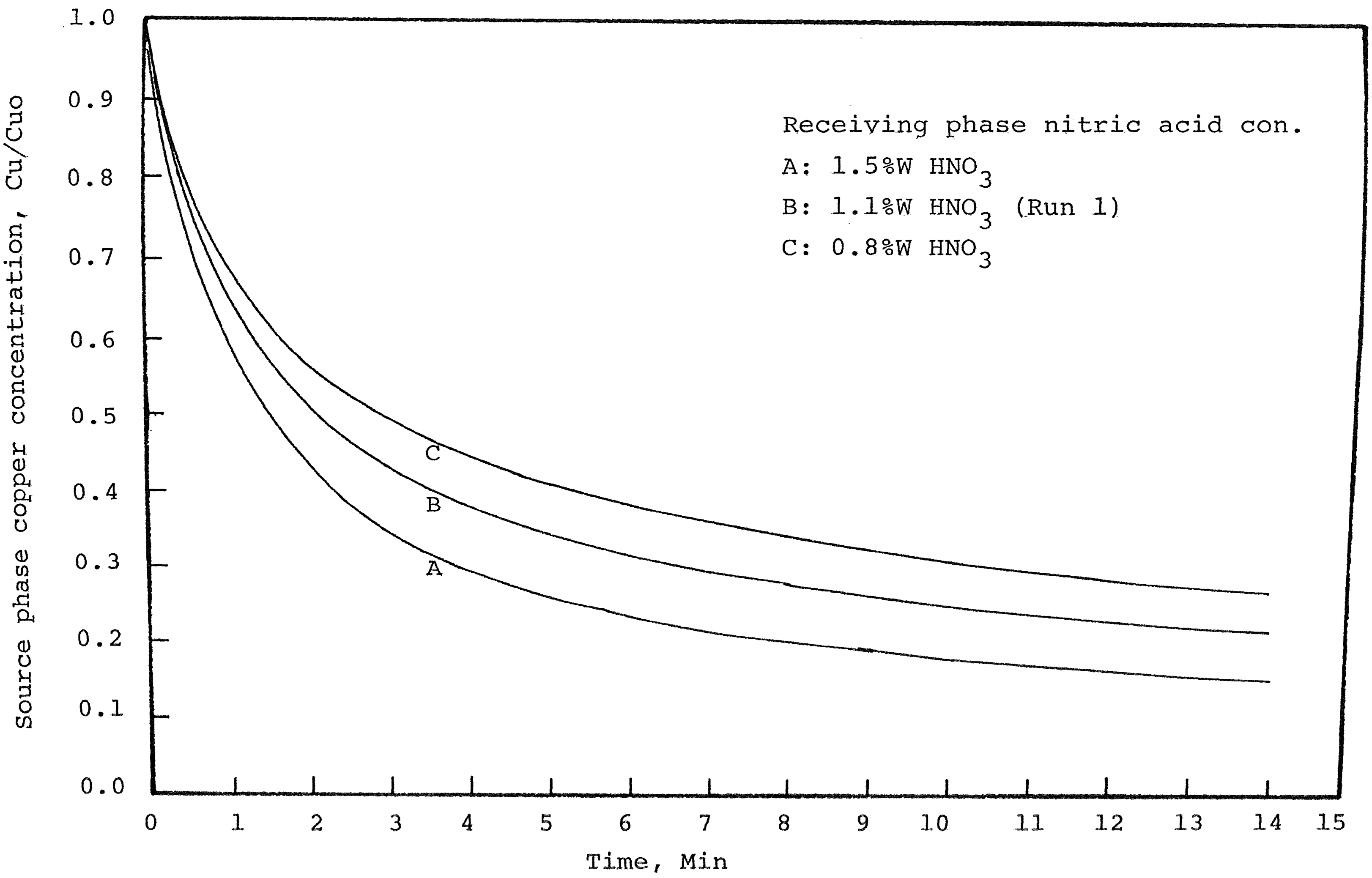


Fig. 7.5 Effect of receiving phase concentration on copper extraction rate.

B. PHENOL REMOVAL BY DISPERSED LIQUID MEMBRANE SYSTEMS.

The experimental data by Teramoto et al. (1983) are used to compare with the models developed in Chapter III. Globule diameter and partition coefficient were measured before experimental run. Diffusivities and mass transfer coefficients were estimated by the correlations in Chapter V. The experimental conditions for three cases and their parameter values are summarized in Table 7.3 and Table 7.4. The theoretical predictions and the experimental data are shown in Figs. (7.6), (7.7) and (7.8). From the predictions and experimental data, similar to the copper extraction process, we have the same comclusion that the model with both resistances considered, curves C, and the model with only external resistance, curves B, are very good in agreement with the experimental data, while the model with out film resistance shows appreciable deviation from the data. We also note that curve B and curve C in each figure, are almost indistinguishable. So, we have the same conclusion as for the copper extraction process, the external film resistance is very important, while the internal film resistance is negligible.

Effect of Surfactant Concentration

The surfactant used in the phenol removal experiments

Table 7.3

Experimental conditions for phenol removal

	Run 1	Run 2	Run 3
Vol. of membrane phase, ml	50	50	50
Vol. of receiving phase, ml	50	50	50
Vol. of source phase, ml	650	650	650
Con. of NaOH in rec. phase, M	0.1	0.3	0.3
PhOH conc. in source phase,ppm	150	500	500
Partition coefficient	1.0	1.0	1.0
Globule diameter, cm	0.152	0.152	0.082
Droplet diameter, μm	1	1	4

Table 7.4

Parameter values for phenol removal

	Run 1	Run 2	Run 3
ε	0.5	0.5	0.5
α	1.0	1.0	1.0
ϕ	0.462	0.462	0.462
D_p, cm^2/s	$1.12x10^{-5}$	$1.12x10^{-5}$	$1.12x10^{-5}$
D_{wp} (in water)	$0.998x10^{-5}$	$0.998x10^{-5}$	$0.998x10^{-5}$
g	1280	1280	1280
R, cm	0.076	0.076	0.041
d_r, cm	0.0001	0.0001	0.0001
k_o, cm/s	0.0282	0.0282	0.0280
k_i, cm/s	0.224	0.224	0.056

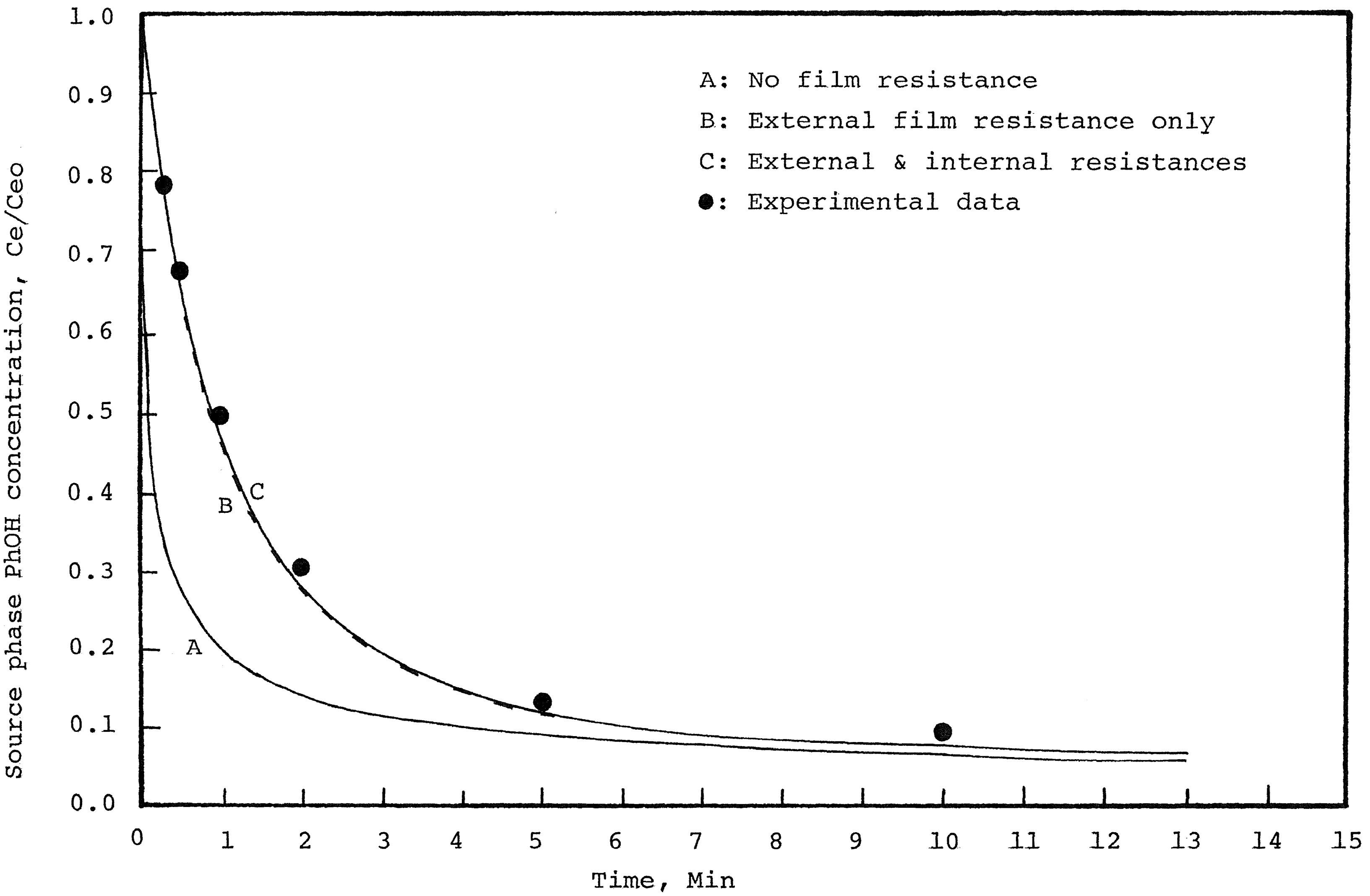


Fig. 7.6 Phenol removal - Run 1

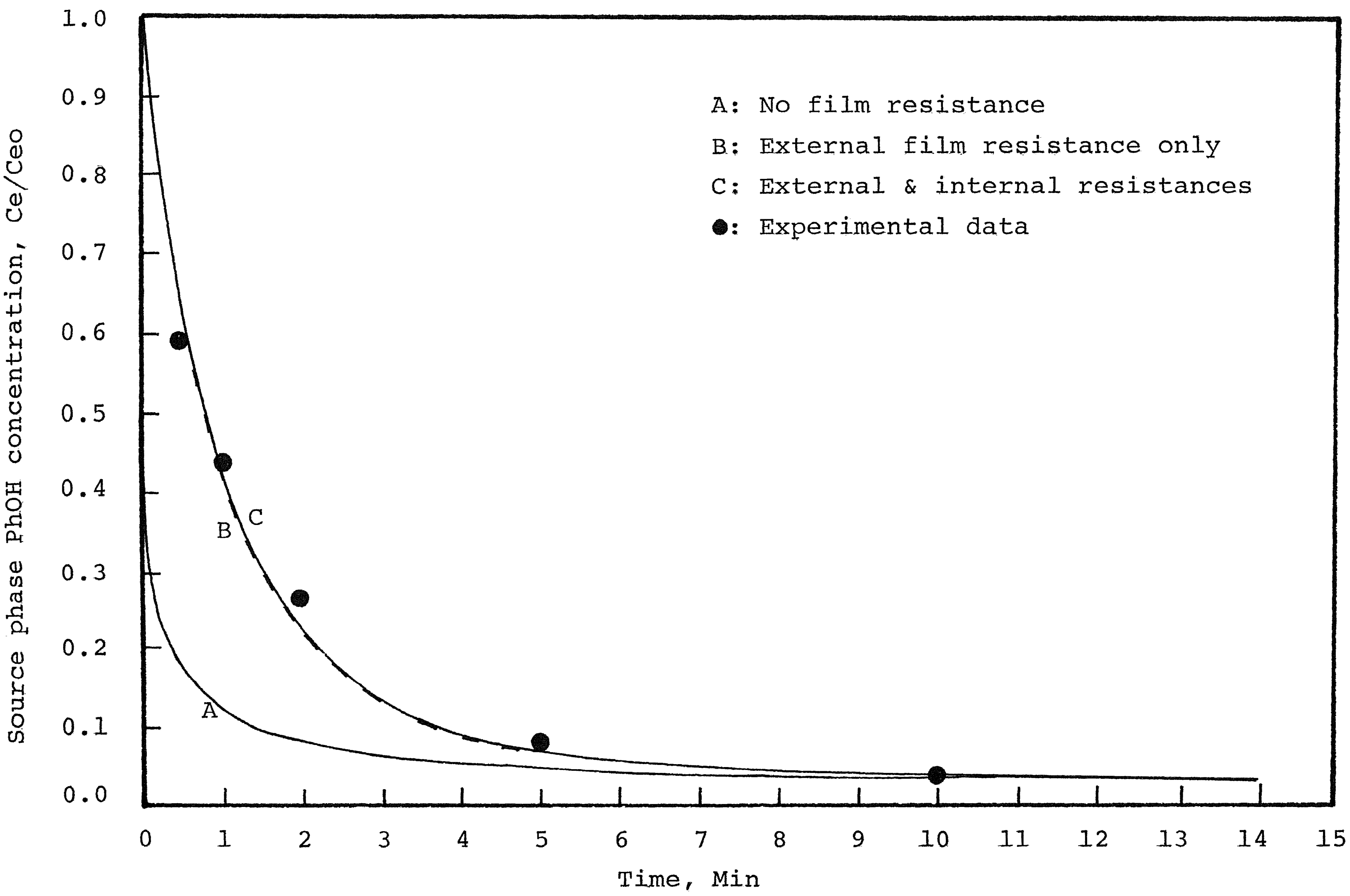


Fig. 7.7 Phenol removal - Run 2

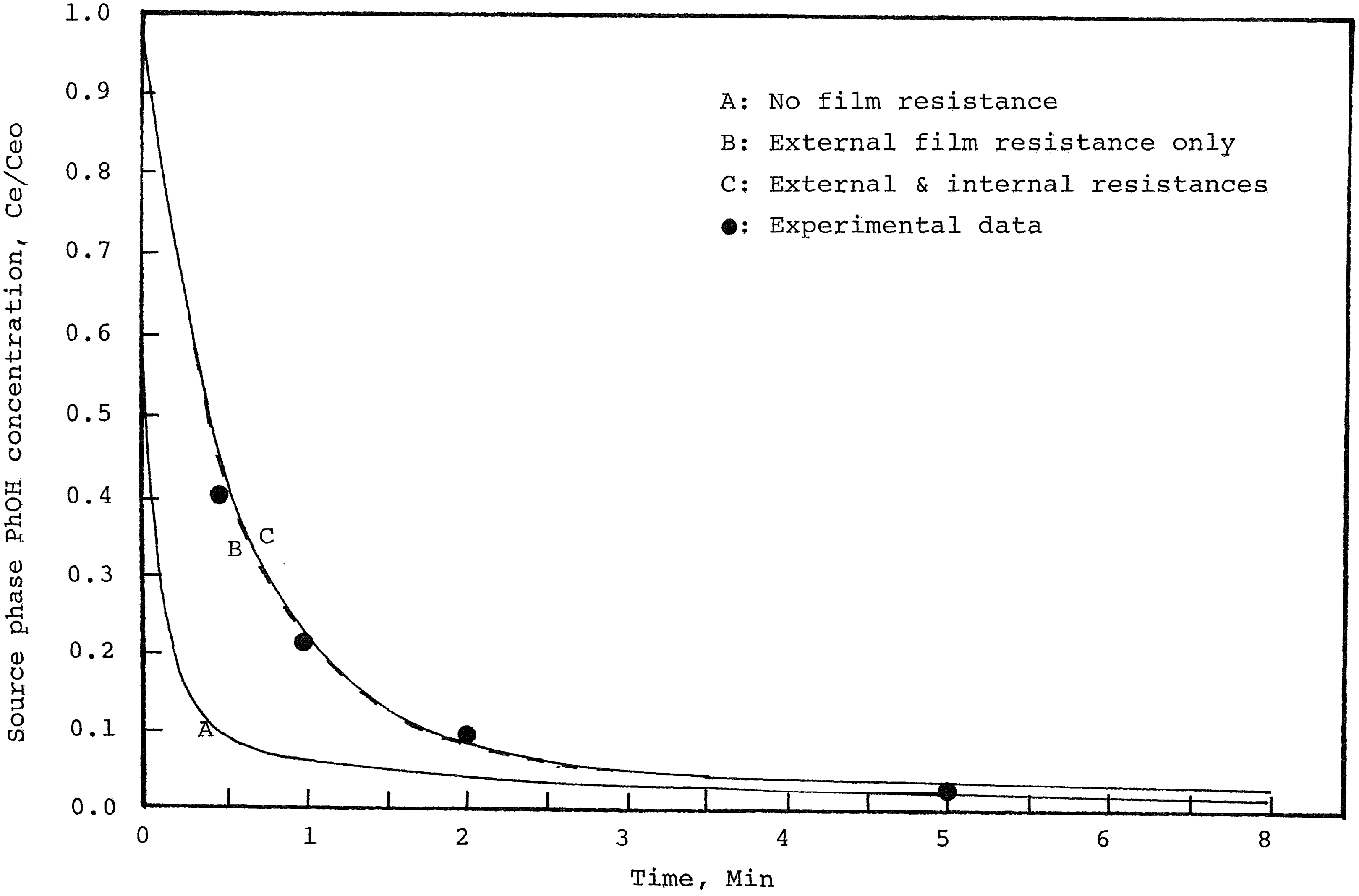


Fig. 7.8 Phenol removal - Run 3

was Span 80. The partition coefficient is a function of the concentration of Span 80 as shown in Fig. (7.9).The primary purpose of surfactants is to stabilize the emulsion. But the surfactant concentration also affect the extraction rate. Fig. (7.10) shows the effect of Span 80 concentration on the phenol removal rate. As shown in the figure, higher surfactant concentration results in higher phenol extraction rate. But too much surfactant is not desirable, since it will cause some difficulty in breaking emulsion phase in a subsequent process.

Effect of receiving phase NaOH concentration

Fig. (7.11) shows the effect of NaOH concentration on the phenol removal rate. The effect of NaOH concentration on the phenol removal rate is similar to the nitric acid conc. on the copper extraction rate. But again, because the leakage problem, the receiving phase NaOH concentration can not be too high.

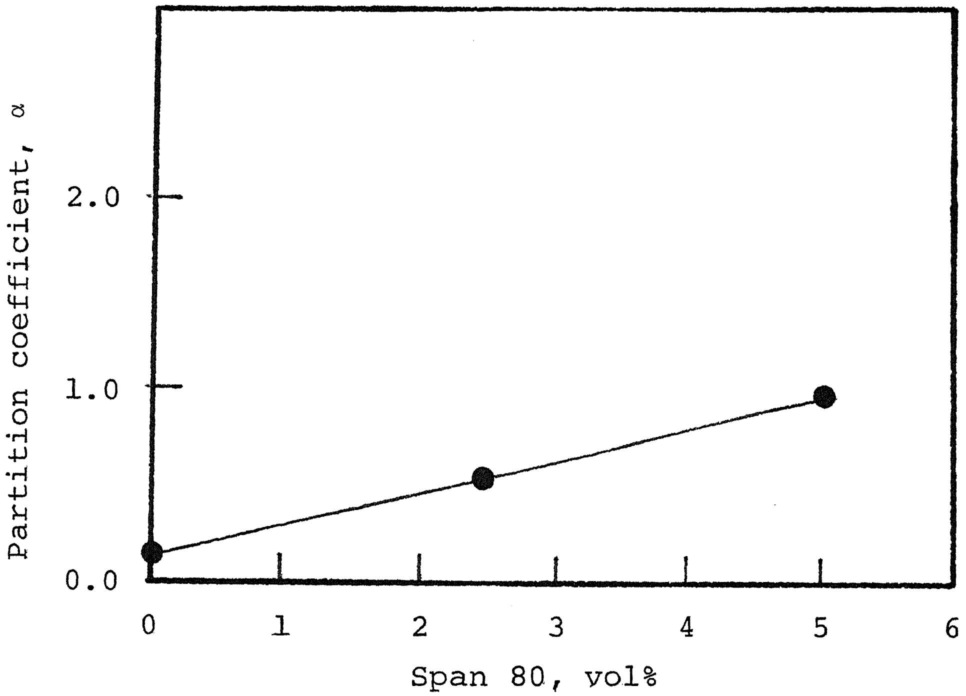


Fig. 7.9 Effect of the concentration of Span 80 on the partition coefficient of phenol

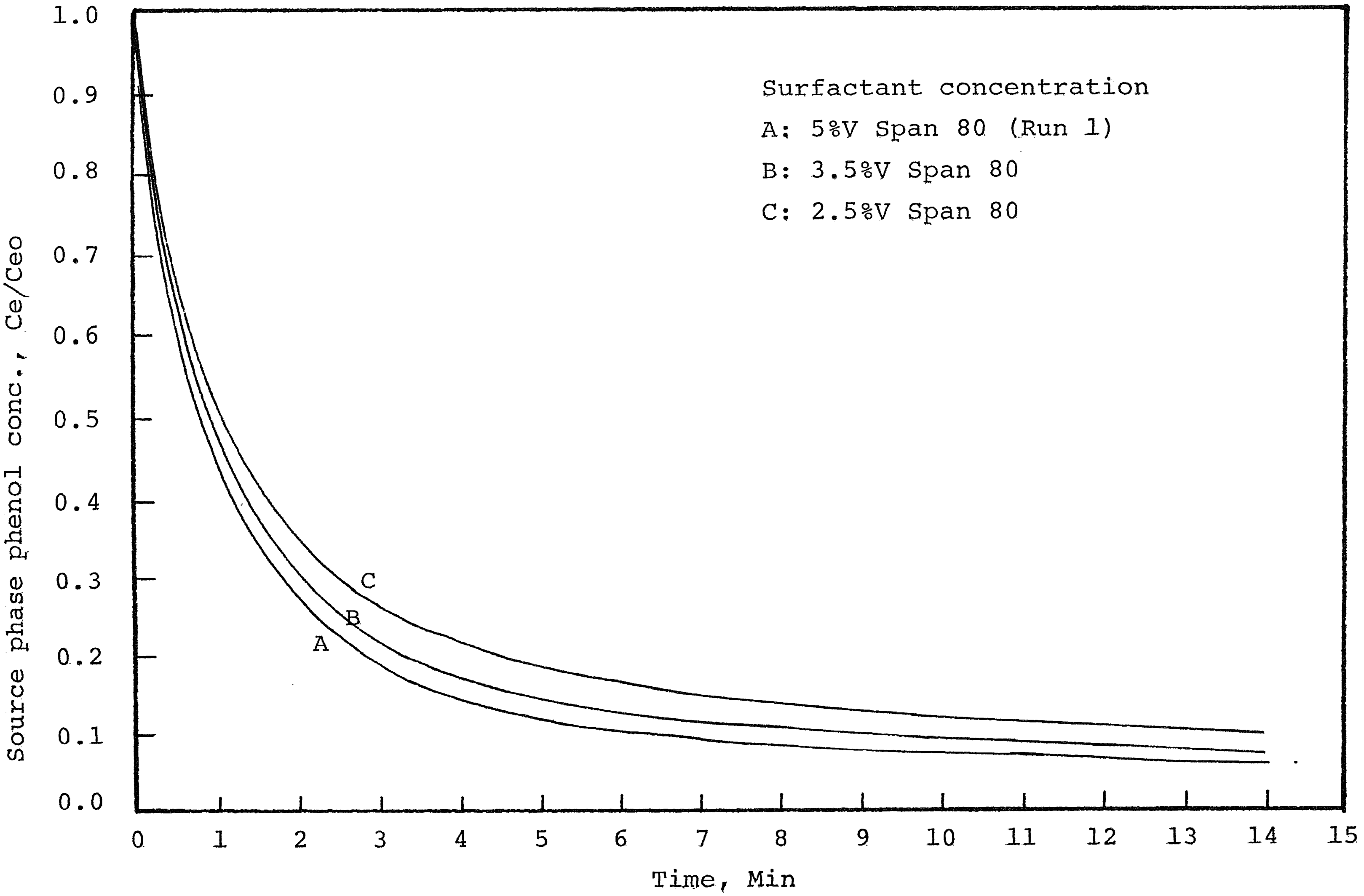


Fig. 7.10 The effect of surfactant concentration on phenol removal rate.

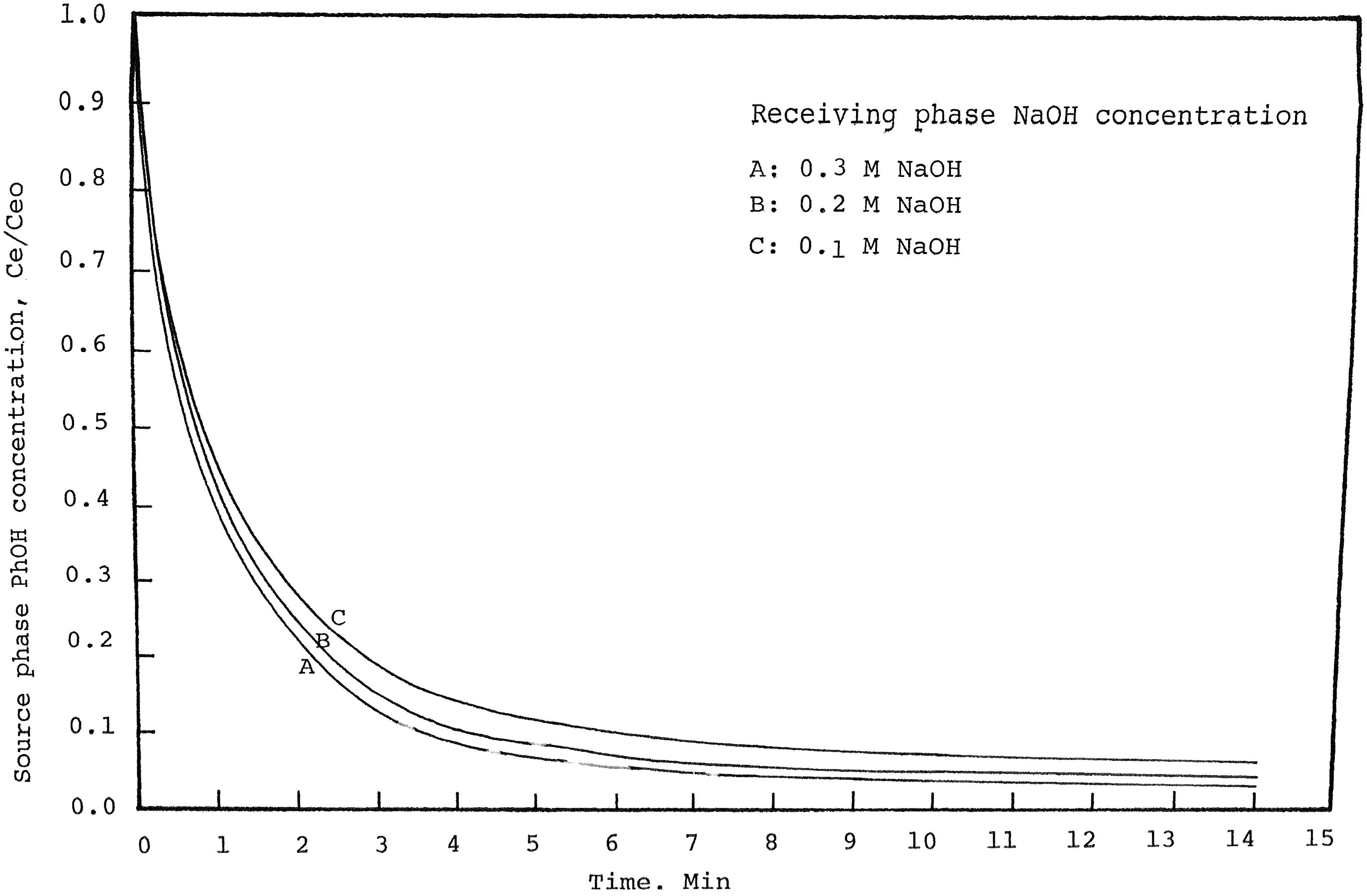


Fig. 7.11 The effect of receiving phase NaOH concentration on phenol removal rate.

C. SOLVENT EXTRACTION.

The models developed in Chapter IV involve two hydrocarbons, A and B, diffusing fron the internal phase to the external phase, and a solvent C diffusing from the external phase to the internal phase. The calculation procedures are shown in Chapter IV. The experimental conditions and physical properties are shown in Table 7.5 and Table 7.6. Following the calculation procedured, the theoretical predictions are shown in Figs. 7.12 and 7.13. Experimental data by Kremesec and Slattery are used to compare the predictions and are plotted in Figs. 7.12 and 7.13.

Fig. 7.12 shows the predictions and data for the mass fractions of hydrocarbons A and B as a function of time. The curves indicated by $\Delta t=0.125$ are for the case when the parameters were adjusted for every 0.125 hour. We see from the figure, when parameters were adjusted for every o.125 hour, the predicted mass fraction of toluene in the extract phase is very close to the experimental data, while the predicted mass fraction of n-heptane shows some deviation from data. For the curves indicated by $\Delta t=0.25$ shows some different results. These may be resulted from experimental errors as indicated by Kremesec & Slattery in their paper. The mass fraction of n-heptane in the extract phase is so

Table 7.5

Initial component masses in solvent extraction

Internal raffinate phase	
toluene, g	42.73
n-heptane, g	33.53
Membrane phase	
water, g	60.01
glycerol, g	143.6
External extract phase	
o-xylene, g	436.0

Table 7.6

Physical properties for solvent extraction

Distribution Coef.			
membrane/internal	5.12×10^{-4}	3.68×10^{-5}	2.22×10^{-4}
membrane/external	4.67×10^{-4}	5.82×10^{-5}	2.22×10^{-4}
Diffusion coef. in membrane phase, cm^2/s	5.24×10^{-7}	4.35×10^{-7}	4.7×10^{-7}

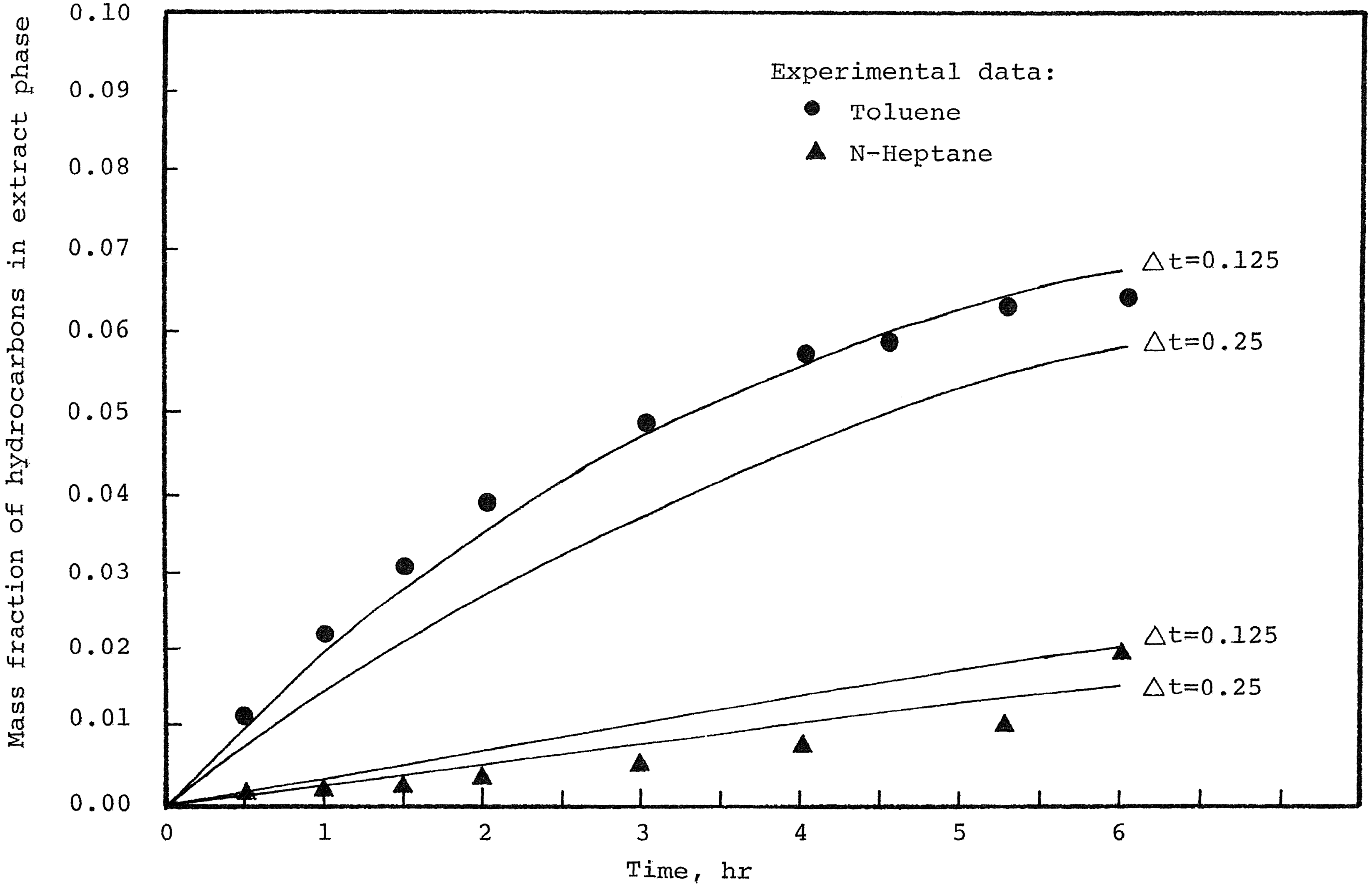


Fig. 7.12 Solvent extraction - hydrocarbons.

small that some experimental errors will cause a large change in percentage.

Fig. 7.13 shows the predicted result of o-xylene mass fraction in the extract phase. The agreement for the curve indicated by =0.125 with data is reasnoable good. Fig. 7.14 shows the separation factor as a function of time. The factor rise sharply for the initial period and then increase slowly. Theoretically, if the extraction time is long enough, the separation factor will decrease after a maximum separation factor value. Since the solvent extraction rate is very slow and the stability problem of the emulsion phase, the maximum point can not be reached in this case.

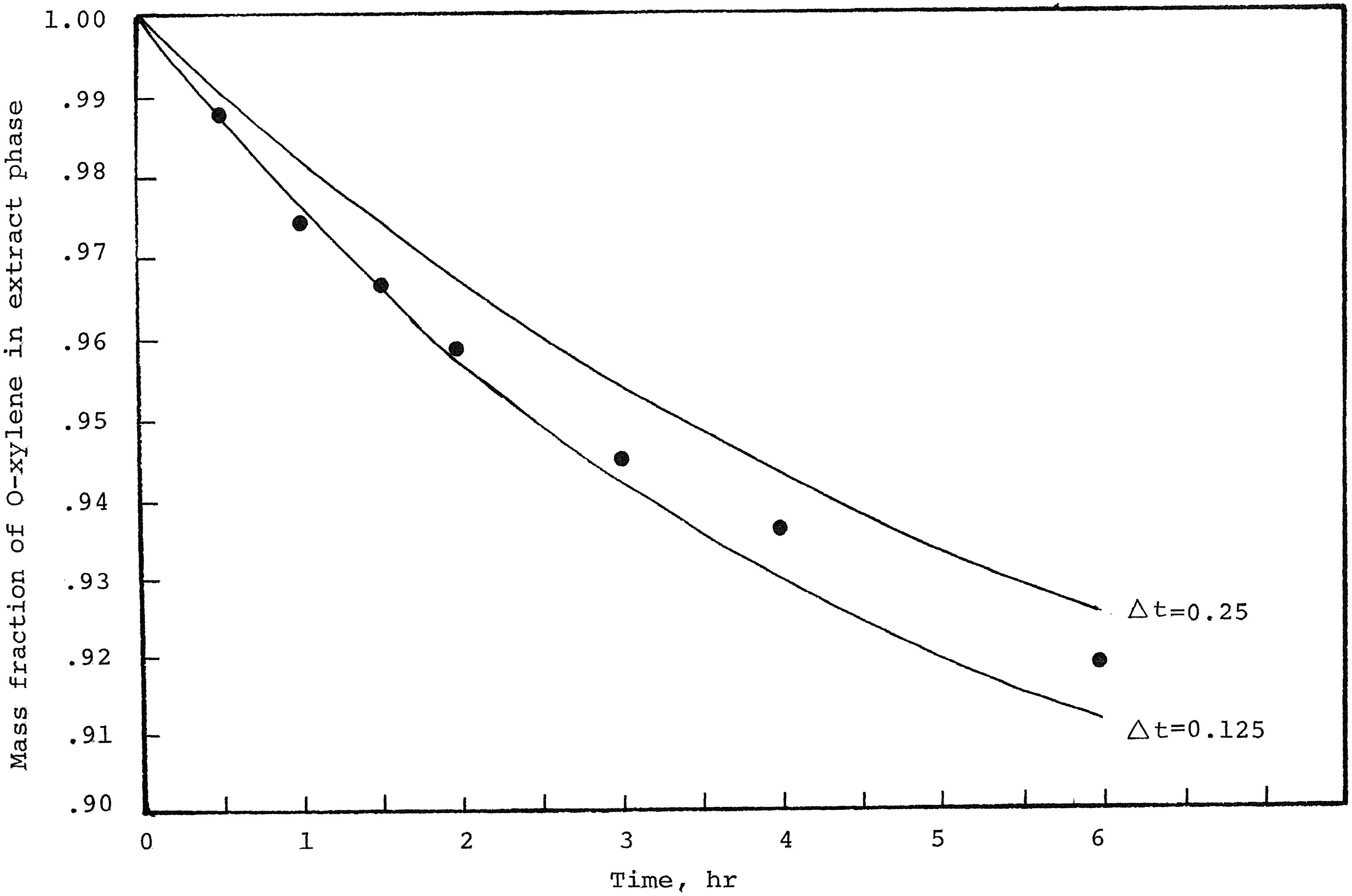


Fig. 7.13 Solvent extraction - solvent.

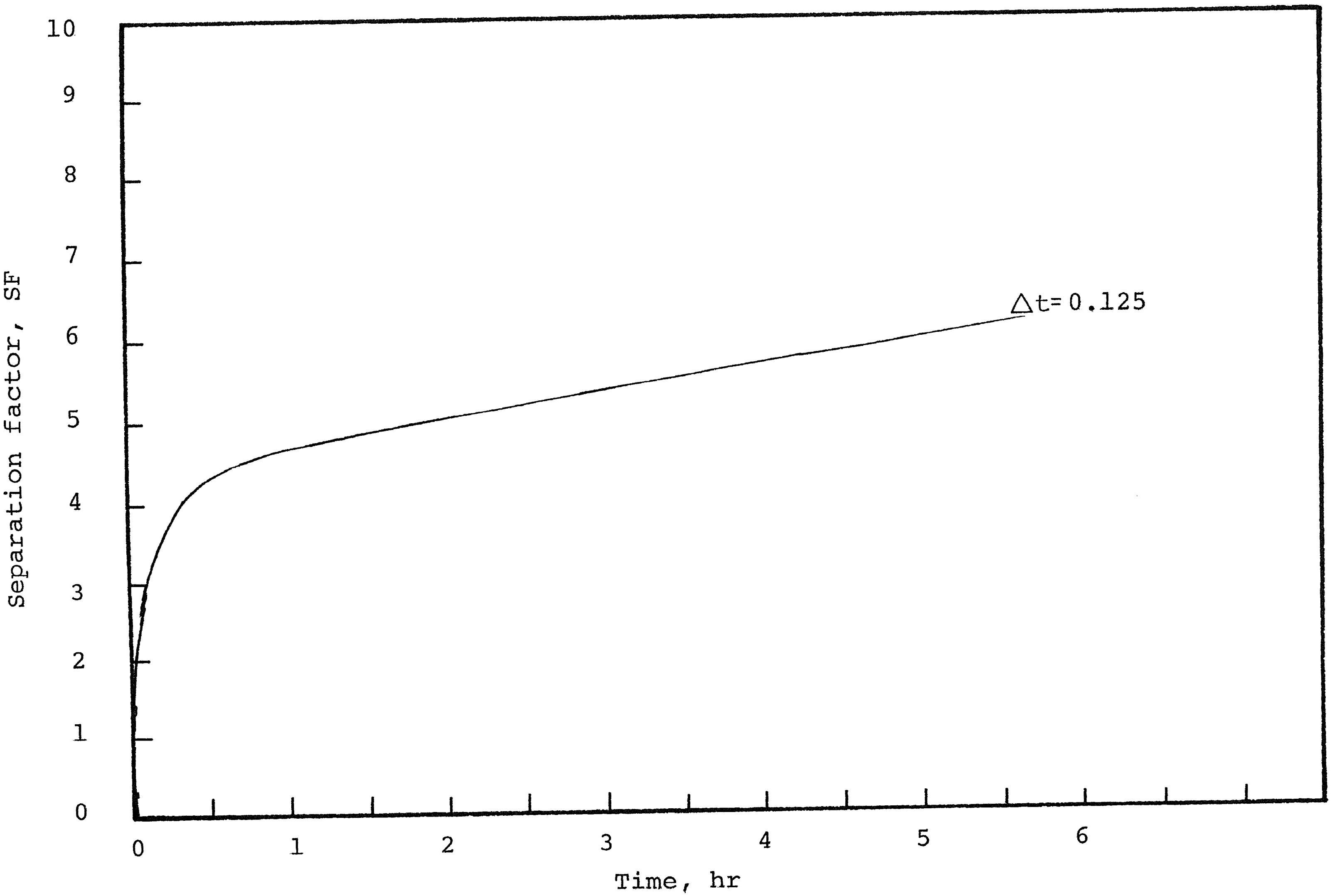


Fig. 7.14 Separation factor

CHAPTER VIII

INDUSTRIAL APPLICATIONS

As mentioned before that the field of liquid membrane technology is currently undergoing a rapid expansion of both research and industrial applications. Dispersed liquid membrane systems have demonstrated considerable potential as effective tools for an increasingly wide variety of separation. Typical applications for each type of liquid membrane systems are summarized below.

(1) Carrier mediated mass transfer through liquid membranes.

Typical applications are the recovery of heavy metal ions from a dilute solution of the removal of heavy metals from waste water streams. Metals such as copper, uranium, lead and chromium etc. all can be treated by this type of liquid membrane system.

(2) Mass transfer through liquid membranes with reaction in the receiving phase.

Typical applications are the removal of contaimnates of weak acids or weak bases from waste water. Acidic materials that can be removed by "caustic" liquid membrane systems are phenol, H_2S, HCN, acetic acid and other organic acid. Basic contaimnates that can be removed by "acidic" liquid membrane systems are NH_3, and amines etc.

(3) Solvent extraction by liquid membrane systems.

The membrane systems of this type are in O/W/O form. The O/W/O liquid membrane systems can be applied to solvent extraction process, specially for isomeric mixtures, azeotropes, thermally unstable compounds of mixtures of components having similar constitution and identical boiling points. Those mixtures are not quite easy separated by traditional methods.

Fig. (8.1) shows a typical process block flow diagram for a dispersed liquid membrane system. Most equipment required for the liquid membrane systems are very common in chemical process industries. For the particular processes and special equipment related to the liquid membrane systems are described below.

Emulsification

The choice of emulsifiers for a particular formulation will sometimes also be dictated by the method one intends to use in making the emulsion. Most of the mechanical devices depend, for their effectiveness, on forcing a mixture of the two phases through small apertures to produce high-shear

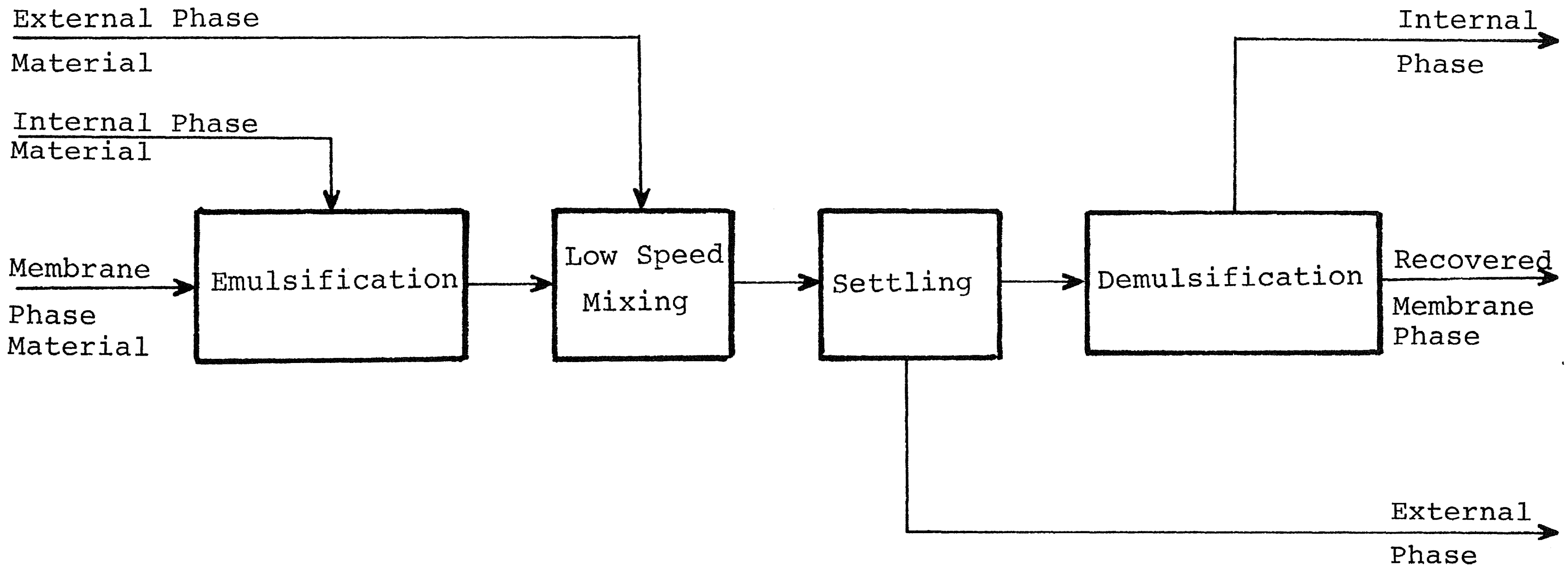


Fig. 8.1 Process block diagram for a dispersed liquid membrane system.

situations. This can be done by pumping the mixtures through small holes in orifice plates where a high pressure drop occurs or by forcing them between a tightly fitting rotor and stator. There are two types of commercial equipment,

(1) Ultrasonic equipment

In this type of devices the high shear is produced by passing the mixture of phases through an area where an ultrasonic field is developed. The acoustical energy may be generated either by a piezoelectric device or by a mechanical "whistle." In either event the effect is to produce rapid local variations in the pressure supplied to the system, and as a result cavitation occurs. In this situation a very high local shear is produced as well as a fairly energetic shock wave. Also in some instances this method employs the principal of the introducing a vapor of one phase into the other liquid.

(2) The colloid mill.

When one gets into the area of dedium or high internal phase ratio emulsions, where the viscosity of the formulation is much higher,it is increasingly difficult to achieve high shear levels, and in these situations the colloid mill is one of the most commonly used commercial devices. In a mill of this kind arotor, often conically shaped and with grooves or other irregularities machined into its surface, rotates at high speed in a concial cavity that fits very closely. Clearance between the rotor and stator usually can be adjusted and is on the order of a few thousandths of an inch. Since such devices are driven by high horspower engines and generate considerable , heat they must be so designed that this heat can be dissipated (Kenneth Lissant, 1974).

Demulsification

Demulsification is the complete break up of an emulsion into its component parts. This is the passage from the metastable condition to the thermodynamically stable state of separate bulk phases. It is found in many systems that two stages may be distinguished in the break up. In the first stage, called flocculation, the droplets of the dispersed phase form clusters or aggregates in which the droplets have not entirely lost their identity. These clusters are easily redispersed by slight agitation. In the second stage, called coalescence, the droplets in a cluster units together into a single large drop.

Practical techniques for demulsification.

(1) Chemical methods.

Chemical methods are probably the most widely used technique for breaking up emulsions. They operate on the principle of removing the barriers that hinder coalescence. The demulsifiers counteract the influence of the protective films that surround the dispersed drops and the double layer forces in several ways. Agents such as polyvalent salts and acids neutralize the electrical fields of the double layer. It is true obvious that for each given emulsion there is a specific demulsifier which will produce optimum results, and this choice must be made after careful study the properties of the emulsion.

(2) Gravity settling tank.

Emulsion phase can be separated from external phase by gravity settling. A simple form of a settling tank for continuous operation is shown in Fig. (8.2). It is obvious that the liquids should not mixed by the fluid flows, especially after pahse separation has taken place. In Fig. (8.2) this is ensured by the baffles near the inlet and hy controlling the flow rates. Typically, the residence time in such equipment is of the order of one hour.

(3) Centrifugal separator.

For the separation of the internal phase from an

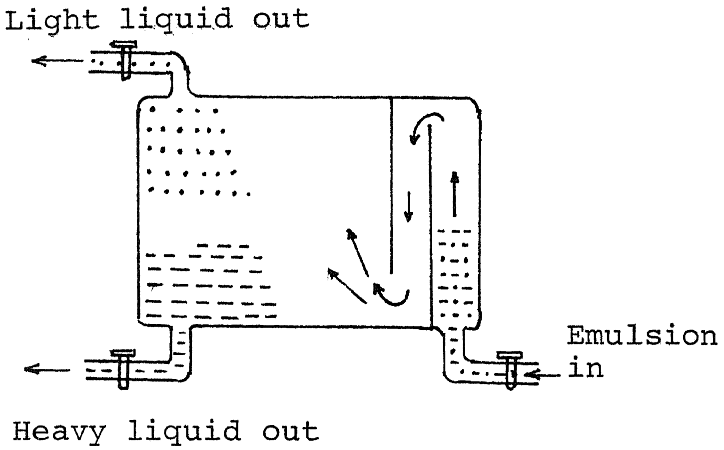


Fig. 8.2 Gravity separator

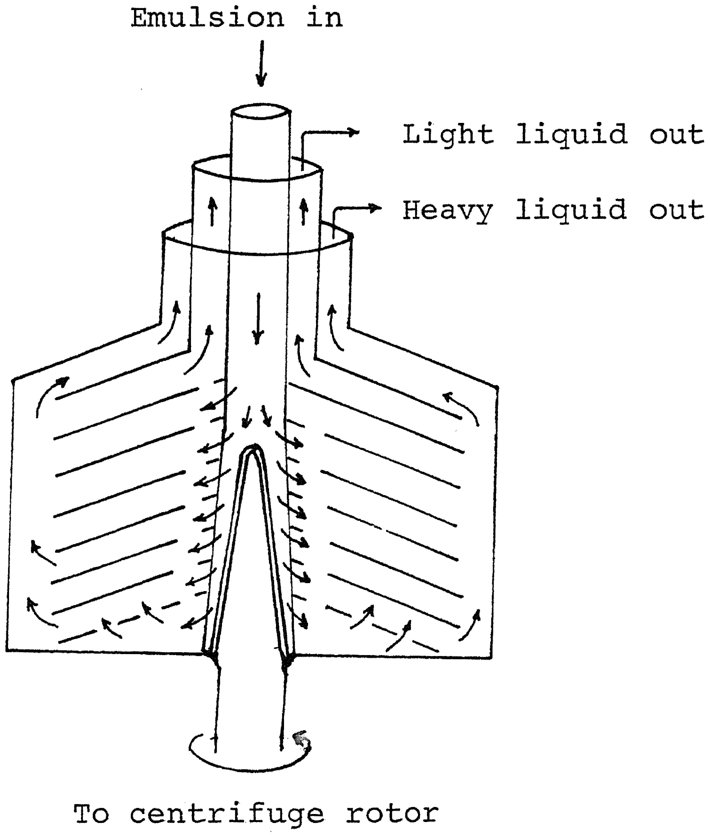


Fig. 8.3 Centrifugal separator

emulsion phase, a centrifugal separator can be used. Fig. 8.3 shows a typical centrifugal separator . Conical discs are placed inside the centrifue. The acceleration is supplied on a film of emulsion forced between the discs and this results in improved separation. Holding times are usually of the order of afer minutes. The heavy liquid is pushed out to the rims of the centrifuge and is withdrawn. The light liquid collects near the central inlet passage and is drawn out at the top.

(4) Electrical methods.

Electrical methods of inducing coalescence are based on one of the two mechanisms, the forces exerted on particles having net charges, and the forces between neutral particles resulting from their acquiring induced dipoles on an a.c. or d.c. field. In emulsions when the particles are uncharged, dipolar coalescence is the operative mechanism. The electric field and the fluid velocity gradient must be reduced when the liquid drops have a large diameter. In the typical arrangement shown in Fig. (8.4), this is achieved by applying the voltage to the lower of the two electrodes and injecting the emulsion in between the electrodes and the continuous body of water at the bottom (impure water is a relatively good conductor of electricity) is small and this the region where large water drops are present. The liquid

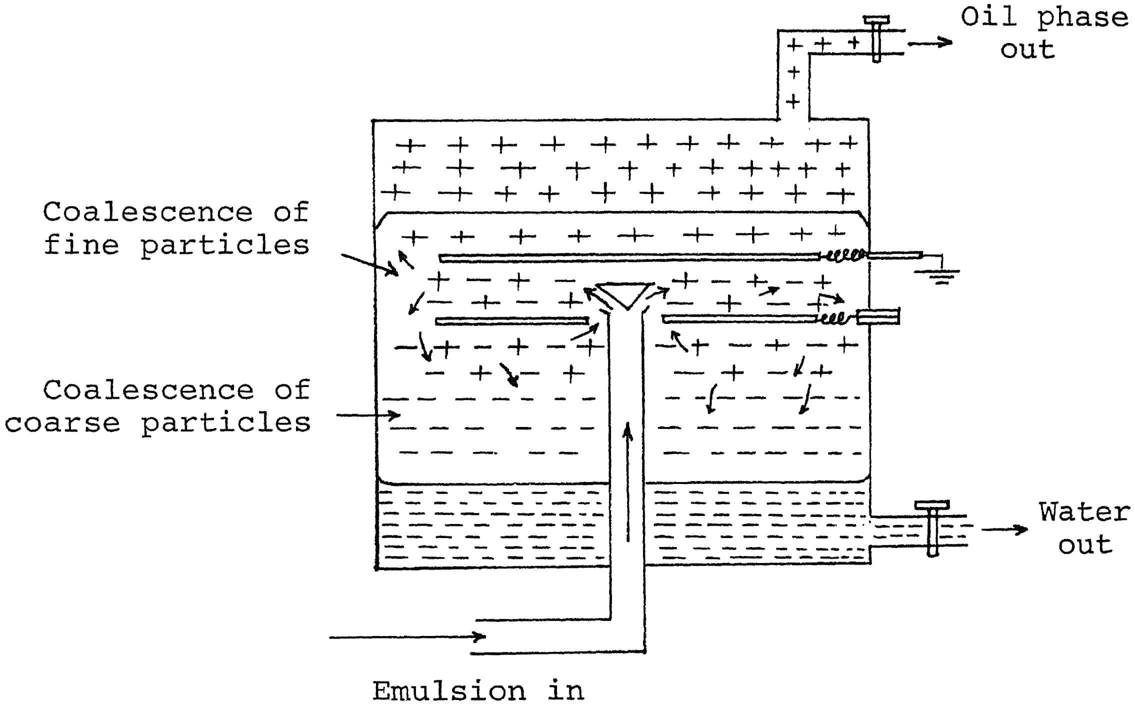


Fig. 8.4 Electric demulsification diagram

flow pattern is such that any part of the emulsion, in which the particles have not attained a large diameter, is recycled into the the region between the electrodes, where coalescence proceeds rapidly.

(5) Heat treatment.

Heat treatment of the emulsion is also a very common technique. Indeed many emulsion may be separated by simply heating them to high temperature and then allowing them to settle. Probably this accelerates any chemical reaction that may be going on, changes the nature of the interfacial film and reduces the viscosity so that conditions favorable to demulsification are produced.

Having all the process and equipment information, now we can propose a workable process flow diagram for the phenol removal by a dispersed liquid membrane system. Fig. (8.5) shows such a flow diagram. The process can be either a continuous process or a batch process. The flow diagram showed in Fig. (8.5) is for a continuous process. The models developed in Chapter III can be used directly for the design of a low speed mixer of a batch process. The design method is similar to the design of a batch reactor. For a continuous process, the models in Chapter III can easily be modified to design the low speed mixer of a continuous process. In practical

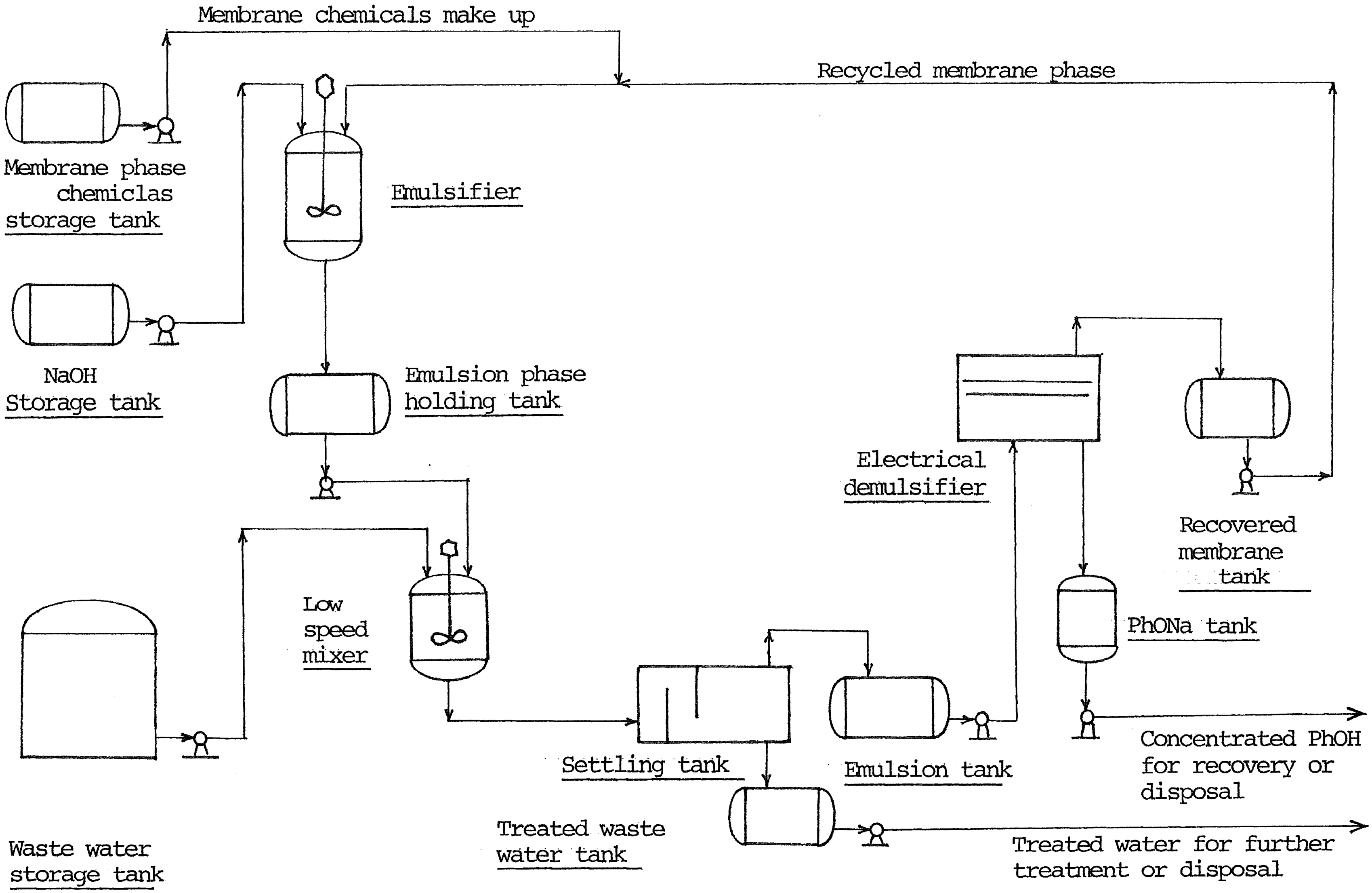


Fig. 8.5 A proposed process flow diagram for phenol removal by a dispersed liquid membrane system.

applications, the low speed mixing unit could be one reactor or several reactors in series or in parallel connection. Fig. (8.6) and Fig. (8.7) show some possible configurations of the low speed mixing unit.

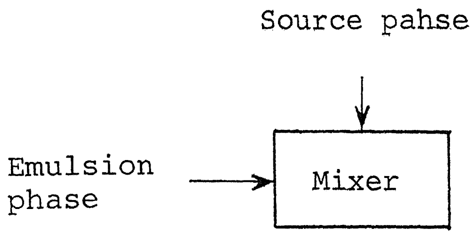
Cost comparison of uranium recovery by a dispersed liquid membrane and a traditional method.

Liquid membrane systems have the following possible advantages over some traditional methods:

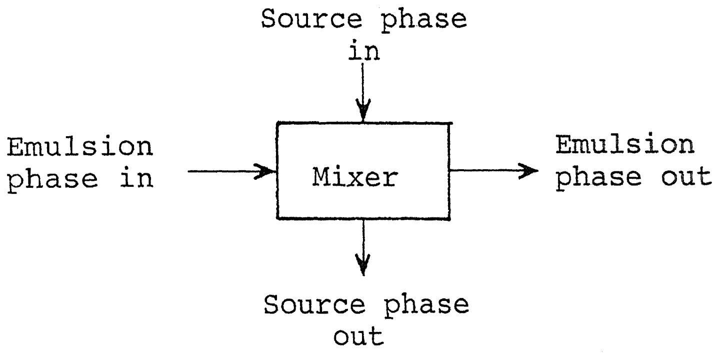
(1) save energy.
(2) reduce cost.
(3) reduce solvent consumption.
(4) produce very high concentrated solution from dilute solution.

In this section, we provide the economic comparition of uranium recovery by a liquid membrane system and the method current in practice. The information and data for the comparition come from the paper by Hayworth et al. (1983).

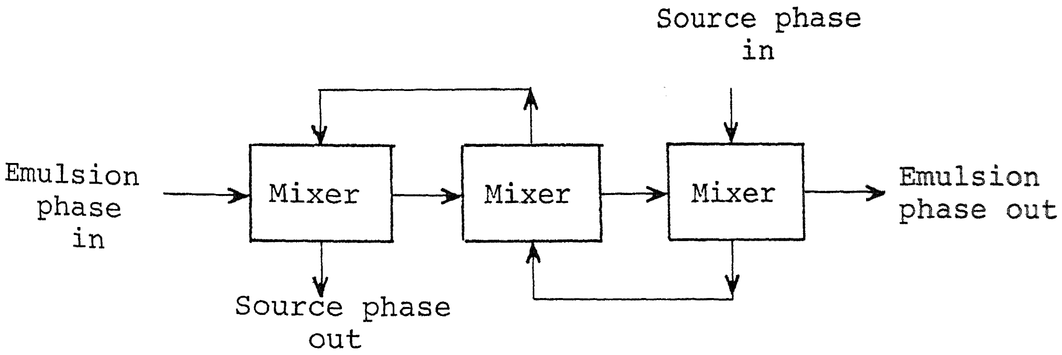
For both solvent extraction (SX) and liquid membrane (LM) technology the uranium in phosphate rock has to be solubilized before extraction can take place. In the manufacture of wet process phosphoric acids (WPPA). both the P and U values in phosphate rock are solubilized. In the



(a) Batch process

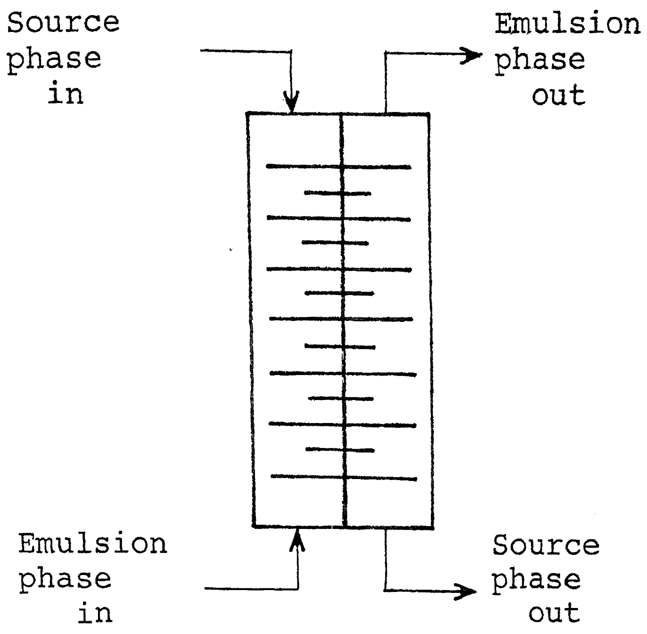


(b) Continuous flow

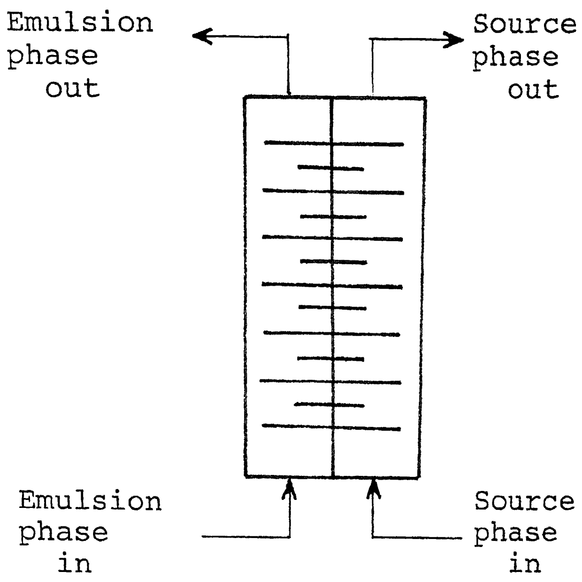


(c) Multiple stage process

Fig. 8.6 Possible configurations for low speed mixer -staged process.



(a) Countercurrent flow



(b) Cocurrent flow

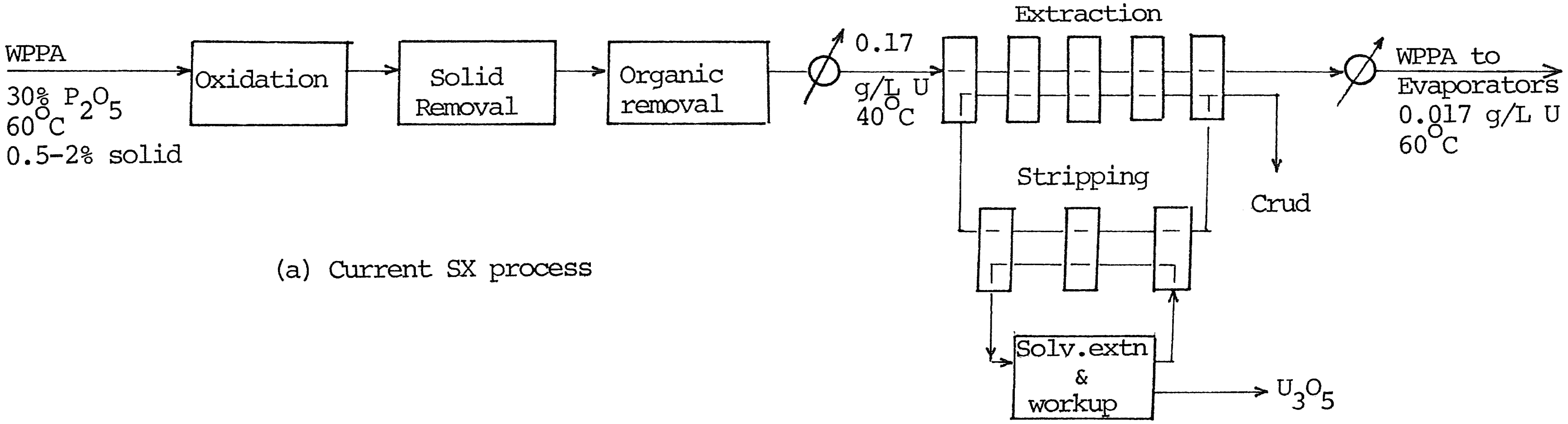
Fig. 8.7 Possible configurations for low speed mixer-continuous contact process.

WPPA process, phosphate rock is contacted in an attack tank with sulfuric acid to produce gypsum and phosphoric acid. The aic so produced from thedihydrate process is normally about 30% P_2O_5, containing about 0.14 to 0.18 g/L of uranium, depending on the uranium content in the rock. 0.17g/L corresponds to about a 1 lb U_3O_8 per ton of P_2O_5 and is representative of most of the currently mined Florida rock. In most phosphoric acid plants, this 30% acid is further concentrated to produce higher strength acid. Because of viscosity and equilibrium considerations, all of the uranium extraction plants currently in operation in the United states operate on the 30% acid stream. Basically, the 30% acid stream is diverted to the uranium extraction plant from its normal source. This would also apply for LM. The raffinate from theuranium extraction plant, appropriately treated to keep any organic carryover from the extraction operation to a minimum, is returned to the acid plant for further concentration via evaporation. The extraction chemistry for the LM technology is essentially the same as that employed in SX. SX.

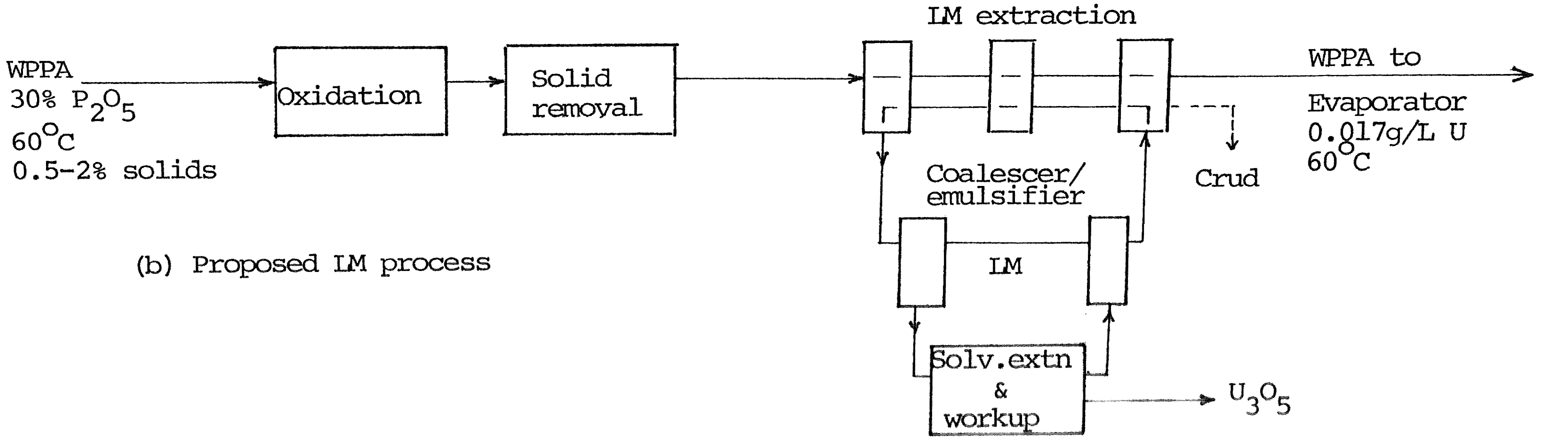
Uranyl ion in the feed or WPPA phase is complexed by complexingagents, di-2-ethylhexyl phosphoric acid (DEHPA), and trioctyl phosphine oxide (TOPO), predissolved in the membrane. The resultant comples is transported across the membrane to the internal phase. Since DEHPA-TOPO does not effectively comples the U(IV) ion, a reductant is used in the internal phase to strip the uranyl complex from the membrane and from the acid soluble U(IV) species, which is efficiently trapped and concentrated in the internal phase.

The main differences between liquid membranes and solvent extraction are shown in Fig. (8.8) and Table 8.1. In pretreatment, LM requires no soluble organic removal or cooling, while SX may require some of these steps. I extraction, we have a maximum of three LM stages versus eight SX satges for extraction and stripping. LM, however, requires a separate coalescer and emulsifier-offsetting to some extent the capital cost savings associated with the elimination of the stripping stages. The secondary solvent step is identical for both processes.

In addition to the equipment related advantages, there are additional advantages to using the LM technology. They lie primarily in the amount of crud that is formed and organic losses associated with extraction in the LM organic phase is 1/5th the concentration normally employed in SX, the amount of crud formed is only 1/4th to 1/5th that normally experienced in SX with equivalent feed pretreatment. Finally because simultaneous extraction and stripping takes place in LM, the organic phase never is the bulk carrier of the uranium. Therefore, the organic circulation rate can be reduced to as low as a feed-to-organic ratio of 18:1 compared to the 1:1



(a) Current SX process



(b) Proposed LM process

Fig. 8.8 Comparison of the LM and SX process for uranium recovery from WPPA.

Table 8.1

Differences between LM and solvent extraction

	LM	SX
Feed pretreatment	Oxidation Solids removal	Oxidation Solid removal Cooling Soluble organics Removal
Extraction/stripping	Max. 3 stages Coalescer Emulsifier	Eight stages
Secondary extraction	Identical for both	
DEHPA/TOPO conc.	1/5	1
Crud make	1/4-1/5	1
Feed/organic ratio	18:1	1:1

normally found in SX plants. Because pf these characteristics of LM, hydrocarbon circulation losses are cut by at least a factor of 10 and chemical make-up cost costs are considerable low. Not only is less organic lost in the crud, but the cost of the organic phase is materially less than that employed in solvent extraction because of lower DEHPA/TOPO concentration.

The design basis for the uranium extraction and recovery is shown on Table 8.2. For LM, the extraction section would contain three counter current stages; for the two SX cases, four countercurrent stages would be required. With respect to the stripping operation, LM would not require this step, while the two SX cases would have four stages.

Table 8.3 shows the capital cost estimates. The capital cost estimate was based on grass roots facilities capable of extracting uranium from a 400,000 ton per year P_2O_5 plant in central Florida location, constructed in the second quarter of 1979. The uranium production capability was estimated at 350,000 lb/yr, allowing for a 5% phase dislocation between operations of the uranium extraction plant and the phosphoric acid plant. All capital costs have an allowance for a 25% project contingency over and above the estimated installed equipment cost, and in the case of LM an additional process allowance of $2.7MM has been added to compensate for some of

Table 8.2

Cost estimate design basis:
Uranium extraction recovery

		SX	
	LM	Minimum Pretreatment	Extensive Pretreatment
Extraction mode		Countercurrent	
Extraction stages	3	4	4
Stripping stages	-	4	4
Emulsifier/coalescer	1/1	-	-
Crud treatment	Mechanical	Mechanical/ Chemical	-
Uranium recovery		Solvent extn.	
Raffinate treatment		Flotation cells	

Table 8.3

Capital cost estimates (Basis: 400,000 tons/yr P_2O_5 acid capacity, central Florida location,2nd Qtr 1979)

		SX ($MM)	
	LM ($MM)	Minimum Pretreatment	Extensive Pretreatment
On-site	14.0	15.4	19.6
Off-site	5.8	6.3	6.6
	19.8	21.7	26.0
Proj contingency	4.8	5.4	6.5
Process allowance	2.7	-	-
	27.3	27.1	32.5
Solvent inventort	o.1	0.9	0.9
Total investment	27.4	28.0	33.4

the remaining uncertainties in the process design. LM facilities are estimated to cost $27.4MM, including the associated off-sites and solvent inventory as company to $28 and $33.4MM for the two SX cases. It should be pointed out that these estimates are based on detailed equipment estimates. Further development activity on LM will probably permit the elimination of feed filtration and one extraction stage, thereby reducing the estimated cost by $4.+MM, to a possible $23MM.

Table 8.4 shows the operating costs for the extraction facilities expressed in dollars per pound of uranium recovered. One of the major differences between the LM and SX costs are associated with organic make-up. A circulation loss of 1/10 of 1% of the organic circulation is assumed which amounts to 10¢/lb of uranium for the liquid membrane case as compared to $3.90/lb for solvent extraction. The very low cost of LM is due to the fact that, compared to SX, only 1/18th the volume of organic is circulating in the LM process and that the cost of the organic membrane is only about 1/4 the unit cost of the solvent extraction hydrocarbon phase. This also accounts for the lower ocst of the raffinate losses for LM.

The LM technology appears to have sufficient return on capital at today's uranium prices to warrant extraction from phosphoric acid plants.

Table 8.4

Operating Cost Estimates (Basis: 400,000 tons/yr acid capacity, 350,000 lbs/yr U_3O_8 recovery, 2Qtr,1979)

	Dollar per lb of U_3O_8		
		SX	
	LM	Minimum pretreatment	Extensive pretreatment
Organic make-up			
Circulation loss	0.1	3.9	3.9
Raffinate loss	0.1	0.2	0.2
Crud loss and treatment	1.0	2.9	0.0
Chemicals & Cupplies	1.4	0.9	1.6
Utilities	0.7	0.9	1.0
Labor, maintenance, taxes,& insurance	7.1	7.1	8.6
Depreciation	4.6	4.7	5.6
Total operating cost	15.0	20.6	20.9

CHAPTER IX

CARRIER MEDIATED MASS TRANSFER IN BIOLOGICAL MEMBRANES

Carrier mediated mass transfer also takes place in life processes. Here we will describe only briefly about the carrier mediated mass transfer in biological membranes. The cell membrane is of vital importance to maintenance of the living organism because it must provide for access to metabolic substrates, for disposal of end products and for regulation of species concentration gradients, all at rates consistent with the cell's functions. It is essential to consider how membrane transpoort processes in a wide variety of tissues are related, how various factors modulating these functions are expressed, and to related these parameters to clinical disorders.

Various substrates utilize different mechanisms with different proteins imbeded in the lipid membranes acting as catalysts and mediators either via active transport with the expenditure of energy or via passive transport via a favorable concentration gradient.

Within certain thermodynamic and structural constraints the membrane-associated proteins can provide pathways for the transport of solutes on a basis other than lipid solubility.

Such a specific site-mediated mechanism for the translocation of solutes istermed facilited transport, which derives its characteristics from the properties of the sites as well as the permeate. Among these the following may be noted:

(1) Facilitated transport is mediated by discrete sites, therefore the rate of transport shows amaximal rate (saturation) as a function of solute concentration.

(2) The transport sites have a finite affinity for a given solute. Thus the sepcificity of the transport system and selectivity among a series of solutes would be determined by relative affinities of a series of solutes for the transport sites.

(3) Since binding is only a prelude to transport, the overall specificity and selectivity for transport will be determined not only by the binding affinity of a solute but also by the ability of the occupied site to translocate solute from one interface to the other and to leave the site.

(4) The transport step may be coupled to binding of yet another solute (for example, hormones and neurotransmitters), to membrane potential to a chemical reaction or to the gradient of another solute (cotransport).

The facilited transport systems in general lower the energy barrier for the transport of solutes. Operationally this can be achieved by one of the following two mechanisms:

(1) A carrier mechanism invokes a site which binds stoichometrically to the permeate, and the site appears alternately at the two interfaces. The translocation step may be achieved by free diffusion, by rotation, or by conformational change. In any event the two compartments separated by the membrane remain somotically separate during the translocation.

(2) A channel or pore mechanism implies fixed opening in the membrane through which a permeate can pass. The passage through a chahel or pore does not necessarily involve binding.

Passive facilitated transport

Transport of polar solutes across the hydrophobic barrier of biological membranes is facilitated by a variety of mechanisms. Like passive diffusion, the driving force for facilitated transport is simply the electrochemical gradient which eventually leads to equalization of concentrations. Sicne these solutes are continuously meatbolized, a concentration gradient of the solutes is maintained.
One of the distinguishing characteristics of transport process that occur through a limited number of sites is that they exhibt saturation kinetics, that is, the rate of transport is limited by the number of transport sites. Examples of

the permeants and cells have the above characteristics are:

Permeant	Cell type
D-Glucose	Erythrocyte
Phosphate ion	Erythrocyte
Sugars and amino acids	Tumor cells
Chloride ion	Erythrocyte

Active transport

Most living organisms survive in an environment which has a low and fluctuating concentation of nutrients. This observation alone suggests that some honeostatic mechanism operates to regulate the intracellular concentration of solutes, which is often higher than the extracellular concentration of these same solutes. Indeed some organisms are able to estabish more than a million-fold gradient of certain solutes. For example, the external pH of acid-secreting parietal cells of gastric mucosa is about one, whereas the intracellular pH is maintained at about 7. Such a transport of solutes against their concentration gradient is called active, or uphill transport. These transport processes exhibit the characteristics of the facilitated transport system: substrate specificity, saturable rate of transport mediated by a few sites on the membrane, competitive, modulation by protein reagents, genetic inducibility, constitutive synthesis, and genetic impairment. Moreover the uphill transport systems are unidirectional, have large temperature coefficients, and are sometimes inhibited by anoxia and metabolic poisons.

Energy for some transport systems can be supplies by coupling to a gradient of another solute as in cotransport system. In other cases the free energy of an exergonic chemical reaction is directly utilized for the uphill transport.

(1) Cotransport

The uphill transport of a solute coupled to a downhill movement of another solute. Acarrier mediated transport system requires formation of a binary complex as a prelude to the translocation step. As shown in fig. 9.1, if such a carrier-solute binary complex CS is not able to translocate or does not have enough driving force, a more mobile ternary CXC would be able to cotranslocate the solute S, even against its gradient, as long as X is transported down its concentration gradient. Several cotransport systems driven by sodium ions, protons, and perphaps potassium ions are known to exist an a wide variety of organisms. Among these the best-characterized cotransport systems are the sodium ion-coupled cotransport systems for sugars and amino acids.

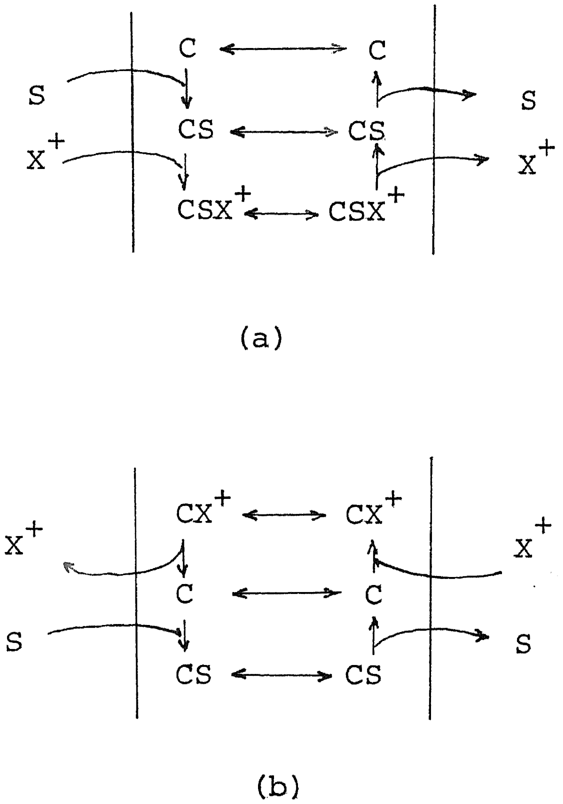


Fig. 9.1 Steps involved in the uphill transport of a solute (S) coupled to a downhill transport of another solute (X^+) by cotransport mechanisms.

(2) Transport energized by ATP

In some of the most widely distributed uphill transport mechanisms the driving force is provided by the free energy liberated by the hydrolysis of ATP to ADP and Pi. In such systems the hydrolysis of ATP and uptake of solutes is obligatorily and stoichiometrically coupled. The sodium-potassium pump is the best characterized transport of this type.

In most cells the transport of sodium (from inside to outside) and potassium ions (from outside to inside) occurs as a stoichimetrically coupled process mediated by ATPase (Glynn and Karlish, 1975): under physiological conditions the pump utilizes the free energy of hydrolysis of one molecule of ATP to extrude three Na^+ ions and to accumulate two K^+ ions. Active transport of Na^+ and K^+ ions is mediated by a Na^++K^+ activated ATPase (Skou, 1975). Several properties attest to this: the ATPase is a membrane-localized enzyme; it is present in all cells that actively transport Na^+ and K^+; the requirements of Mg^{2+} and the binding constants for Na^+ and K^+ for phospholipids are strongly associated with purified Na^++K^+ ATP preparations.

Kinetic studies of the ATPase reaction have yielded a scheme that is consistent with the following partial reactions in a transport cycle (Albers and Koval, 1973):

$$E_1 + ATP + Na_i^+ \rightleftharpoons E_1\text{-}P(Na_i^+) + ADP$$

$$E_1\text{-}P(Na_i^+) + Mg \rightleftharpoons E_2\text{-}P + Na_o^+$$

$$E_2\text{-}P + K_o^+ \rightleftharpoons E_2(K_o^+) + Pi$$

$$E_2(K_o^+) \rightleftharpoons E_1 + Mg^{2+} + K_i^+$$

Thus phosphorylation of the native enzyme E_1 by ATP requires N_a^+. The phosphorylated enzyme undergoes a conformational change after Mg^{2+} binding. It is this step that is most probably regulated by the lipid environment. Loss of phosphate from E_2-P is accelerated by K^+ but is insensitive to ADP. In this reaction sequence Na^+ is discharged durning a conformational change of E_1-P to E_2-P. This permits Na_i^+-Na_o^+ exchange when the external low affinity sites are siturated, requires only the presence of ATP, is promoted by ADP, and is inhibited by oligomycin. Further kinetic studies suggest that the Na^+ and binding sites are separate but strongly couples; that is either both sites are oriented inwardly or both sites are oriented outwardly (Swann and Albers, 1975). Although Na^++K^+ ATPase also shows K^+-activated phosphatase activity, it cannot transfer phosphate from acetyl phosphate to ATP. This suggest that the phosphatase reaction with these substrate can bypass the initial sodium-dependent formation of E_1-P.

The scheme presented above is consistent with the available evidence that suggests that the transport and ATPase activities cannot be uncoupled (Jain & Wagner, 1980).

CHAPTER X

CONCLUSIONS

The agreements of the theoretical predictions for the copper extraction, phenol removal and solvent extraction with experimental data are very good. A very important contribution of this research is that we can predict the extraction rate of a dispersed liquid membrane system without the need of experimental extraction run. No adjustable parameter in the models has to be curve fitted. All parameters can be determined from literature or by correlations or through operating conditions.

Span 80 is added to membrane phase to stabilize the emulsion and to reduce membrane breakage. From our experiments, at 5%V Span 80, the leakage rate was below 1% . In practical applications, the leakage problem can be neglected. Too high surfactant concentation should be avoided. Since too much surfactant in membrane phase would cause some problems in breaking up the emulsion in a subsequent process.

When chemical reaction is involved in the receiving phase, increase the receiving phase reagent concentration will also increase the extraction rate. Since the membrane rupture problem exists, the receiving phase reagent concentration can not be too high.

From the comparison of the models with experimental data, we have concluded in Chapter VII that for practical purpose, the internal film resistance is negligible and the external film resistance can not be neglected. The models developed in this study are for batch process, but they can easily be modified for a continuous process.

The dispersed liquid membrane technology is in the stage of potential industrial commercialization. The advantages over traditional methods were discussed in Chapter VIII. There still some area need further study, such as optimum composition and the best configuration for a low speed mixing unit etc. Although further research and pilot plant test are needed, the results from this study represent a very significant step toward the practical applications of the dispersed liquid membrane technology.

APPENDIX A

EXPERIMENTAL DATA FOR COPPER EXTRACTION

1. Leakage Test
2. Equilibrium constant
3. Copper extraction run

1. Leakage Test

Leakage Test

(Run 1)

Conditions:

Membrane phase: 32.5 ml n-heptane containing 5%V Span 80 and 3%W LIX-64N.

Internal phase: 32.5 ml 1000 ppm copper solution.

External phase: 400 ml deionized water.

Mixing speed: 290 rpm.

Emulsion phase was added slowly.

Time (min)	External phase copper conc. (ppm)	Leakage rate (%)
0	o	0.
3	0.5	0.63
6	0.5	0.63
9	0.5	0.63
12	0.5	0.63
15	0.75	0.94

1. Leakage Test

Leakage Test
(Run 2)

Conditions:

Membrane phase: 35 ml n-heptane containing 5%V Span 80 and 3%W LIX-64N.

Internal phase: 35 ml 1000 ppm copper solution.

External phase: 400 ml deionized water.

Mixing speed: 263 rpm.

Emulsion was added abruptly.

Time (min)	External phase copper conc. (ppm)	Leakage rate (%)
0	0	o
3	1	1.14
6	1.5	1.71
9	1.5	1.71
12	1.5	1.71
15	1.5	1.71

1. Leakage Test

Leakage Test
(Run 3)

Conditions:

Membrane phase: 35 ml n-heptane containing 5%V Span 80 and 3%W LIX-64N.

Internal phase: 35 ml 1000 ppm copper solution.

External phase: 400 ml deionized water.

Mixing speed: 280 rpm.

Emulsion phase was added slowly.

Time (min)	External phase copper conc. (ppm)	Leakage rate (%)
0	0	0
3	0.5	0.57
6	0.5	0.57
9	0.5	0.57
12	0.5	0.57
15	0.5	0.57

1. Leakage Test

Leakage Test

(Run 4)

Conditions:

Membrane phase: 40 ml n-heptane containing 5%V Span 80 and 2%W LIX-64N.

Internal phase: 40 ml 1000 ppm copper solution.

External phase: 400 ml deionized water.

Mixing speed: 280 rpm.

Emulsion phase was added slowly.

Time (mim)	External phase copper conc. (ppm)	Leakage rate (%)
0	0	0
3	0	0
6	0.5	0.5
9	0.5	0.5
12	0.5	0.5
15	1.0	1.0

2. Equilibrium Constant

100 ml of 100 ppm copper aqueous solution was shaked with 100 ml membrane phase solution which containing 5%V Span 80 and 2%W LIX-64N. After about 20 minutes the pH value and copper concentration were measured.

	pH Value	$[H^+]$ Moles/L	$[Cu^{++}]$ ppm	$K_{eq}[RH]^2$
Run 1	2.65	2.24×10^{-3}	28.5	1.26×10^{-5}
Run 2	2.60	2.51×10^{-3}	33.07	1.28×10^{-5}

$$K_{eq} = \frac{[CuR_2][H^+]^2}{[Cu^{++}][RH]^2}$$

$$\left[K_{eq}[RH]^2\right]_{avg} = 1.27\times10^{-5}$$

3. Copper Extraction

Copper Extraction

(Run 1)

Conditions:

Membrane phase:	40 ml n-heptane containing 5%V Span 80 and 2%W LIX-64N.
Internal phase:	40 ml 1.1%W HNO_3 solution.
External phase:	460 ml 130 ppm copper solution.
Mixing speed:	280 rpm.
Temperature:	25°C.
pH (external):	2.3
pH (internal):	0.77
Globule radius:	0.045 cm.

Time (min)	External phase copper conc. (ppm)	Relative to original conc. (%)
0	130.4	100
1	88.6	67.9
2	73.6	56.4
4	57.3	43.9
6	40.9	31.4
9	34.1	26.1
12	24.6	18.9

3. Copper Extraction

Copper Extraction

(Run 2)

Conditions:

Membrane phase:	40 ml n-heptane containing 5%V Span 80 and 2%W LIX-64N.
Internal phase:	40 ml 1.1%W HNO_3 solution.
External phase:	460 ml of 174 ppm copper solution.
Mixing speed:	280 rpm.
Temperature:	25°C.
pH (external):	2.3
pH (internal):	0.77
Globule radius:	0.045 cm.

Time (min)	External phase copper conc. (ppm)	Relative to original conc. (%)
0	174	100
1	114	65.5
2	90	51.8
4	74	42.5
6	64	36.8
9	53	30.5
12	42	24.1

APPENDIX B

COMPUTER PROGRAMS

1. Phenol Removal with External Film Resistance Only.
2. Phenol Removal with External & Internal Resistances.
3. Solvent Extraction.

1. Phenol Removal with External Film Resistance Only.

```
C THIS PROGRAM IS FOR PHENOL REMOVAL CASE B,FILE BB-1
      DIMENSION B(500)
      REAL K
      R(X,K,ALP,P)=(P-ALP*K*X**2)*X/((1.-ALP*K)*X**2+P)
90    READ,K
      IF (K .GE. 10.) STOP
C  A=1-E+EG
C  P=ALPHA*PHI*A
      E=0.5
      ALP=1.
      PHI=0.46154
      DEP=(1.-E)*1.12E-5
      RADIU=0.076
      G=1280.
      A=1.-E+G*E
      P=ALP*PHI*A
      X=4.0
      Q=X-3.14
      DO 120 I=1,500
100   QQ=ATAN(R(X,K,ALP,P))
      X=X+(QQ-Q)
      DIF=QQ-Q
      IF (ABS(DIF) .LT. 0.000001) GO TO 110
      Q=QQ
      GO TO 100
110   B(I)=X
      X=X+3.1415
120   CONTINUE
      WRITE (2,125) K, (B(I),I=1,10)
125   FORMAT(1X,'EXTERNAL FILM RESISTANCE K=',F7.5,/,10F10.3)
      TT=0.
      DO 230 J=1,30
      T=DEP/RADIU**2*60*TT
      CE=3./(3.+P)
      DO 200 I=1,500
      BB=((1.-ALP*K)*R(B(I),K,ALP,P)+ALP*K*B(I))*EXP(-B(I)**2/
A*T)/
     C ((1.-ALP*K-ALP*K*B(I)**2/2.+P/2.)*R(B(I),K,ALP,P)+(0.5+
     C ALP*K)*B(I))
      CE=CE+BB
      IF (ABS(BB) .LT. 0.000001) GO TO 210
200   CONTINUE
210   WRITE (2,220) I, TT,CE
220   FORMAT(1X,'CONVERGENT AT',I4,'TH EIGEN TERM AT TIME='
     C ,F5.2,'  MIN  CE/CE0=',F6.3)
      TT=TT+0.5
230   CONTINUE
      GO TO 90
      END
```

2. Phenol Removal with External & Internal Resistances.

```
C  THIS PROGRAM IS FOR PHENOL REMOVAL CASEE C, FILE BC-1
      DIMENSION HB(199),HR(600)
      COMMON A,E,G,RKI,PHI,RKO,ALP
      REAL KO,KI
90    READ, KO, KI
      IF (KO .GE. 10.) STOP
C  A=1-E+GE
C  P=ALP*PHI*A
      E=0.5
      ALP=1.0
      PHI=0.462
      RADIU=0.076
      RD=0.0001
      DEP=(1.-E)*1.12E-5
      G=1280.
      RKO=DEP/RADIU/KO
      RKI=DEP/(KI*(3.*E/RD)*RADIU**2)
      A=1.-E+G*E
      P=ALP*PHI*A
C  NEXT TO FIND EIGEN VALUES HB
      X=4.
      Q=X-3.14
      DO 120 I=1,199
      CALL EIGB(X,EB,ROTB,QB)
100   QQ=ATAN(EB)
      X=X+(QQ-Q)
      CALL EIGB(X,EB,ROTB,QB)
      DIF=QQ-Q
      ESP=0.000001
      IF(ABS(DIF ) .LT. ESP ) GO TO 110
      Q=QQ
      GO TO 100
110   HB(I)=X
      X=X+3.1415
120   CONTINUE
C  SIMILAR FOR EIGEN VALUES HR
      X=4.0
      Q=X-3.14
      DO 121 I=1,199
      CALL EIGR(X,ER,ROTR,QR)
101   QQ=ATAN(ER)
      X=X+(QQ-Q)
      CALL EIGR(X,ER,ROTR,QR)
      DIF=QQ-Q
      EPS=0.000001
```

```
      IF (ABS(DIF) .LT. EPS ) GO TO 111
      Q=QQ
      GO TO 101
  111 HR(I)=X
      X=X+3.1415
  121 CONTINUE
      WRITE (2,125) RKO,RKI
  125 FORMAT(1X,'EXTERNAL RKO=',F7.5,'    INTERNAL RKI=',E10.3)
      WRITE(2,126) (HB(I),I=1,10)
  126 FORMAT(1X,' EIGENVALUES FOR HB',/,1X,10F10.4)
      WRITE(2,127) (HR(I),I=1,10)
  127 FORMAT(1X,'EIGENVALUES FOR HR',/,1X,10F10.4)
      TT=0.
      DO 230 J=1,30
      T=DEP/RADIU**2*60.*TT
      CE=3./(3.+P)
      BR=1.
      DO 200 I=1,199
      CALL EIGB(HB(I),EB,ROTB,QB)
      BB=((1.-ALP*RKO)*EB+ALP*RKO*HB(I))*EXP(-ROTB*T)/
     C ((1.-ALP*RKO+0.5*(ALP*PHI-ROTB*ALP*RKO)*(HB(I)**2/ROTB
     C +QB))*EB+(0.5+0.5*ROTB/HB(I)**2*
     C QB+ALP*RKO)*HB(I))
      IF (BR .LT. 0.000001) GO TO 150
      CALL EIGR(HR(I),ER,ROTR,QR)
      BR=((1.-ALP*RKO)*ER+ALP*RKO*HR(I))*EXP(-ROTR*T)/
     C ((1.-ALP*RKO+0.5*(ALP*PHI-ROTR*ALP*RKO)*(HR(I)**2/ROTR
     C +QR))*ER+(0.5+0.5*ROTR/HR(I)**2*
     C QR+ALP*RKO)*HR(I))
      CE=CE+BB+BR
      GO TO 151
  150 CE=CE+BB
  151 IF(ABS(BB) .LT. 0.000001) GO TO 152
      GO TO 200
  152 IF(ABS(BR) .LT. 0.000001) GO TO 210
  200 CONTINUE
  210 WRITE(2,220) I,TT,CE
  220 FORMAT (1X,'CONVERGENT AT',I4,'TH EIGEN TERM AT TIME=',
     C F5.2,'  MIN  CE/CEO=',F6.3)
      TT=TT+0.5
  230 CONTINUE
      GO TO 90
      END
      SUBROUTINE EIGB(X,EB,ROTB,QB)
      COMMON A,E,G,RKI,PHI,RKO,ALP
      DOUBLE PRECISION DA,DE,DG,DRKI, DX
      DX=X
      DA=A
      DE=E
      DG=G
```

```
 DRKI=RKI
 ROTB=(DA+DG*DE*DRKI*DX**2-((DA+DG*DE*DRKI*DX**2)**2
C -4.D0*(1.D0-DE)*DG*DE*DRKI*DX**2)**0.5)/
C (2.D0*(1.D0-DE)*DG*DE*DRKI)
 EB=(PHI-ROTB*RKO)*X/(PHI+(1./ALP-RKO)*ROTB)
 QB=(G*E)**2*RKI*ROTB/(G*E*RKI*(-ROTB)+1.)**2
 RETURN
 END
 SUBROUTINE EIGR(X,ER,ROTR,QR)
 COMMON A,E,G,RKI,PHI,RKO,ALP
 DOUBLE PRECISION DA,DE,DG,DRKI, DX
 DX=X
 DA=A
 DE=E
 DG=G
 DRKI=RKI
 ROTR=(DA+DG*DE*DRKI*DX**2+((DA+DG*DE*DRKI*DX**2)**2
C -4.D0*(1.D0-DE)*DG*DE*DRKI*DX**2)**0.5)/
C (2.D0*(1.D0-DE)*DG*DE*DRKI)
 ER=(PHI-ROTR*RKO)*X/(PHI+(1./ALP-RKO)*ROTR)
 QR=(G*E)**2*RKI*ROTR/(G*E*RKI*(-ROTR)+1.)**2
 RETURN
 END
```

3. Solvent Extraction.

```
C  PROGRAM FOR SOLVENT EXTRACTION FILE D-1
C  A=TOLUENE
C  B=N-HEPTAN
C  C=O-XLENE (SOLVEN)
C  MEMBRANE G=GLYCEROL, WATER
      DIMENSION BETA(300),GAMA(300),PHI(300)
      RF(X,P)=P*X/(P+X**2)
C  MOLECULAR WEIGHT
      WA=92.13
      WB=100.2
      WC=106.16
      WG=92.09
C  DENSITY
      DA=0.886
      DB=0.684
      DC=0.881
      DG=1.260
C  DIFFUSIVITY
      DFA=5.24E-7
      DFB=4.35E-7
      DFC=4.74E-7
C  DISTRIBUTION COEFFICIENT
      RMAI=5.12E-4
      RMAO=4.67E-4
      RMBI=3.68E-5
      RMBO=5.82E-5
      RMCI=2.22E-4
      RMCO=1.95E-4
C  FEED RATES IN GRAMES
      FAO=42.73
      FBO=33.52
      FW=60.01
      FG=143.6
      FCO=436.0
C  VOLUME  AND RO
      VM=FW/1.+FG/DG
      VRO=FAO/DA+FBO/DB
      RMM=(FG/WG+FW/18.)/VM
      RO=0.1
      RN=3.*(VM+VRO)/4./3.1416/(RO)**3
      A=0.
      B=0.
      C=FCO/WC
      T=0.125
      TIME=0.125
```

```
      TPRINT=0.5
C  PARAMETETRS
90    FA=FAO-A*WA
      FB=FBO-B*WB
      FC=FCO-C*WC
      RMT=C+A+B
      VR=FA/DA+FB/DB+FC/DC
      E=VR/(VR+VM)
      RMR=(FA/WA+FB/WB+FC/WC)/VR
      R=(3.*(VM+VR)/(4.*RN*3.1416))**(1./3.)
      CAO=RMAI*RMM*(FA/WA)/(FA/WA+FB/WB+FC/WC)
      CBO=RMBI*RMM*(FB/WB)/(FA/WA+FB/WB+FC/WC)
      CCO=RMCI*RMM*(FC/WC)/(FA/WA+FB/WB+FC/WC)
      DEA=(1.-E)*DFA
      DEB=(1.-E)*DFB
      DEC=(1.-E)*DFC
      AA=1.-E+E*RMR/RMAI/RMM
      D=3.*(VRO+VM)*(R/RO)**3
      AB=1.-E+E*RMR/RMBI/RMM
      AC=1.-E+E*RMR/RMCI/RMM
      BA=D*RMAO*RMM/RMT
      BB=D*RMBO*RMM/RMT
      BC=D*RMCO*RMM/RMT
      PA=AA*BA
      PB=AB*BB
      PC=AC*BC
C  EIGEN VALUES FOR BETA AND GAMA
      X=4.0
      Q=X-3.14
      DO 120 I=1,299
100   QQ=ATAN(RF(X,PA))
      X=X+(QQ-Q)
      DIF=QQ-Q
      IF (ABS(DIF) .LT. 0.000001) GO TO 110
      Q=QQ
      GO TO 100
110   BETA(I)=X
      X=X+3.1416
120   CONTINUE
      X=4.
      Q=X-3.14
      DO 121 I=1,299
101   QQ=ATAN(RF(X,PB))
      X=X+(QQ-Q)
      DIF=QQ-Q
      IF (ABS(DIF) .LT. 0.000001) GO TO 111
      Q=QQ
      GO TO 101
```

```
111    GAMA(I)=X
      X=X+3.1416
121   CONTINUE
      X=4.
      Q=X-3.14
      DO 122 I=1,299
102   QQ=ATAN(RF(X,PC))
      X=X+(QQ-Q)
      IF (ABS(QQ-Q) .LT. 1.E-6) GO TO 112
      Q=QQ
      GO TO 102
112   PHI(I)=X
      X=X+3.14
122   CONTINUE
      ATO=(D*AA*CAO+3.*A)/(AA*BA+3.)
      BTO=(D*AB*CBO+3.*B)/(AB*BB+3.)
      CTO=(D*AC*CCO+3.*C)/(AC*BC+3.)
      DO 200 I=1,299
      TRMA=((BETA(I)**2*A+AA*D*CAO)*RF(BETA(I),PA)
     C -D*CAO*BETA
     C (I)*AA)/((1.+BA*AA/2.)*BETA(I)**2*RF(BETA(I),PA)
     C +0.5*BETA(I)**3)*EXP(-BETA(I)**2*DEA/
     C (AA*R**2)*3600.*T)
      ATO=ATO+TRMA
      IF (ABS(TRMA) .LT. 1.E-7) GO TO 210
200    CONTINUE
210   IF (ABS(TIME-TPRINT) .GT. 0.0001) GO TO 240
      WRITE(2,220) I,TIME,ATO
220   FORMAT(1X,'CONVENGENT AT ',I4,'TH EIGEN TERM AT TIME='
     C,F5.2,' HR, A=',F7.4)
240   DO 300 I=1,299
      TRMB=((GAMA(I)**2*B+AB*D*CBO)*RF(GAMA(I),PB)
     C -D*CBO*GAMA
     C (I)*AB)/((1.+BB*AB/2.)*GAMA(I)**2*RF(GAMA(I),PB)
     C +0.5*GAMA(I)**3)*EXP(-GAMA(I)**2*DEB/
     C (AB*R**2)*3600.*T)
      BTO=BTO+TRMB
      IF(ABS(TRMB) .LT. 1.E-7) GO TO 310
300   CONTINUE
310   IF (ABS(TIME-TPRINT) .GT. 0.0001) GO TO 321
      WRITE(2,320) I,TIME,BTO
320   FORMAT(1X,'CONVENGENT AT ',I4,'TH EIGEN  TERM AT TIME=',
     C F5.2,' HR,  B=',F7.4)
321   CONTINUE
      DO 301 I=1,299
      TRMC=((PHI(I)**2*C+AC*D*CCO)*RF(PHI(I),PC)
     C -D*CCO*PHI
     C (I)*AC)/((1.+BC*AC/2.)*PHI(I)**2*RF(PHI(I),PC)
     C +0.5*PHI(I)**3)*EXP(-PHI(I)**2*DEC/
     C (AC*R**2)*3600.*T)
```

```
      CTO=CTO+TRMC
      IF (ABS(TRMC) .LT. 1.E-7) GO TO 311
301   CONTINUE
311   IF (ABS(TIME-TPRINT) .GT. 0.0001) GO TO 322
      WRITE(2,333) I,TIME,CTO
333   FORMAT(1X,'CONVENGENT AT ',I4,'TH EIGEN TERM AT TIME=',
     C F5.2,' HR, C=',F7.4)
322   CONTINUE
      A=ATO
      B=BTO
      C=CTO
      IF (ABS(TIME-TPRINT) .GT. 0.0001) GO TO 260
      YA=A*WA/(C*WC+A*WA+B*WB)
      YB=B*WB/(C*WC+A*WA+B*WB)
      YC=1.-YA-YB
      SEPF=A*(FBO/WB-B)/B/(FAO/WA-A)
      WRITE (2,250) YA,YB,YC,SEPF,E
250   FORMAT(1X,'YA=',F6.4,'  YB=',F6.4,'  YC=',F6.3,
     C ' SEPTN FACTOR=',F6.3,' E=', F5.3)
      TPRINT=TPRINT+0.5
260   CONTINUE
      T=0.125
      TIME=TIME+T
      IF (TIME .GE. 6.1) STOP
      GO TO 90
      END
```

NOMEMCLATURE

a	interphase area of membrane and internal phases per unit volume of emulsion phase.
a_A, b_B, a_C	as defined by eqn. (4.17).
A	moles of A in external extract phase.
A_o	moles of A in extract phase at time t_o.
A_{Oi}	initial moles of A in internal raffinate phase.
b_A, b_B, b_C	as defined by eqns. (4.43), (4.45) and (4.47).
B	moles of B in extract phase.
B_o	moles of B in extract phaseat time t_o.
B_{Oi}	initial moles of B in internal raffinate phase.
C_A, C_B, C_C	concentration of A,B,C in membrane phase.
C_{AO}, C_{BO}	concentration of A,B in membrane phase at time t_o.
C_{CO}	concentration of C in membrane phase at time t_o.
C_e	concentration of phenol in source phase.
C_{eo}	initial concentration of phenol in source phase.
C_e^*	concentration of phenol at membrane external phase.
C_m	concentration of phenol in membrane phase.
C_m^*, C_{mi}^*	concentration of phenol at membrane external,internal interphase.
C_r	phenol conc. in receiving phase.
C_{ri}^*	phenol conc. at membrane internal interphase.
C_{rt}	total phenol conc. in receiving phase.
Cu, C_H	conc. of Cu^{++}, H^+ in source phase.
Cuo, C_{HO}	initial conc. of Cu^{++}, H^+ in source phase.

Cu^*, C_H^*	conc. of Cu^{++}, H^+ in source phase at membrane external interphase.
C_x, C_{RH}	conc. of CuR_2,RH in membrane phase.
C_X^*, C_{RH}^*	conc. of CuR_2,RH at membrane external interphase.
C_{Xi}^*, C_{RHi}^*	conc. of CuR_2,RH at membrane internal interphase.
Cui, C_{Hi}	conc. of C^{++}, H^+ in receiving phase.
Cui^*, C^*_{Hi}	receiving phase conc. of Cu^{++}, H^+ at membrane internal interphase.
Cuo	initial conc. of Cu^{++} in source phase.
C_{RHO}	initial conc. of RH in membrane phase.
C_{HO}	initial conc. of H^+ in source phase
C_{HOi}	initial conc. of H^+ in receiving phase.
D_A, D_B, D_C	diffusion coefficient of A,B,C in membrane phase.
D_p	diffusion coefficient of phenol in membrane phase.
D_x, D_{RH}	diffusion coefficient of CuR_2,RH in membrane phase.
D_{ex}, D_{eRH}	effective diffusivity of CuR_2,RH in emulsion phase.
D_{ep}	effective diffusivity of phenol in emulsion phase.
D_{eA}, D_{eB}	effective diffusivity of A,B in emulsion phase.
D_{eC}	effective diffusivity of C in emulsion phase.
d	as defined by eqn. (4.17).
k_i	membrane internal interphase mass transfer coefficient.
k_o	membrane external interphase mass transfer coefficient.
K_i	membrane internal resistance as defined by eqn. (2.91).
K_o	membrane external resistance as defined by eqn. (2.91).
Ka	acid dissociation constant of phenol.
Kw	ion concentration product of water.

m_A, m_B, m_C	distribution coefficient of A,B,C.
M_R	total number of moles per unit volume of raffinate phase.
M_m	total number of moles per unit volume of membrane phase.
M_t	total number of moles of extract phase.
m	equilibrium constant as defined by eqn. (2.15a)
N	total number of globules in a batch.
q	equilibrium constant as defined by eqn. (2.15b).
r	radial distance from globule center.
R	Sauter mean diameter of globules.
t	time
V_A, V_B, V_C	molar volume of A,B,C.
V_t	total volume of a batch.
V_{EO}	initial volume of emulsion phase.
X_A, X_B, X_C	mole fraction of A,B,C in raffinate phase.
X_{AO}, X_{BO}	mole fraction of A,B at time t_o.
X_{CO}	mole fraction of C at tiem t_o.
y	dimensionless radial distance.

Greek letters

ε	volume fraction of internal phase in emulsion phase.
ϕ'	volume fraction of emulsion phase in a batch.
ϕ	as defined by eqn. (2.22)
τ	dimensionless time
α	partition coefficient of phenol.

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