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Emulsion liquid membrane removal of arsenic and Strontium from wastewater : an experimental and theoretical study

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ABSTRACT

EMULSION LIQUID MEMBRANE REMOVAL OF ARSENIC AND STRONTIUM FROM WASTEWATER: AN EXPERIMENTAL AND THEORETICAL STUDY

by
Ding-Wei Zhou

The emulsion liquid membrane (ELM) technique has been successfully applied on the removal of arsenic (As) from metallurgical wastewater and the removal of strontium (Sr) from radioactive wastewater. This study consisted of experimental work and mathematical modeling.

Extraction of arsenic by an emulsion liquid membrane was firstly investigated. The liquid membrane used was composed of 2-ethylhexyl alcohol (2EHA) as the extractant, ECA4360J as the surfactant, and Exxsol D-80 solvent (or heptane) as the diluent. The sulfuric acid and sodium hydroxide solutions were used as the external and internal phases, respectively. The arsenic removal efficiency reached 92% within 15 minutes in one stage. Extraction and stripping chemistries were postulated and investigated. It was observed that extraction efficiency and rate increase with the increase of acidic strength and alkali strength in the external and internal phases, respectively. It was also observed that the removal selectivity of arsenic over copper is extremely high.

Strontium-90 is one of the major radioactive metals appearing in nuclear wastewater. The emulsion liquid membrane process was investigated as a separation method by using the non-radioactive ^{87}Sr as its substitute. In our study, the membrane

phase was composed of di-(2-ethylhexyl) phosphoric acid (D2EHPA) as the extractant, ECA4360J as the surfactant and Exxsol D-80 as the diluent. A sulfuric acid solution was used in the internal phase as the stripping agent. The pH range in the external phase was determined by the extraction isotherm. Under the most favorable operating condition, the strontium removal efficiency can reach 98% in two minutes.

Mass transfer of the emulsion liquid membrane (ELM) system was modeled mathematically. Our model took into account the following: mass transfer of solute across the film between the external phase and the membrane phase, chemical equilibrium of the extraction reaction at the external phase-membrane interface, simultaneous diffusion of the solute-carrier complex inside the globule membrane phase and stripping of the complex at the membrane-internal phase interface, chemical equilibrium of the stripping reaction at the membrane-internal phase interface and leakage of the solute from the internal phase to the external phase. Resulting simultaneous partial differential equations were solved analytically by the Laplace transform method. Four dimensionless groups were found with special physical meanings to characterize the emulsion liquid membrane systems. It not only predicted the concentration of solute in the external phase versus time, but also gave the concentration profile inside the membrane globule and the interfacial concentration at the external-membrane phase interface at different time. The model predicted very well the experimental data obtained from the removal of arsenic and strontium by the emulsion liquid membranes.

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by
Ding-Wei Zhou

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EMULSION LIQUID MEMBRANE REMOVAL OF
ARSENIC AND STRONTIUM FROM WASTEWATERS: AN EXPERIMENTAL
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This dissertation is dedicated to
my parents, my wife and daughter

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NOMENCLATURE

B   Dimensionless emulsion capacity constant, defined as $m*f*\omega$.

Biot   Biot number, defined as $\dfrac{R*k}{m*De}$.

bn   Eigen values, n=1,2,3....

C_e Solute concentration in the external phase (ppm).

C_e^* Solute concentration in the external phase at external-membrane interface (ppm).

C_{eo} Initial solute concentration in the external phase (ppm).

C_i Solute concentration in the internal phase (ppm).

C_m Solute concentration in the membrane phase (ppm).

C_m^* Solute concentration in the membrane phase an the external phase-membrane interface (ppm).

D_e Effective diffusivity of the solute-carrier complex in the emulsion phase (m^2/sec.).

Di   Diffusivity of the solute in the aqueous phase (m^2/sec.).

D_m Diffusivity of the solute-carrier complex in the membrane phase (m^2/sec.).

d_l Diameter of the propeller (m).

d_T Diameter of the tank (m).

e   Internal volume fraction of the emulsion, defined as $\dfrac{Vi}{Vm+Vi}$.

F   Faraday Constant (96500 c/g-equiv).

f   Intermediate variable, defined as $\dfrac{3f'}{1-f'}$.

f'   Emulsion volume fraction of the total volume, defined as $\dfrac{Vm+Vi}{Ve+Vm+Vi}$.

G   Reciprocal of the Biot number, defined as $\dfrac{m*De}{R*k}$.

H   Intermediate variable, defined as $\sqrt{\omega s}$.

I   Intermediate variable, defined as $\dfrac{k_b*R^2}{De}$.

k   External mass transfer coefficient (m/sec.).

k_b Leakage rate (1/sec.).

Ko   Intermediate variable, defined as $\dfrac{R*k*f}{De}$.

m   Extraction partition function at the external phase-membrane interface.

M_B Molecular weight of solvent phase (g/mol).

N   Total number of the emulsion globules druing agitating.

n^+, n^- Valences of cation and anion, respectively.

P   Dimensionless leakage group, defined as $\dfrac{\omega*k_b*R^2}{De}$.

q   Stripping partition function at the membrane-internal phase interface.

r   radius inside emulsion globule (m).

R   Sauter mean radius of the emulsion globule (m).

Re   Renold number, defined as $\dfrac{N*d_I^2*\rho}{\mu}$.

R_x Disappearance of the solute-carrier complex in the membrane phase into the internal phase by stripping (mol/dm^3/sec.).

s   laplace domain.

T   Absolute temperature (K).

t   Time (sec).

U_e Dimensionless solute concentration in the external phase, defined as $\dfrac{Ce}{Ceo}$.

U_e^* Dimensionless solute concentration in the external phase at the external phase-membrane interface, defines as $\dfrac{C^*e}{Ceo}$.

U_m Dimensionless solute concentration in the membrabe phase $\dfrac{Cm}{m*Ceo}$.

U_m^* Dimensionless solute concentration in the membrane phase at the membrane-internal phase interface, defined as $\dfrac{C^*m}{m*Ceo}$.

v   Dimensionless radius, defined as $\dfrac{r}{R}$.

V_A Molar volume of the solute A at its normal boiling temperature (cm^3/mol).

V_e External phase volume (dm^3).

V_i Internal phase volume (dm^3).

V_m Membrane phase volume (dm^3).

GREEK SYMBOLS

ϕ Associate factor of solvent (2.6 for water, 1.0 for unassociated solvent).

ρ Density of the external phase (g/cm^3).

τ Dimensionless time, defined as $\dfrac{De*t}{R^2}$.

ω Intermediate variable, defined as $1+e(q-1)$.

γ Surfacial tension (dyn/cm).

μ Viscosity of the external phase (g/cm/sec.).

λ^+, λ^- Limited (zero concentration) ionic conductance of cation and anion respectively (A/cm^2)(V/cm)(g-equiv./cm^3).

η_B Viscosity of solvent phase (cp).

CHAPTER 1

GENERAL INTRODUCTION

1.1 Emulsion Liquid Membranes and Their Applications

Since Norman N. Li invented emulsion liquid membranes as a separation technique in 1968 [Li,(1968)], emulsion liquid membranes have demonstrated considerable potential as effective tool for wide variety of separations.

Emulsion liquid membranes, also called surfactant liquid membranes or liquid surfactant membranes, are essentially double emulsion, i.e., water/oil/water (W/O/W) systems or oil/water/oil (O/W/O) systems. for the W/O/W systems, the liquid membrane is the oil phase that is between two water phases, and the configuration is stabilized by oil soluble surfactant.

As shown in recent reviews[Ho and Sirkar, (1992); Ho and Li (1992); Noble and Way, (1987a,1987b); Nakashio, (1993)], the separation of variety of chemical compounds by liquid surfactant membrane has been studied by many investigators in past two decades. Dr. W.S. Winston Ho and co-workers have summarized the previous works in their handbook[Ho and Sirkar, (1992)]. They are heavy metals, such as zinc[Draxler, Furst and Marr, (1988); Draxler and Marr, (1986); Lorbach and Marr, (1987)], nickel[Draxler and Marr, (1986)], cadmium, copper, mercury, lead[Marr, Bart and Draxler, (1990)], chromium[Fuller and Li, (1984)], cobalt. and etc.[Marr and Kopp, (1982); Frankenfeld and Li, (1977, 1979)]; alkali metals, such as sodium, potassium, lithium, cesium and etc.[Reusch and Cussler, (1973), Schiffer *et al.*, (1974); Culler and

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Evans, (1980); Bartsch *et al.*, (1987)]; organic and inorganic acids, [Halwachs, Flaschel, and Schugerl, (1980); Terry, Li, and Ho, (1982); Yan, Huang, and Shi, (1987); Qian, Ma, and Shi, (1989)], such as acetic and propionic acid, cresols, hydrocyanic acid and etc.; biochemicals[Thien, Hatton, and Wang, (1986); Ho and Cowan, (1987); Thien and Hatton, (1988)], such as amino acid, antibiotics, phospholipids and etc.; biomedical reagents[Li and Asher, (1973); Asher, *et al.*, (1975, 1976, 1979, 1980)], such as artificial blood cell, cholesterol, toxins and etc.. Among the above applications, removal of zinc from waste water in the viscose fiber industry[Draxler, Marr, and Protsch, (1988)], and removal of phenol from waste water[Zhang, Liu, and Lu, (1987)] have been commercialized in Austria and China respectively.

1.2 General Description of Emulsion Liquid Membranes

Emulsion Liquid membranes are usually prepared by first forming an emulsion between two immiscible phases, and then dispersing the emulsion into a third(continuous) phase by agitation for extraction. The membrane phase is the liquid phase that separates the encapsulated, internal droplets in the emulsion from the external, continuous phase, as shown in Figure 1.1. In general , the internal, encapsulated phase and the external, continuous phase are miscible. However, the membrane phase must be immiscible with either of these two phases in order to be stable. Therefore, the emulsion is of the W/O type if the external, continuous phase is water, and it is of the O/W type if the external, continuous phase is oil. To maintain the integrity of the emulsion during the extraction process, the membrane phase generally contains some surfactant(s) and additive(s) as

stabilizing agents, and it also contains a base material that is a solvent for all the other ingredients. Typically, the encapsulated, internal droplets in the emulsion are 1-3 micrometers in diameter to provide a good emulsion stability for ELM extraction. When the emulsion is dispersed by agitating in the external, continuous phase during the extraction process, many small globules of the emulsion are formed. The size of the globules depends on the characteristics and concentration of the surfactant in the emulsion, the viscosity of the emulsion, and the intensity and the mode of mixing[Ohtake *et al.*, (1987); Rautenbach and Machhammer, (1988); Ho, (1986)]. Usually, the globule size is controlled in the range of 100 to 2000 μm in diameter. Thus, a very large number of the emulsion globules can be formed easily to produce a very large mass transfer area adjacent to the external, continuous phase. Each emulsion globule contains many 1 to 3 μm internal droplets. Thus, the internal mass transfer area, typically 10^6 m^2/m^3, is even
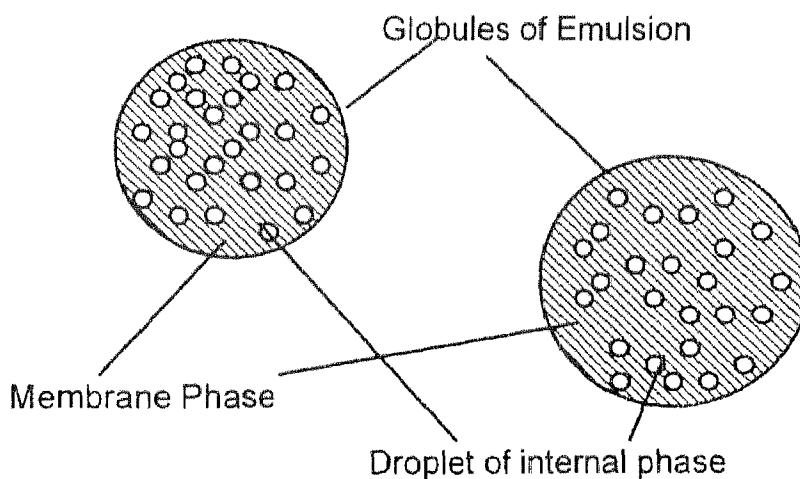
Figure 1.1 Schematic of an Emulsion Liquid Membrane System

much larger than the external mass transfer surface area. Therefore, a rapid mass transfer in the ELM process can occur from either the external, continuous phase to the internal, encapsulated phase.

The configuration of an ELM process is given in Figure 1.2. It consists of four unit operations: (1) Emulsification: the membrane phase and the internal phase are mixed and formed a water-in-oil emulsion. It generates an tremendous interfacial area about 10^6 M^2/M^3 of the emulsion for mass transfer of metal ions in the next operation.(2) mass transport operation: the emulsion is dispersed in the external phase by agitating. Droplets of the W/O emulsion are formed and suspended in the external phase. In the mixing tank, mass transport of metal ions occurs. It takes only a few minutes of mixing time to achieve the mass transport operation. (3) Settling: The droplets (globules) of the emulsion and the external phase are separated in a settling tank after the droplets regaining its form of the
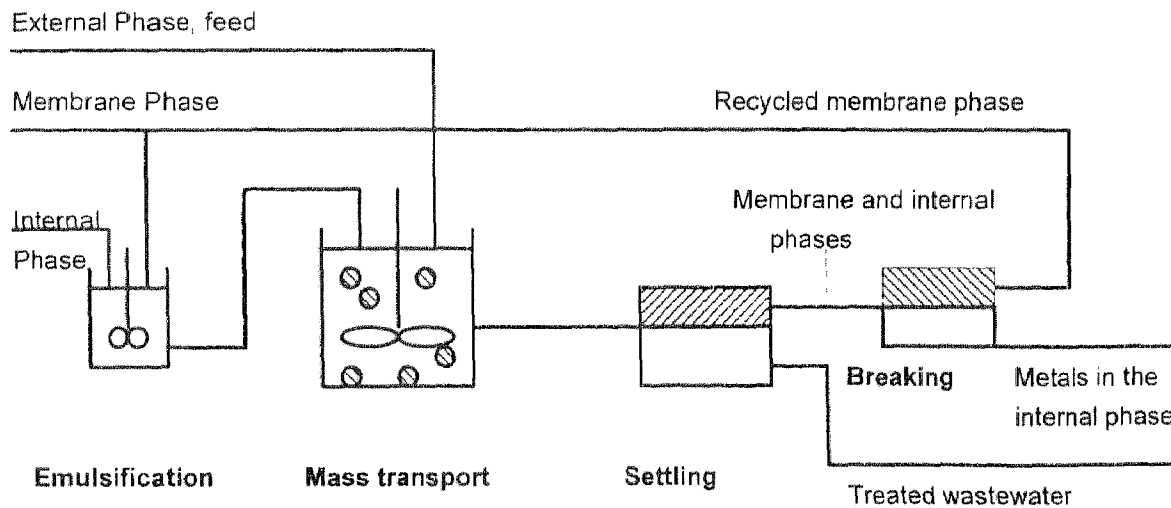
Figure 1.2: Schematic of a Continuous Emulsion Liquid Membrane Process

continuous emulsion on top of the external phase. (4) Breaking operation: The emulsion of membrane phase and internal phase with metal ions in it is then demulsificated and separated using an electrical demulsification apparatus. The metal ions in the internal phase are in the form of an aqueous concentrated solution. The membrane phase will be recycled and used again in the emulsification operation.

1.3 Facilitated Mechanisms

The effectiveness of emulsion Liquid membranes is a result of two facilitated mechanisms called Type 1 and Type 2 facilitations[Matulevicius and Li, (1975), Li, (1978, 1981)]. In Type 1 facilitation, the reaction in the internal phase of the ELM maintains a solute concentration of effectively zero. This is the minimization of the diffusing solute species in the internal phase. The reaction of the diffusing species with a chemical reagent in the internal phase forms a product incapable of diffusing back through the membrane. Extraction of phenol from aqueous phase is a very good example.

Type 2 facilitation is also called carrier facilitated transport. In this type of facilitation, the diffusing species is carried across the membrane phase by incorporating a "carrier" compound (complexing agent or extractant) in the membrane phase, and reactions involving the diffusion species and the carrier compound take place both at the external interface between the external and membrane phases and the internal interface between the membrane and internal phases. In this thesis, all the investigated systems belong to this type. Extraction of strontium ion via di(2-ethylhexyl)phosphoric acid

(D2EHPA, HR) from wastewater can used as an example to illustrate the mechanism of carrier facilitation.

The mechanism involves the following steps:

(1) Mass transfer of strontium ion from the external bulk phase through the mass transfer film resistance to the external interface between the external phase and membrane phase.

(2) Sr ions (Sr^{+2}) reacts with the carrier or extractant (HR) of the membrane phase at the interface between the external and membrane phases.

$$Sr^{2+}\big|_{external} + 2HR\big|_{interface(ext./memb.)} \longrightarrow SrR_2\big|_{interface(ext./memb.)} + 2H^+\big|_{external}$$
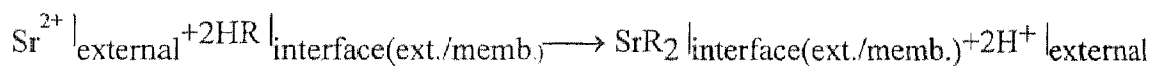
where SrR_2 is the membrane-soluble complex in the membrane phase.

(3) Mass transfer of SrR_2 in the membrane phase from the external/membrane interface to the membrane/internal interface

$$SrR_2\big|_{interface(ext./memb.)} \longrightarrow SrR_2\big|_{interface(memb./int.)}$$
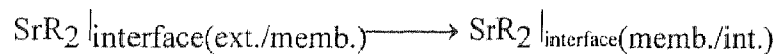
(4) The membrane-soluble complex(SrR_2) at the membrane/internal interface reacts with hydrogen ions from the internal phase.

$$SrR_2\big|_{interface(memb./int.)} + 2H^+\big|_{internal} \longrightarrow 2HR\big|_{interface(memb/int.)} + Sr^{2+}\big|_{internal}$$

The metal ions are released from the membrane phase into the internal phase.

(5) Mass transfer of extractant(HR) in the membrane phase from the membrane/internal interface to the external/membrane interface.

$$HR\,|_{interface(memb./int.)} \longrightarrow HR\,|_{interface(ext./memb.)}$$

This facilitated transfer of strontium ions occurs when the pH value of the internal phase is lower in value than the external phase.

1.4 Advantages of Emulsion Liquid Membrane

For both type 1 and type 2 facilitations, there are several advantages of the emulsion liquid membrane process over the solvent extraction process. They are (1) Simultaneous extraction and stripping take place in one single step rather than two separate steps as required by solvent extraction. This is one of important advantages of ELM extraction versus solvent extraction. (2) The ELM feature of simultaneous extraction and stripping removes the equilibrium limitation inherent in solvent extraction. Therefore, the complete removal of the solute from feed can be achieved with single-step ELM extraction. (3) Another advantages resulting from non-equilibrium feature of an ELM process is the significant reduction of the extractant inventory required for the ELM extraction versus solvent extraction. The reduction by a factor of more than 10 is possible so that expensive extractant can be used. (4) High flux is possible. By combining the advantages of high diffusion coefficient in the liquid phase with the added carrying capacity of the carrier, larger flux than polymer membrane is possible. (5) Very selective separation are possible. The selective nature of the carrier provides much better separation than those obtainable based solely on relative solubility and diffusion. (6) Ions can be concentrated. Coupled transport allows one to pump ions against their concentration gradients. (7) ELM is reported up to 40% less expensive than solvent extraction.[Noble and Way, (1987b)]

1.5 Scope of this Study

This study focused on the application of emulsion liquid membranes on wastewater treatment. For the treatment of arsenic ion from metallurgical wastewater, 2-ethylhexyl alcohol was determined by experiment as an effective carrier. Sulfuric acid and sodium hydroxide solutions were used as external and internal phases, respectively. The effects of operating conditions on extraction performance, such as dosage of the emulsion, acidic strength in the external phase and alkali strength in the internal phase were investigated and optimized. For the treatment of strontium ion from radioactive wastewater, di-(2-ethylhexyl) phosphoric acid was determined as an effective carrier. Sulfuric acid solution was used as the internal phase and a buffer solution of acetic acid and sodium acetate was used as the external phase. The operating conditions were investigated and optimized. In addition, a mathematical model was derived to the model emulsion liquid membrane system and predicted the experimental data. This model not only predicts concentration of solute in the external phase versus time, but also gives the concentration profile inside the membrane globule and the interfacial concentration on external phase-membrane interface. A theoretical investigation of emulsion liquid membrane systems through the mathematical model was conducted.

CHAPTER 2

EXTRACTION OF ARSENIC ION BY EMULSION LIQUID MEMBRANE

2.1 Introduction

Arsenic ranks 20th in abundance in the earth's crust[National Research Council, (1977)],

Most of the arsenic product commercially accumulates as a byproduct in the smelting of

nonferrous metal ores containing copper, gold, silver, lead, nickel and cobalt[Cullen and

Reimer, (1989)]. Today arsenic is almost always an unwanted accompanying element in

metallurgy. In the mining industry, some mine water and tailing water from mineral

processing plants, particularly from nonferrous metal mines, usually contain arsenic. The

discharge of the waste water containing arsenic to an aquatic system poses a potential

threat to the environment. Therefore, it is necessary to treat waste water containing

arsenic[Wolf, (1976)]. In addition, arsenic is well-know as a toxic component, among its

four stable states, (+5, +3, -3 and 0), As(III) is the most toxic one and is reportedly 25-60

times as toxic as As(V) and several hundreds times as toxic as other organic arsenic

compounds so that As(III) is mostly concerned. It has also been suggested that arsenic

may cause neurological damage to those who drink water contaminated with slightly

greater than 0.1mg/l[Korte et $al.$, (1993)]. U.S. EPA demands that waste water

containing less than 0.05mg/L of arsenic can be disposed of. Due to its high toxicity, rare

research has been conducted on arsenic, even its chemistry, but it is clear that pH

determines which arsenate species is dominant. For AS(III), it changes its forms from

H_3AsO_3 to $H_2AsO_3^-$ to $HAsO_3^{2-}$ to AsO_3^{3-} when pH increases. It was reported that As(III)

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has large solubility in basic surroundings(up to 32g/l in 5%NaOH solution), almost 10 times of its solubility in neutral aqueous phase[Baradel, *et al.*, (1986)]

We first successfully applied an emulsion liquid membrane(ELM) process for the removal of arsenic. The membrane was composed of 2-ethylhexyl alcohol(2EHA) as the extractant, ECA4360J as the surfactant and Exxsol D-80 solvent (or heptane) as the diluent. The sulfuric acid solution and the sodium hydroxide solution were used as external and internal phases, respectively. The arsenic removal efficiency reached 92% within around 15 minutes in one stage. Meanwhile, extraction and stripping chemistries were postulated and investigated. It was observed that extraction rate and removal efficiency increase with the increase of acidic strength and alkali strength in the external and the internal phases, respectively. It was also observed that selective removal of arsenic over copper is extremely high. Some other effects were studied, such as diluent properties, agitating speed and initial arsenic concentration. In comparison with solvent extraction process, all the advantages of emulsion liquid membrane were shown on the arsenic removal process, such as mild operating condition, fast removal rate and high removal efficiency at one stage.

2.2 Literature Review

Existing methods of arsenic removal include precipitation, coprecipitation, adsorption, ion exchange, reverse osmosis and solvent extraction. Chemical precipitation and coprecipitation to form insoluble metal hydroxide were the most used treatment methods[Happer and Kingham, (1992); Chou, (1987); Gulledge and O'Connor, (1973)].

Alumina sulfate or ferric sulfate is chosen as coprecipitation reagent, and it was reported that 0.05mg/L of arsenic in effluent could be achieved by adjusting pH value(pH=4.5-8.0 for alumina sulfate, pH=4.0-12.0 for ferric sulfate). The precipitation processes have the advantage of low cost for high volume treatment and easy adjustment for quality control and till now have been the most reliable and effective methods. However, these treatments have their drawbacks. After arsenic and other metals are removed from wastewater, the sludge must be further treated. The toxic arsenic in the sludge is always needed to be separated from other metals such as copper, cadmium etc.

Adsorption was another choice for arsenic removal[Gupta and Chen, 1978; Huang and Fu, (1984); Rosenblum and Clifford, (1983); Bellack, (1971), Diamadopoulos, et al., (1993)]. The adsorbents commonly used are activated alumina and activated carbon. Activated alumina adsorption is highly selective for arsenic. Therefore, from two of them, activated alumina adsorption shows better. The typical alumina used in water treatment is 28-48 mesh (0.3-0.6 mm diameter) mixtures of amorphous and γ-Al_2O_3 prepared by low-temperature(300-600°C) dehydration of $Al(OH)_3$. They have surface area of 50-300 m^2/g. After treatment, Concentration of arsenic in solution can be reduced to less than 0.01 mg/L, so that adsorption is always used as last step for purification. Activated alumina adsorption is highly selective for arsenic, possible to reach low effluent contaminant level and insensitive to flow conditions and the total dissolved solids background. But, it has the disadvantages of slow adsorption kinetics, low capacity treatment, frequent regeneration of packing, and disposal of spent regenerate.

Ion exchange was an innovative method for arsenic treatment by EPA[Clifford and Lin,(1991), Hofheins, (1984)]. A cation exchange resin is chosen when arsenic is As^{3+}, and an anion exchange is chosen when arsenic is AsO_3^{3-} or AsO_4^{3-} . Selection of particular resin also depends on pH of the solution and what other ions in the same solution. Ion exchange makes an essentially zero level of effluent contamination possible, relatively insensible to flow variations and allowable for large quantity treatment. Most ion-exchange resins are completely regenerable and can be operated for thousands of cycles before they are replaced. However, their useful lives can be shortened drastically by fouling, the accumulation of deposit in or on the resin bead. The most common foulants for cation exchangers are clays and iron; humic materials and silica typically foul anion resin. Therefore, ion exchange is a high-cost process and it is always applied as last step for purification .

Reverse osmosis was applied to arsenic treatment as an innovative method by U.S. EPA[Clifford and Lin, (1991)]. The mechanism is that the water is forced from a concentrated salt solution through a semi-permeable membrane into a solution of low salt concentration by the application of hydraulic pressure. The hydraulic pressure must be applied larger than the osmosis pressure, and the rate of water flow through the membrane is proportional to the net pressure difference of hydraulic pressure and osmosis pressure across the membrane, whereas the salt flux is proportional to the concentration difference and independent of the pressure. The reverse osmosis process can treat large quantity of wastewater, and effluent arsenic concentration can also be reduced to very low level. But this process is not selective, all contaminant ions and most dissolved non-

ions are also removed, and because it is one kind of membrane process, membranes are prone to fouling and a high level of pretreatment is required.

Rare reports have been found on arsenic treatment by solvent extraction[Baradel, et al., 1986; Wai, Mok, and Shah, (1986), Rein, et al., (1961); Lyerly and Brerd, (1961)], and almost all the existing papers describing the arsenic extraction were based on analytical point of view. See Table 2-1. In application, Baradel et al. used 2-ethylhexyl-alcohol (2EHA) as the extractant to extract arsenic in 1986, they found that 80-85% of removal efficiency could be achieved in three stages with an organic/aqueous ratio of 5/1 and a very high sulfuric acid concentration in the aqueous phase (200g/l). NaOH solution(5%) was used as the stripping phase. Severe operating conditions restricted its industrial application, but it gave some background for the emulsion liquid membrane process.

Although there is a great deal of interest in emulsion liquid membranes in academic research, up till now, no paper has been found about arsenic removal by ELMs. Because there existed chemistry of solvent extraction for arsenic, together with the matured double emulsion technique, application of emulsion liquid membrane to arsenic treatment is very much interested. The objectives of this study are to find out the workable extractant-surfactant systems and their operating conditions, to determine the extraction mechanism of arsenic and to investigate effects on the mass transfer operation from the external phase to internal phase by parameters, such as formula of the emulsion, external extraction conditions, internal stripping conditions, etc..

Table 2-1 List of the Previous Work on the Extraction of Arsenic

Author	Extractant	Extraction Condition	Efficiency	Stripping
Baradel, A. *et al*, , 1986	Long Chain Alcohol 2-Ethylhexyl Alcohol (2EHA) in TBP	1-10g/L of As total H_2SO_4 solution(200g/L)	80-85%	Na(OH)
Wai, C.M.*et al*, 1986	Ammonium pyrrolidinecarbodithioate(APCDT) or diethyldithiocarbamate(NaDDTC) in Chloroform	1g/L of As total pH=1-1.5	100%	HNO_3
Rein, J.E. *et al*, 1961	(Propyl, Butyl, Hexyl) Amine Complexes	Not given High HCl solution (5N HCl)	around 50%	Not given
Lyerly,L.A. *et al*, 1961	Catechol or Catechol in Benzene	1.0g/L of As total High HCl solution (8-10N)	80-100%	Not given

2.3 Experimental

The arsenic solution(feed) was prepared by dissolving the arsenic trioxide(Sigma Chemical Co.) in a sodium hydroxide(Aldrich Chemical Company) solution. pH was adjusted by adding a sulfuric acid solution and then the arsenic(III) solution was diluted to 100 ppm (Approx.) for further usage. The emulsion consisted of membrane and internal phases. The membrane phase was formulated with a diluent, such as heptane(Fisher Scientific), Exxsol D-80 and Isopar M (Exxon Chemical Company), a carrier, such as 2-ethylhexyl alcohol (2EHA, Aldrich Chemical Company), and a surfactant, such as ECA4360J(Exxon Chemical Company). See Figure 2.1 for their chemical structures. ECA4360J is a nonionic polyamine with a molecular weight of about 1800.

The typical volume fractions of three components in the membrane phase were 88:10:2. The emulsion was prepared by adding the internal aqueous phase(0.5-2.0 N NaOH) in the formulated membrane phase at a ratio of 1/9-1/5, and then emulsified by use of a Warring blender for 30 minutes at the fixed agitated speed of 10,000 rpm, then cooling down to room temperature. The emulsion was freshly prepared each time before the permeation experiment.

The prepared emulsion was then dispersed in an agitated vessel with the feed arsenic solution in a volume ratio of 1/5. Agitated speed was controlled at 300 rpm(others if indicated) and detected by a digital stroboscope(Cole-Parmer). pH value was measured by pH meter (PHCN-31, OMEGA), and samples were taken periodically for further separation, dilution and instrumental analysis. Inductively coupled plasma-mass spectrometry(ICP-MS, VG PLasma Quad, VG Elemental Limited) was used for quantitative analysis.

$$CH_3\text{-}(CH_2)_3\text{-}\underset{\underset{\displaystyle C_2H_5}{|}}{CH}\text{-}CH_2\text{-}OH$$

2-ethylhexyl alcohol(2EHA)
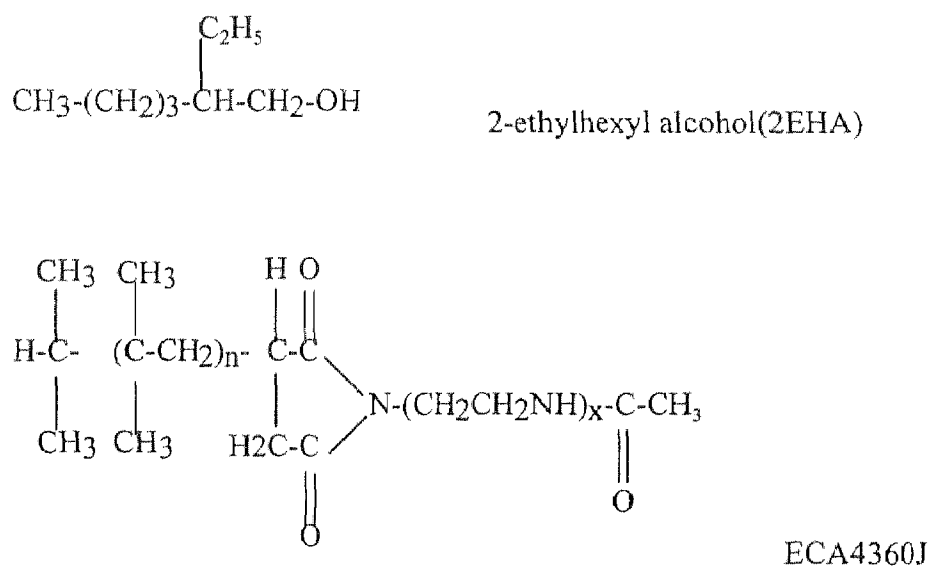
ECA4360J

Figure 2.1 Chemical Structures of 2EHA and ECA4360J

Equilibrium data were achieved by extraction and stripping experiments in separatory funnels. Extraction was conducted in O/A = 2:1 when the organic phase was formulated as 90 v% of heptane and 10 v% of 2EHA, and the aqueous phase contained 100 ppm of arsenic in 0.2 M sulfuric acid solution. Stripping was conducted in A/O = 1:1 where the stripping phase was a 1.0 N NaOH solution. Both extraction and stripping were conducted in closed vessel with magnetic stirring for 24 hours.

2.4 Mechanism

Baradel's work proved that arsenic can be extracted by 2EHA in an acid solution and stripped by an alkali solution, and the higher of the acidity in the extraction phase and the higher of the alkalinity in the stripping phase, the higher is the removal efficiency of arsenic. All these facts substantiated the possibility of arsenic removal by application of an emulsion liquid membrane(ELM), because one of the advantages of ELM is to separate two aqueous phases with extremely different conditions by an organic membrane phase. Thus, the extraction and stripping of the arsenic can happen simultaneously at interfaces of either side of liquid membrane. A surfactants, such as ECA4360J, is used to stabilize the liquid membrane. A extractant, such as 2EHA, acts as the carrier to transport arsenic from the external aqueous phase to the internal aqueous phase.

The dissociation of three proton ions of arsenic acid is at pH=2.25, 6.67 and 11.52(refer to $K_1=5.6*10^{-3}$, $K_2=1.7*10^{-7}$ and $K_3=3*10^{-12}$ respectively), that means arsenic exists as H_3AsO_3 in a strong acidic solution, such as 0.2M H_2SO_4, and exists as AsO_3^{-3} in

a strong alkali solution, such as 1N NaOH solution, together with the assumption of 2EHA acting as basic extractant, the postulated mechanism of arsenic transport by the ELM is follows:

Extraction:

$$nROH + AsO_3^{-3} + 3H^+ \equiv\!\equiv\!\equiv (H_3AsO_3)*(ROH)_n \tag{2.1}$$

Organic Phase   Aqueous Phase   Organic Phase

Stripping:

$$(H_3AsO_3)*(ROH)_n + 3OH^- \equiv\!\equiv\!\equiv nROH + 3H_2O + AsO_3^{-3} \tag{2.2}$$

Organic Phase   Aqueous Phase   Organic Phase   Aqueous Phase
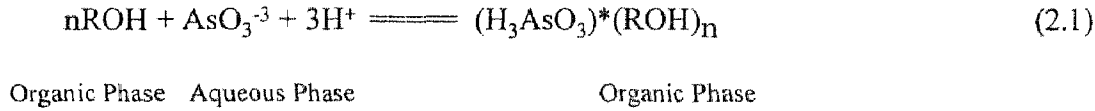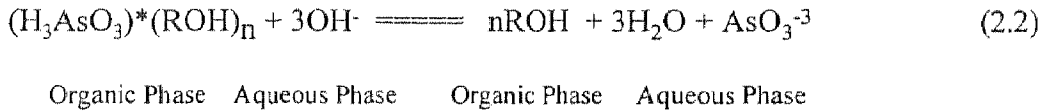
Excess hydrogen ions in the external phase and excess hydroxide ions in the internal phase are used as driving force to pump arsenic ions across the membrane so that recovery can be achieved. Although this mechanism has not been fully proven in this dissertation, it is consistent with our results, as well as the results obtained by others who have studied liquid-liquid extraction.

The distribution coefficient (m)of arsenic in the membrane phase and the external phase increases with acidity of the external phase and the concentration of 2EHA in the membrane phase.

From chemical equilibrium of equation (2.1)

$$Keq = \frac{[(H_3AsO_3)\bullet(ROH)_n]}{[H^+]^3 \bullet [AsO^{-3}_3] \bullet [ROH]^n}$$

$$\tag{2.3}$$

$$m = \frac{[(H_3AsO_3)\bullet(ROH)_n]}{[AsO^{-3}_3]} = Keq \bullet [H^+]^3 \bullet [ROH]^n$$

The exponential of proton ion concentration must be 3 due to the chemical ion charge balance. The value of n, order of ROH concentration, should be determined experimentally. The result shows in Figure 2.2. It may be found that the distribution coefficient m ranges from 0.16 to 0.59 when 5 to 100% volume fractions of 2EHA in the membrane are applied, other experimental conditions are shown on the figure. After regression, n is found at around 1/3, which implies the solute-carrier complex is in the form of $3(H_3AsO_3)*(ROH)$. But, the chemical structure of this complex can't be easily figured out and so that further investigations are needed. However, this coefficient is useful for calculating some parameters, such as diffusivity for model prediction.

ECA4360J, as a nonionic polyamine, has been used as the surfactant to stabilize the double emulsion. Its advantage of preventing serious swelling has been proven by many researchers[Nakashio, Goto, Matsumoto, and Kondo, (1988); Qian, Ma, and Shi, (1989)]. It is sparingly soluble in water[[Draxler, Furst, and Marr, (1988)], and shows high chemical stability, especially against bases[Zhang and Xiao, (1990)]. The dosage of ECA4360J in the membrane phase was optimized at around 3wt% to overcome the emulsion break-up and swelling problems[Nakashio, (1993)], which reflected to about 2v% in our experimental conditions. Thus, 2 v% of ECA4360J was chosen for all our experiments.
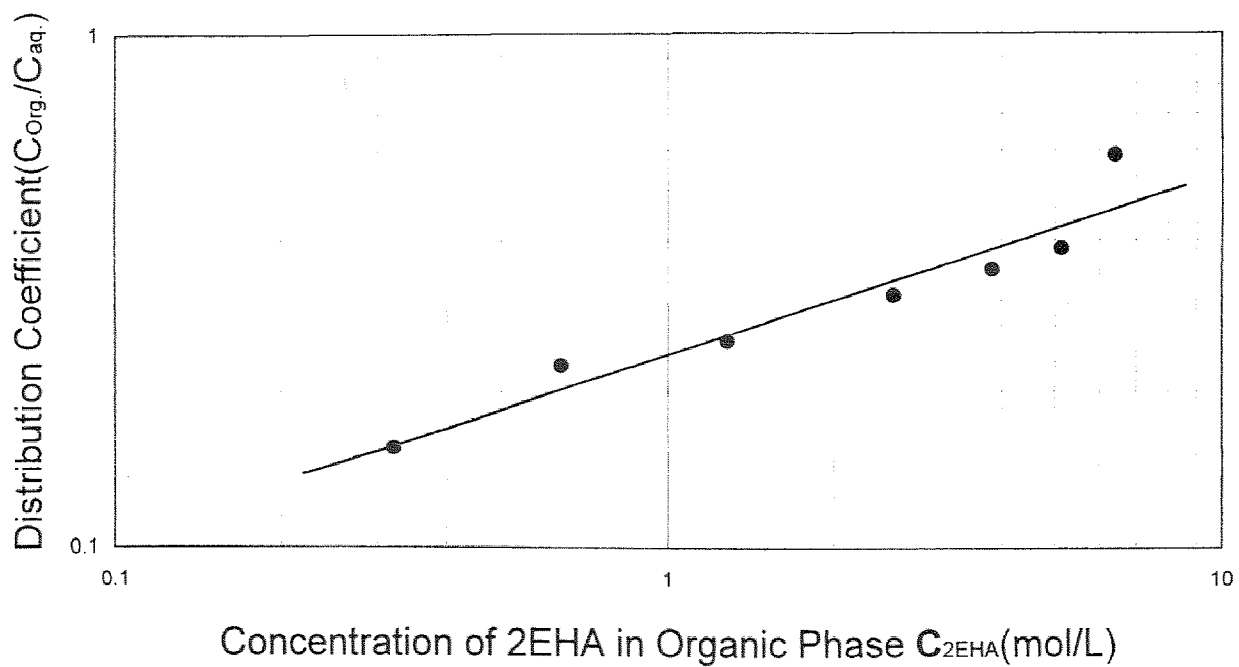
Figure 2.2 Determination of Arsenic-2EHA Distribution Coefficient
Aqueous phase: 10ml, Initial As Concentration: 85.90ppm, acidic strength: 0.2 M H_2SO_4
Organic phase: 20ml, Extractant: 2EHA, Diluent: Heptane, 2EHA Conc. see figure
Experimental condition: magnetic stirring in closed vessel for 24 hours at room temp.

2.5 Results and Discussion

2.5.1 Effect of 2EHA Concentration on As Removal via ELM

The concentration of 2-ethylhexyl alcohol (2EHA) in the membrane phase was investigated. The experimental results are shown in Figure 2.3. Both extraction rate and removal efficiency increase as the concentration of 2EHA increases from 5v% to 10v%. But, with further increase to 50v%, the dimensionless arsenic concentration drops at a quicker rate initially, and rebounds after 5 minutes. These phenomena can be explained as that the high-concentration extractant is helpful to increase the extraction kinetics and solubility of arsenic from the external aqueous phase to the organic membrane phase, both facts will accelerate the removal rate. However, emulsion liquid membranes have their own characters, such as swelling and break-up. High-concentration 2EHA would help transport of water from the external phase to the internal phase which causes swelling. If swelling is very serious, internal droplets will enlarge in volume so as to have a possibility to break the outside membrane when the membrane-internal interfacial tension can't resist. Break-up causes instability of the emulsion and liberty of already extracted arsenic into the external aqueous phase. It could be visualized that the emulsion was unstable when 50v% 2EHA was used, but was very stable in the cases of 5v% and 10v% extractant. Further, due to its low price, nontoxity and physical and chemical stability, 10v% of 2EHA in the membrane phase was used for all following experiments, because it gave faster extraction rate and higher removal efficiency when compared to 5v% concentration.
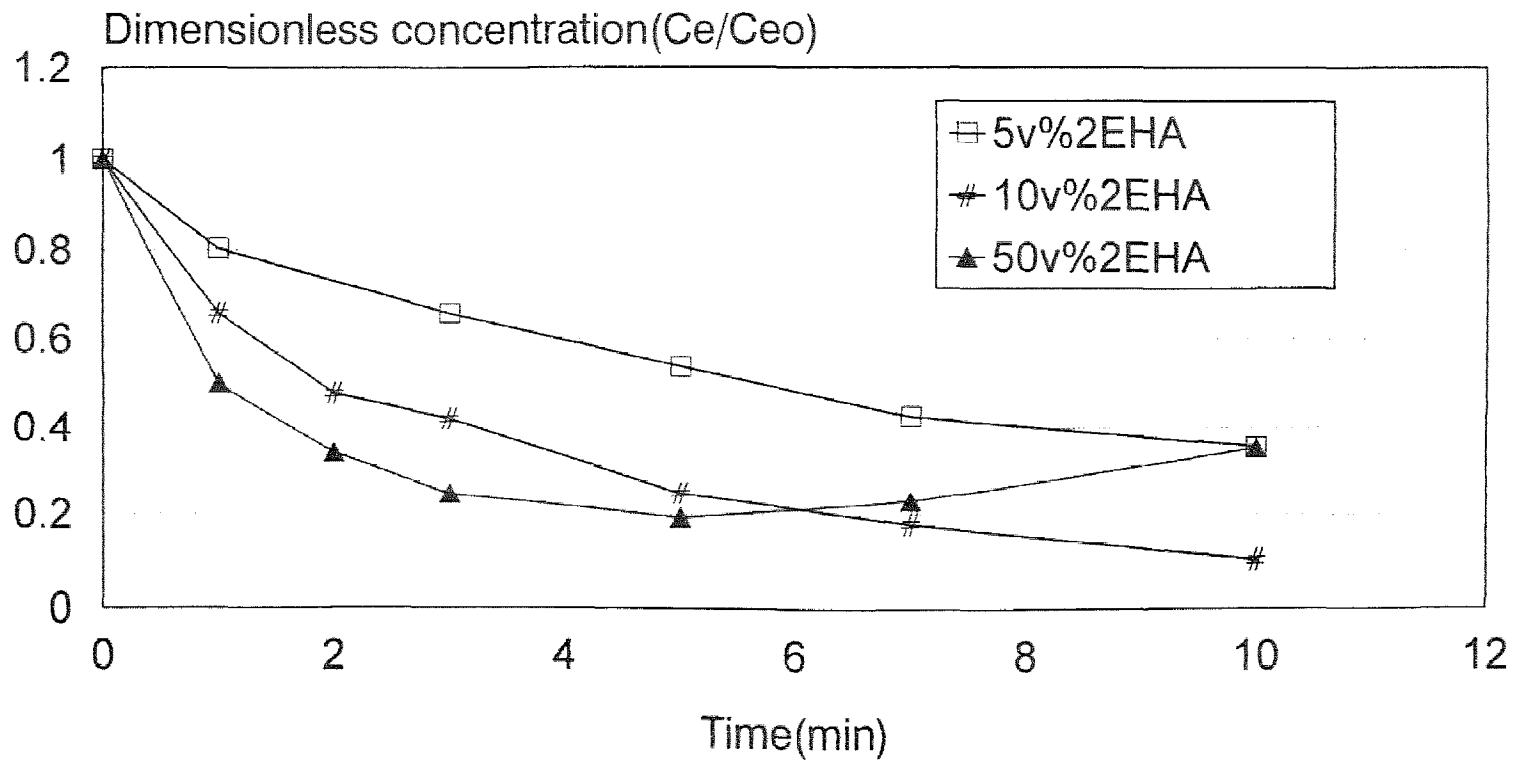
Figure 2.3 Extraction of Arsenic by ELM, Effect of Carrier Concentration
Ve=500ml, Co=100ppm(Approx.), 100ml Emulsion, 300rpm, 0.1M H2SO4
Emulsion: 20v%NaOH(1.0M), 2v% ECA4360, 2EHA(see above), rest: Heptane

2.5.2 Effect of External Acidic Strength

Acid strength in the external phase was adjusted by use of a sulfuric acid, and its effect is shown in Figure 2.4. With the increase of sulfuric acid concentration from 0.1M to 0.4M, arsenic removal efficiency increased from 78% to 92%, and the permeation rate increased too, implying high acidity beneficial to transport. The reason is that high proton concentration moves the extraction equilibrium forward (see extraction equation). In other way, it can also be explained by the positive effect of proton concentration on distribution coefficient m. Therefore, a relative higher concentration of the complex at the external phase-membrane interface is achieved that enlargers its permeation driving force into the membrane-internal phase interface when arsenic is stripped. However, the increase of $[H_2SO_4]$ will cost more money, increase difficulty in operation and is also harmful to surfactant since it decreases emulsion stability. Thus, $[H_2SO_4]$ =0.2-0.4(M) is a suitable range for the arsenic removal process.

We also tried chloride acid instead of sulfuric acid, the experiment showed worse performance when same acid strength was used. It can be interpreted that chloride acid may react with ECA4360J so as to destroy the emulsion stability.

2.5.3 Effect of Internal Alkali Strength

Internal alkali strength was adjusted by use of the sodium hydroxide, and its effect on ELM performance is shown in Figure 2.5. The higher the alkali strength, the better the stripping. Arsenic removal efficiency increased from 72% to 92% at the extraction time of 15 min. when [NaOH] was increased from 0.5N to 1N. However, the efficiency increased slightly when [NaOH] was further increased to 2N. the results implied that
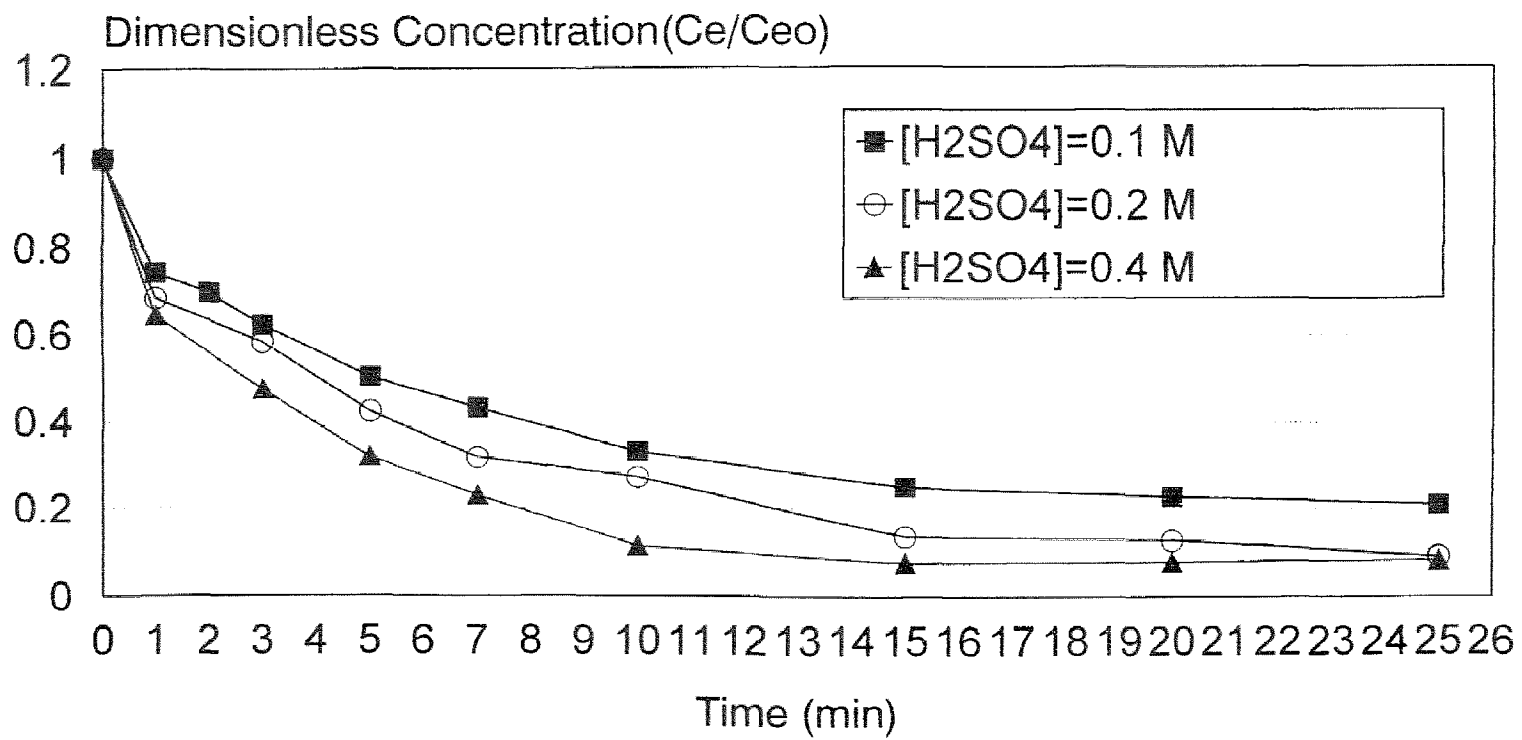
Figure 2.4 Extraction of Arsenic by ELM, Effect of External Acidic Strength
Ve=500 ml, 100ppm As, 300rpm, Acidic strength(see above)
Vi+Vm=100ml, 10v%2EHA, 10v%NaOH(2N), 2v%ECA4360, Rest:Heptane
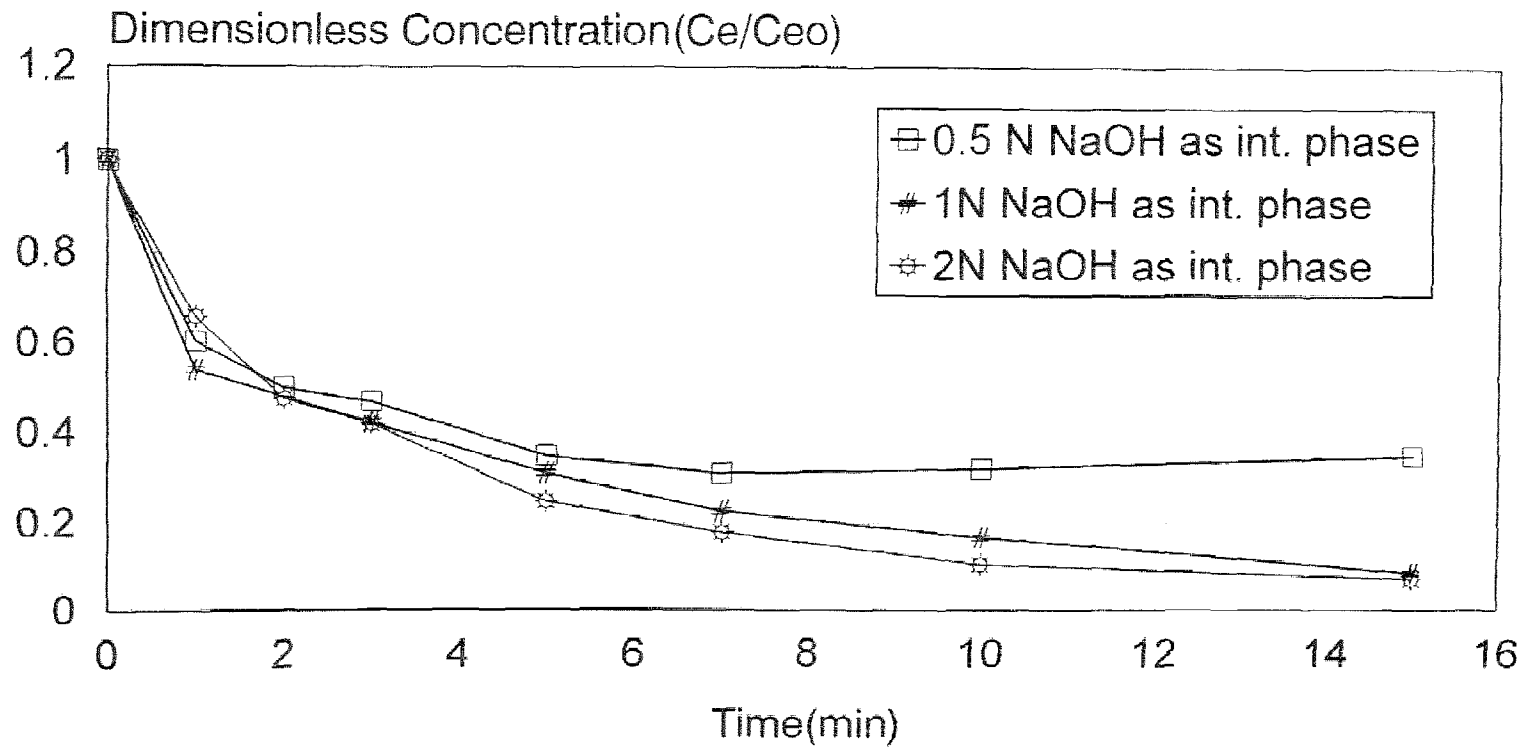
Figure 2.5 Extraction of Arsenic by ELM, Effect of Internal Alkali Strength
Ve=500ml, Co=100ppm(Approx.), 100ml Emulsion, 300rpm, 0.1M H2SO4
Emulsion: 20v%NaOH, 2v% ECA4360, 10v% 2EHA, Rest: Heptane

stripping was completed by 1N NaOH at that operating condition, and the overall arsenic permeation process was not limited by the stripping step. The reason is from the consumption ratio, which is defined as ratio of total mole of arsenic over total mole of hydroxide ion that can accept arsenic ion, was about 10% in this case when [NaOH] is 1N, implying that hydroxide ion is 90% in excess. If [NaOH] was increased from 1N to 2N, the consumption ratio decreased to 5% and hydroxide was 95% in excess. Hydroxide ion not only acted as a receiving agent, but also created a large driving force for facilitated arsenic transport. Thus, excess hydroxide increasing from 90% to 95% would not make a big increase of the driving force. Another reason is that the stripping phase already dispersed stably inside the emulsion globule in very small diameters(1-3 μm) that created huge interfacial area, resulting in complete stripping. This is another advantage of emulsion liquid membrane, when compared with solvent extraction.

2.5.4 Effect of Concentrated Volume Ratio

Concentrated volume ratio is defined as the volume ratio of the external aqueous phase and the internal aqueous phase. A high concentrated volume ratio represents a large reduction of the wastewater volume to a highly concentrated waste which is easy for further treatment. However, when other operating conditions are kept the same, a high concentrated volume ratio will lower the removal efficiency and rate. Figure 2.6 shows experimental results of arsenic removal under the ratios of 25 and 50. Doubling the concentrated volume ratio would half the consumption ratio and decrease the dispersion density of the internal phase in the emulsion globule which causes longer diffusion path
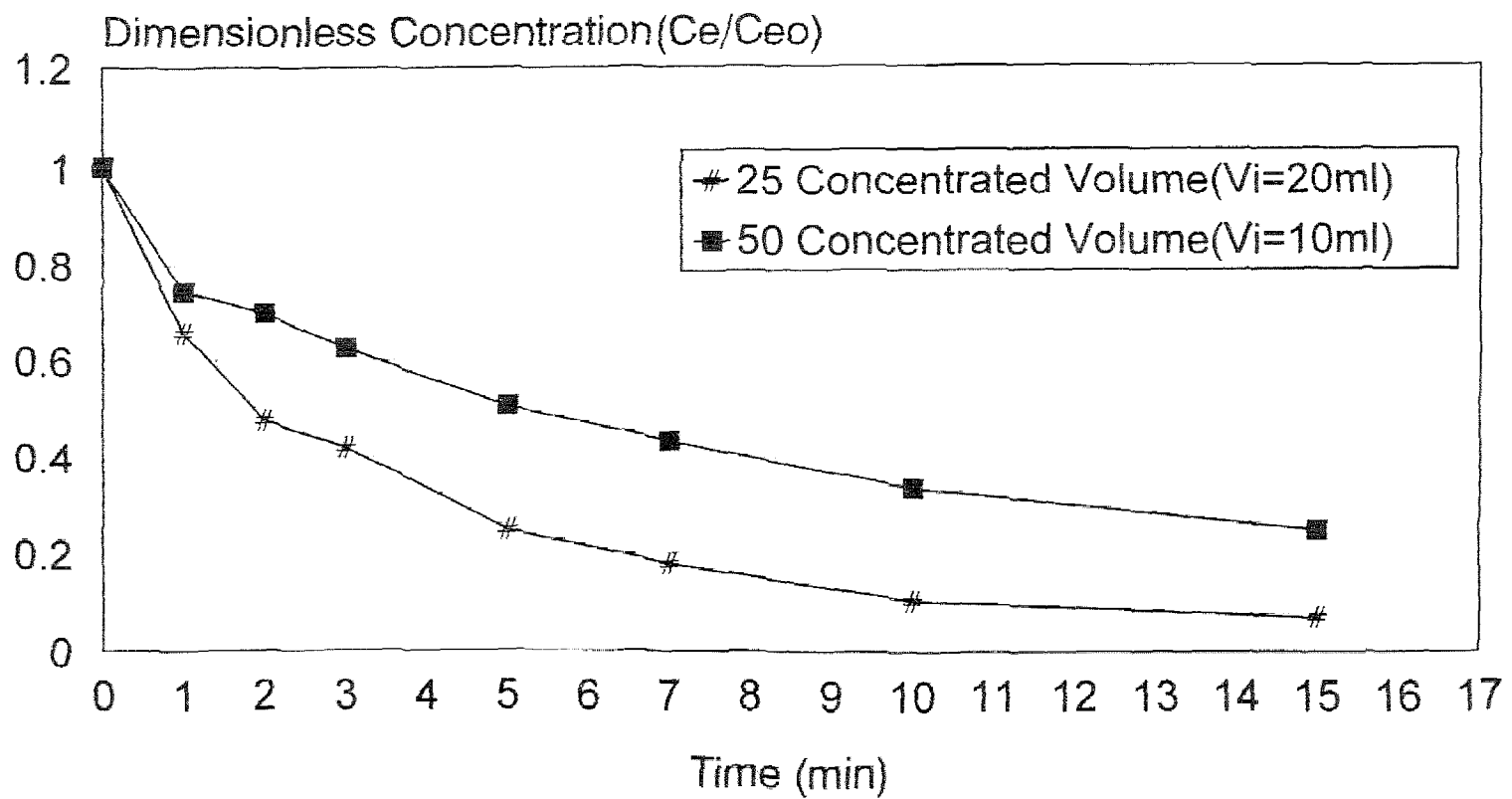
Figure 2.6 Extraction of Arsenic by ELM, Effect of Concentrated Volume Ratio
Ve=500ml, 100ppm[As], 0.1M H2SO4, 300rpm
Vi+Vm=100ml, 2v%ECA4360, 10v%2EHA, Vi(see above), rest:Heptane

of the complex from the external phase-membrane interface to the membrane-internal phase interface. However, an increase of internal alkali strength can make up the loss of consumption ratio. But in this case, in order to keep same consumption ratio, the concentration of NaOH must be doubled to 4N. However, from the conclusion on the effect of internal alkali concentration, stripping will be completed by the 1-2N NaOH solution. Thus, the main reason for lowering the performance was due to the long diffusive path of the complex. It could be overcome by using an extremely high speed emulsifier during the emulsion preparation, but this was restricted by behavior of emulsification apparatus used.

2.5.5 Effect of Initial Arsenic Concentration

Figure 2.7 shows the experimental results of two initial arsenic conditions, 100.9 ppm and 5.51 ppm. They surprisingly gave almost the same performance. The interesting phenomena could be explained as following: in these two experimental conditions, the consumption ratios were very small, 3.36% and 0.18%, respectively. Hydroxide ions, as a receiving reagent in the internal phase, were very large in excess so that almost remained the same for two processes. Together with the same external acid concentration, change of initial arsenic concentration didn't affect the driving force. This information technologically implies that similar arsenic removal efficiency can be achieved if further lower initial concentration is used, and that removal efficiency can be raised if several ELM stages are arranged in series.
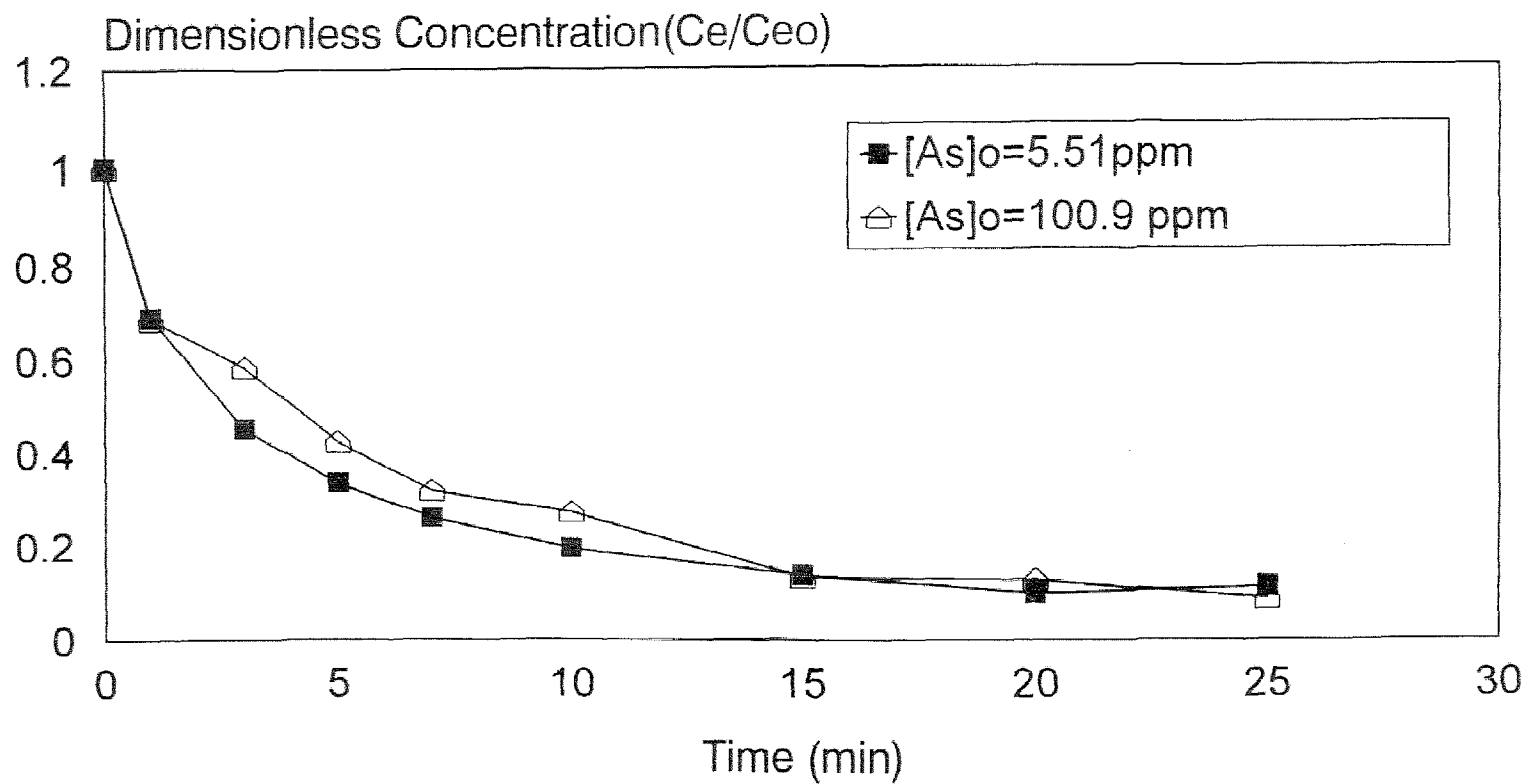
Figure 2.7 Extraction of Arsenic by ELM, Effect of Initial Arsenic Concentration
Ve=500 ml, 5.51ppm As, 300rpm, [H2SO4]=0.2 M
Vi+Vm=100ml, 10v%2EHA, 10v%NaOH(2N), 2v%ECA4360, Rest:Heptane

2.5.6 Selectivity of Arsenic over Copper

Wastewater containing arsenic mostly comes from mineral processing plants, particularly from non-ferrous metal mines. Selective removal of arsenic from other metals is very important. The Figure 2.8 shows the result of its selectivity over cupric ion, as a representative alkali-earth metal. Initial As and Cu concentrations were chosen as 100 ppm and 1000 ppm, respectively, other experimental conditions are shown in the figure. It could be observed that Cu was almost not extracted at all, while arsenic concentration dropped gradually to 10% of its original at 15 min. Extremely high selectivity of arsenic over copper came from that fact that 2EHA, as a extractant, would not form a complex with cupric ion, a alkali-earth metal ion in the acidic surrounding. Due to totally different extraction mechanisms of arsenic and alkali-earth metals, extremely high selectivity can be achieved.

2.5.7 Effect of Diluent Properties

Membrane diluent plays a significant role in the ELM process. It should have low solubility in aqueous phase, its molecular weight and viscosity will determine the diffusivity of metal-carrier complex in the membrane phase, its viscosity will affect the stability of the emulsion and the size of emulsion globule during the agitation, its volatility will affect the loss of the membrane phase and its polarity will affect the distribution of solute between the external aqueous and membrane phases. All its properties will affect ELM process performance. We tried heptane, usually for laboratory research and two other industrial petroleum solvents, Exxsol D-80 and Isopar M. Figure 2.9 shows the results of experiments that were conducted at the same dosage of
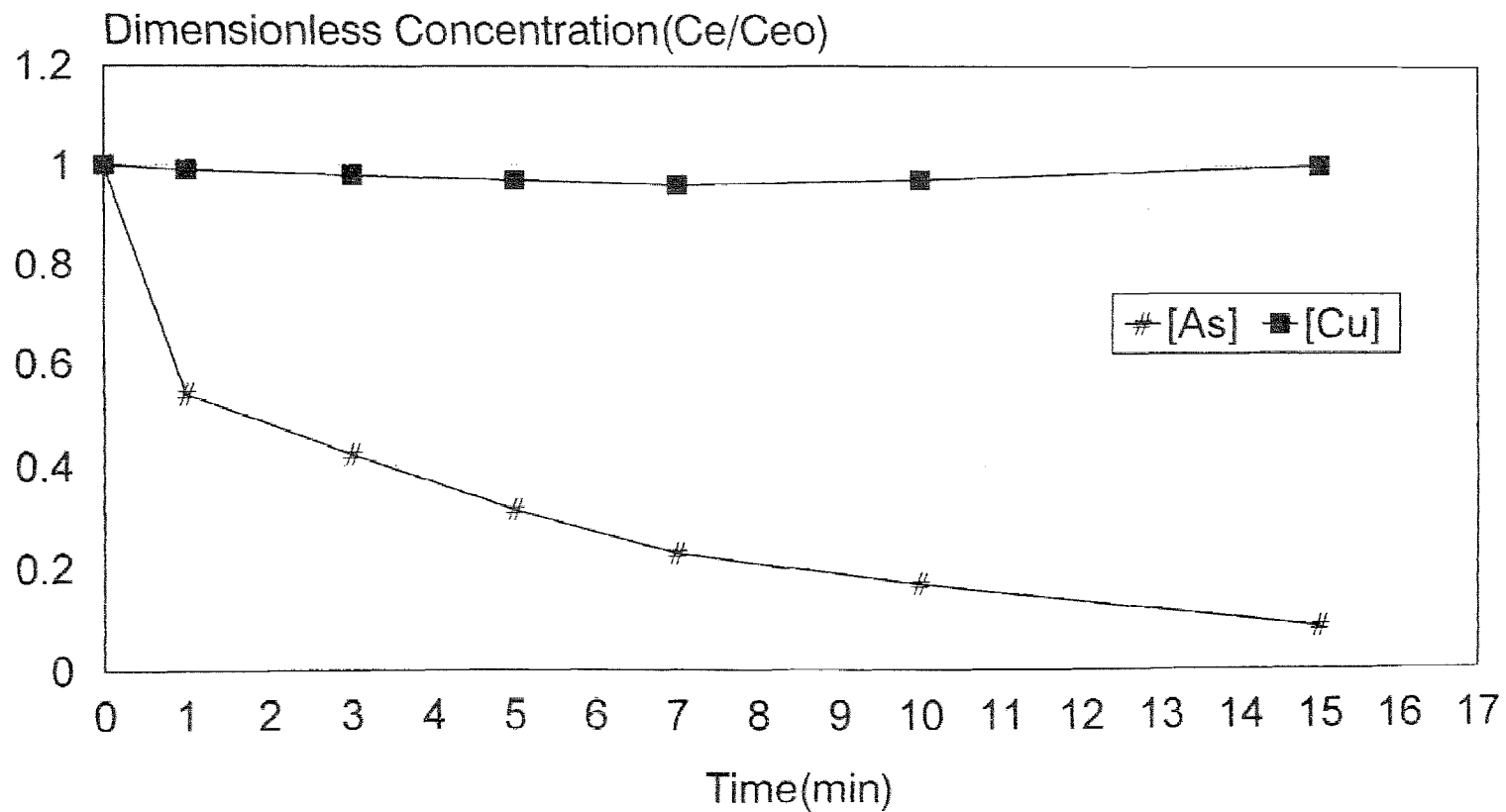
Figure 2.8 Extraction of Arsenic by ELM, Selectivity of Arsenic over Copper
Ve=500ml, 100ppm[As], 1000ppm[Cu], 0.1M H2SO4, 300rpm,
Vi+Vm=100ml, 10v% 2EHA, 2v%ECA4360, 20v%NaOH(1M), 68v%Heptane
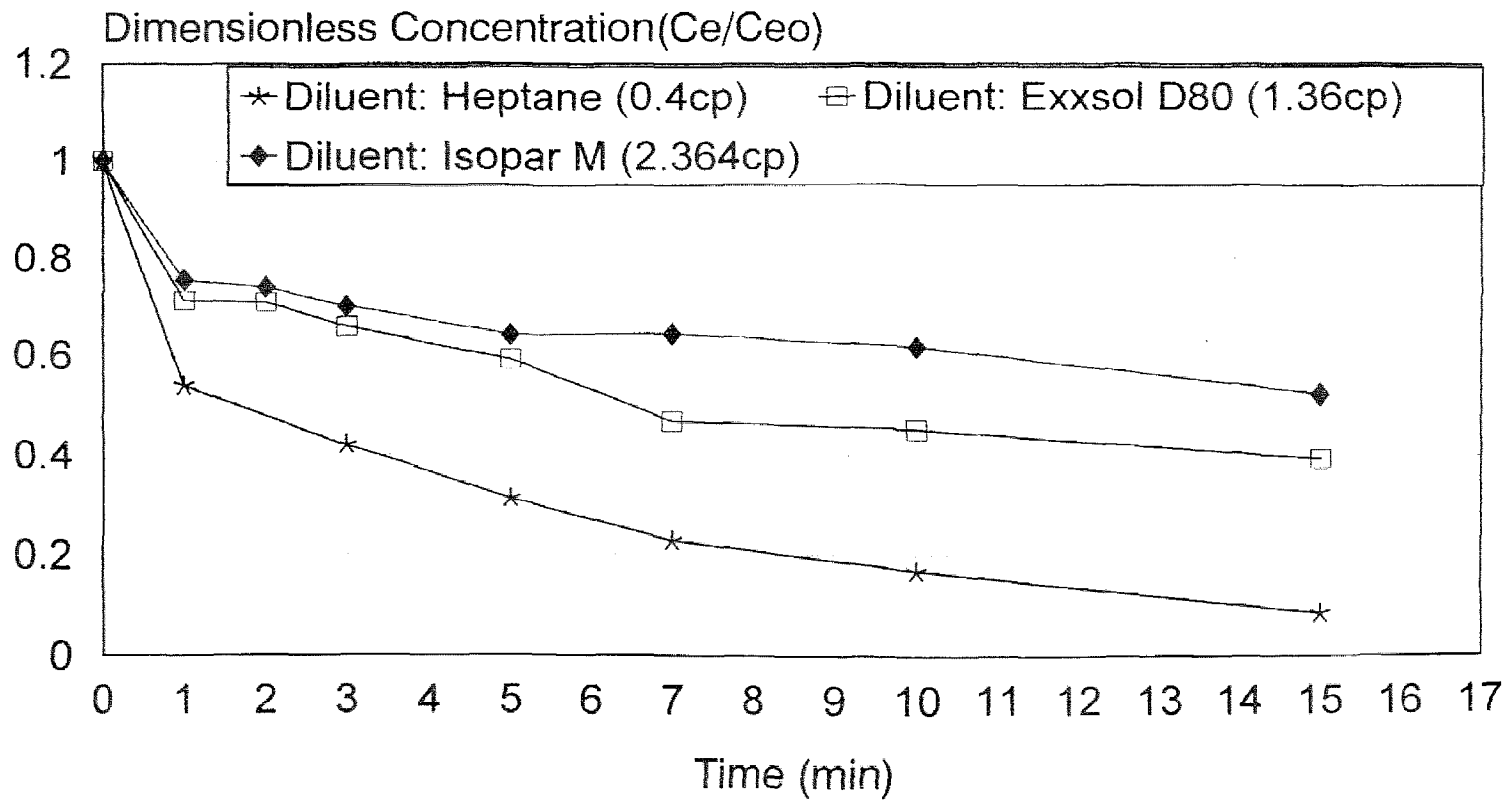
Figure 2.9 Extraction of Arsenic by ELM, Effect of Diluent Viscosity
Ve=500ml, 100ppm As, 0.1M H2SO4, 300rpm,
100ml Emulsion, 10v% 2EHA, 2v% ECA4360J, 20v%NaOH(1M), Rest:Diluent

membrane, external and internal phases and the same agitating speed(300 rpm approx.), but only with the change of the diluents. The arsenic removal rate and efficiency decreased from heptane to Exxsol D-80 to Isopar M. The phenomena can be interpreted by their different viscosity. Heptane, with the lowest viscosity(0.4 cp), resulted in the highest complex diffusivity (De is inverse proportional to viscosity in the Wilke-Chang equation) and the smallest globule size inside agitating vessel (the Sauter mean diameter d_{32} is proportional to $\mu^{0.3-0.7}$). Therefore, it will show better performance over other two solvents. But, from the viewpoint of its physical properties, heptane can't escape its drawbacks of high volatility so that it is only be used as laboratory diluent. Exxon Isopar M, with the highest viscosity, slow down the As permeation so that it showed the worst performance Another drawback of Isopar M was so viscose that the emulsion sticks to the permeation vessel and agitator, so as to affect the separation speed of the membrane phase and the external phase after the permeation process. Thus, it is not practical for industrial use. Exxsol D-80, with viscosity of 1.36 cp, in between heptane and Isopar M, overcome drawbacks of both. It has neglectable volatility, moderate viscosity, not too large to slow down the permeation, or not too small to decrease membrane strength. It also has a high flash point of 80 °C for safety and an enough low density of 0.798 for fast phase separation. But at an agitating speed of 300 rpm, the As permeation rate and removal efficiency were both low, Thus, an increase of agitating speed was investigated.

2.5.8 Effect of Agitating Speed

Agitating is used to disperse the emulsion to form emulsion globules in the external phase. The higher the agitating speed, the smaller is the globule size, resulting in a larger
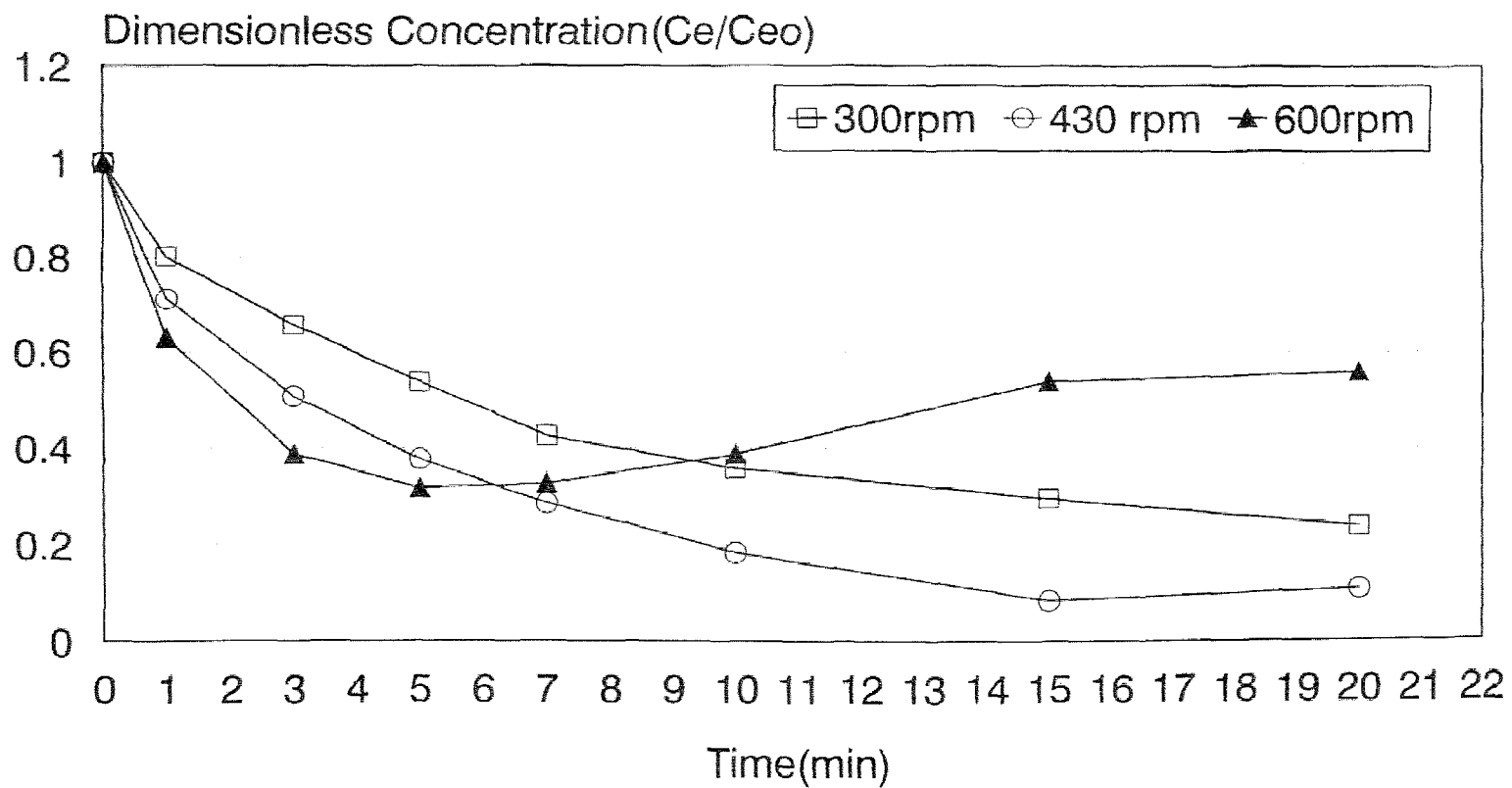
Figure 2.10 Extraction of Arsenic by ELM, Effect of Agitating Speed
Ve=500ml, 100ppm(apr.), 0.2M H2SO4,D-80 as Diluent(1.36cp)
100ml Emulsion, 10v% 2EHA, 2v%ECA4360, 10V%NaOH(1N), Rest:D-80

interfacial area, and a higher external mass transfer coefficient. Both advantages are helpful to mass transfer. But agitating with too much high speed will destroy the stability of the emulsion globules. Figure 2.10 gives the results of three agitating speed conditions. It can be observed that the arsenic permeation rate and removal efficiency were both low at 300 rpm. when increasing to 430 rpm, 93% efficiency was achieved at 15 minutes. However, the curve slightly went up after 15 minutes, representing a small breakup of the emulsion globules. When the speed was further increased to 600 rpm, the dimensionless concentration went down to 32% at 5 minutes and went up quickly, which implied a serious break-up of the emulsion. Actually, the critical agitating speed for serious break-up depends on the type and dosage of the diluent, surfactant and internal phase, the properties of the external phase, and the type of mixer and mixing vessel. In this particular case, the agitating speed should be controlled at 430 rpm or slightly less.

2.6 Summary of Arsenic Extraction via ELM

The feasibility of using the emulsion liquid membrane for the recovery of arsenic(III) has been firstly investigated. 2-ethylhexyl alcohol (2EHA) diluted in some organic diluents was used as the complexing reagent for facilitated transport of arsenic ions in the acidic aqueous phase. An alkali solution was used as the receiving reagent. The maximum of 92% removal efficiency was achieved in one stage within 15 minutes at a concentrated volume ratio of 50(see Table 2.3 for optimal operating conditions). Effect of external acid strength, internal alkali strength, initial arsenic concentration, diluent properties and agitating speed have been investigated. It is found that the arsenic removal rate and

efficiency were increased with the increases of the acidic strength and alkali strength in the external and internal phases, respectively. Almost the same results were found for the cases of 100.9 ppm and 5.51 ppm of the initial arsenic concentrations. This implied that the separation limit of an ELM stage can be removed by use of series stages. The extremely high selective removal of arsenic over copper, a representative alkali-earth metal, has been established.

Table 2-2 Optimal Operating Conditions for ELM Removal of Arsenic

Initial arsenic concentration	100 ppm(Approx.)
Volume ratio of three phases	Ve:Vm:Vi=50:9:1
External phase	0.2M H_2SO_4
Internal phase	2N NaOH
Agitating speed	300 rpm
Membrane phase composition	10 v% 2EHA, 2 v% ECA4360J, Rest: Exxsol D-80

CHAPTER 3

EXTRACTION OF STRONTIUM VIA ELM PROCESS

3.1 Introduction

Radioactive waste is well-known a serious problem facing to the United States. The waste is harmful to human being due to its radioactivity. Its exposure to human being and contamination to water and food will cause severe medical problems including cancer. The waste and environmental problems, located at more than 100 contaminated installations in 36 states and territories, are the result of half a century of nuclear processing activities by the Department of Energy (DOE) and its predecessor organizations. The cost for cleaning up this legacy has been estimated to be of the order of hundreds of billions of dollars.

The emerging problems have attached importance to the U.S. Department of Energy. DOE established its Office of Environmental Restoration and Waste Management(EM) in November, 1989 as the first step toward correcting contamination problems resulting from nearly 50 years of nuclear weapons production and fuel processing activities. Its responsibility included handling, treatment, and disposition of radioactive and hazardous waste. Furthermore, the Efficient Separation and Processing Integrated Program(ESPIP) was created in 1991 to identify, develop and perfect separations technologies and processes to treat wastes and address environmental problems throughout the DOE Complex.

For treatment of radioactive waste in underground storage tank (UST), current approach is to mix the waste with melted glass, and cool it down to normal temperature, so that the radioactive elements, together with all other non-radioactive chemical compounds are fixed inside the glass matrix. Thus, leakage is limited. Then, the whole burden of waste glass is put into a lead metal container to prevent it radioactivity and the lead container is then buried deeply underground the dessert, such as Reno, Nevada[DOE Report, (1994)]. With this technology, the remediation is estimated to cost at least 100 billion dollars for treating 10^8 gal of high level waste at Hanford, Savannah River, Oak Ridge, Idaho and Fernald Sites. Therefore, the greatest technical and financial challenges facing the DOE, EPA and other governmental departments are demonstrating, testing and evaluating new technologies that can reduce costs, improve safety and minimize delays.

The Efficient Separation and Processing Integrated Program(ESPIP) was created in 1991 by DOE to identify, develop and perfect separation technologies. ESPIP's origin came with the realization that if new separations and processes can produce even a marginal reduction in cost then billions of dollars will be saved.

As soon as the mission is established, the urgent needs facing DOE, EPA officials and many research scientists and professors are 1) fully understanding the chemical and physical properties of the waste; 2) classifying the problem priorities; 3) searching for new, safe, fast and low-costly treatment technologies for specific priority; 4) testing, demonstrating and scaling up the reliable technologies.

Priority is being given to (1) the highly radioactive elements, such as strontium-90 and cesium-137, (2) transuranic elements, such as neptunium, plutonium, americium and

cerium (3) long-lived soluble fission products, such as technetium-99 and iodine-129, and (4) soluble activation products, e.g., tritium and carbon-14.

Actually, most of the volume of the waste is composed of non-radioactive materials, such as water and comparatively harmless salts, such as nitrate and nitrite. The source of the radiation, the radionuclides, are typically only a few tenths of one percent of the volume. Strontium-90(Sr-90) and cesium-137(Cs-137) are just two of these radionuclides. Although they, in turn, occur in comparatively small amounts, their physical properties indicate that they are of great importance in waste management considerations. These two substances dominate the fission product radiation, contributing over 90% of the thermal energy and penetrating radiation during the first thirty years after irradiation. These properties lead to major problems in handling the waste in the intermediate processing stages between reclamation of wastes from the tanks and the production of the final waste form, and may have a severely deleterious effect on the behavior of the final waste form. If these two radionuclides could be selectively removed from the waste, there would be an easing of the handling requirements and an improvement in the quality of the glass waste form.

In this study, the emulsion liquid membrane process was investigated as a separation method by using the non-radioactive Sr-87 as its substitute. In our study, the membrane phase was composed of di-(2-ethylhexyl) phosphoric acid (D2EHPA) as the extractant, ECA4360J as the surfactant and Exxsol D-80 as the diluent. The pH range in the external phase was determined by the extraction isotherm. The external pH range was controlled by use of a HAc-NaAC buffer solution. Sulfuric acid was used in the internal

phase as the stripping agent. Under the most favorable operating condition, the strontium removal efficiency reached 98% in two minutes. The other effects, such as selectivity of strontium over sodium and the function of buffer solution, were also studied.

3.2 Literature Review

Solvent extraction is an effective technology to separate strontium ions from an aqueous phase. It was reported that di-(2-ethylhexyl)phosphoric acid (D2EHPA) diluted with tributyl phosphate(TBP) and a hydrocarbon diluent could extract strontium, when pH ranged from 4 to 6. Meanwhile, strong acid, such as nitric acid(HNO_3) and sulfuric acid(H_2SO_4) were proven as effective stripping reagents[Schulz and Bray, (1987)].

Unfortunately, there are a lot of disadvantages for the solvent extraction process. (1). Large amounts of organic extractant and solvent have to used to handle a large volume of the waste, that increase the operating cost. (2). Efficiency of the extraction and stripping is limited by chemical equilibrium of each step, so that a series of extraction and stripping have to applied to increase the total separation efficiency, which increase the capital cost of the separation process. (3). High efficiency requires a series of steps of extraction and stripping, which increase the separation time. (4). A series of extraction and stripping steps requires huge separation facilities which consist of a lot of mixers, settles, pumps, pipes, etc., leading to difficulties of preventing operators from the radioactivity. Thus, the conclusion has been made that solvent extraction is an effective, but not efficient, safe, or cost-effective separation technology for strontium separation.

The emulsion liquid membrane technique has been successfully applied on strontium removal by Inci Eroglu[Eroglu, *et al.*, (1991)] and F. Macasek[Macasek, *et al.*, (1984)]. They both used D2EHPA as the carrier, SPAN-80 as the surfactant and strong nitric acid as the stripping reagent. However, the operating conditions were not optimized so that their removal efficiency only reached 92%-95% by one step, the concentrated volume(volume ratio of the external phase to the internal phase) was low (only 10-20), or extraction operation took a long time(30 min.). In addition, they only used a simple mass transfer model to explain the experimental phenomena. The theory of mass transfer inside the emulsion liquid membrane phase was not discussed.

The objectives of this research were to optimize the extraction conditions and to give clear explanation of emulsion liquid membrane extraction of strontium via detail detailed mathematical model. In our experimental systems, D2EHPA , ECA4360J and Exxsol D-80 were used as the carrier, surfactant and diluent, respectively.

3.3 Experimental

The strontium(Sr-87) solution(feed) was prepared by dissolving strontium chloride (Sigma Chemical Co.) in deionized water. pH was adjusted and controlled by use of a sodium acetate-acetic acid buffer solution. The emulsion consisted of membrane and internal phases. The membrane phase was formulated with the diluent, Exxsol D-80 (Exxon Chemical Company), the carrier, di-(2-ethylhexyl) phosphoric acid (D2EHPA, Sigma Chemical Co.) and the surfactant, ECA4360J (Exxon Chemical Company). The typical volume fractions of three components were 93:5:2. The emulsion was prepared by

adding the internal aqueous phase (3M H_2SO_4) in formulated membrane phase at a ratio

of 1/4-1/2, and then emulsified by use of a Warring blender for 30 minutes at the fixed

agitated speed of 10,000 rpm, then cooling down to room temperature. The emulsion was

freshly prepared each time before each permeation experiment.

RO\
      P=O
RO/   \OH

where

$R=CH_3-(CH_2)_3-CH-CH_2-$

CH_2

CH_3
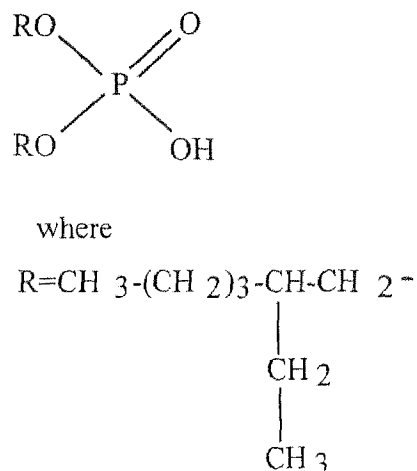
Figure 3.1: Chemical Structure of D2EHPA

The prepared emulsion was then dispersed in an agitated vessel with the strontium

solution in a volume ratio of 1/10. The agitating speed was controlled at 300 rpm (others

if indicated) and measured by a digital stroboscope (Cole-Parmer). The pH value in the

external phase was measured by a pH meter (PHCN-31 OMEGA), and samples were

taken periodically for further separation, dilution and instrumental analysis. Atomic

adsorption spectrometry (AA, Hieftje Smith12) was used for quantitative analysis.

Equilibrium data were obtained via batch extraction and stripping experiments.

Extraction was conducted in O/A = 1:1 when the organic phase was formulated as 95 v%

of Exxsol D-80 and 5 v% of D2EHPA, and the aqueous phase contained 1000 ppm (approx.) of strontium in a 0.1N NaAc-HAc buffer solution. Stripping was conducted in A/O = 1:1 where the stripping phase was a H_2SO_4 (3M) solution. Both extraction and stripping were conducted in closed vessels with magnetic stirring for 24 hours.

3.4 Results and Discussion

3.4.1 Extraction Isotherm

The extraction isotherm of the Sr-D2EHPA system was obtained by changing pH of the aqueous phase in contact with organic solvent. Figure 3.2 shows the dependence of extraction efficiency on pH. It was found that pH has a significant influence on strontium extraction via D2EHPA. Extraction efficiency reached 96-99% when pH ranged 3-4. This implies that D2EHPA is a suitable acidic extractant for strontium ions. It was also found that the lower the pH, the lower the extraction efficiency. This isotherm specified the range of pH for extraction operation. Differing from the solvent extraction process, the emulsion liquid membrane process shows a reduction of the pH in the external phase, due to the back transfer of proton ions from the internal phase to the external phase. Thus, a buffer solution has to be used in the external phase to stabilize the pH. Generally, the NaAc-HAc buffer gives its pH range of 3.5-5.5, which exactly follows this requirement. Another phenomenon was observed that D2EHPA, as an acidic extractant, reacts with aqueous phase with pH greater than 5.5. Thus, the pH of all experiments should be kept lower than 5.5.
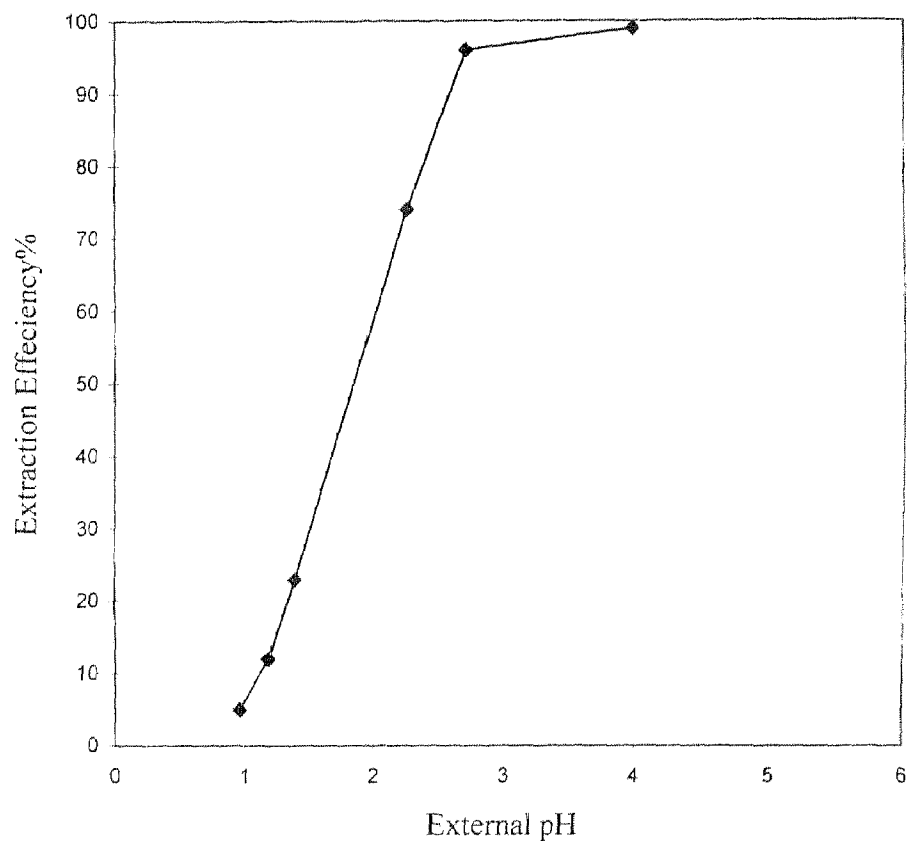
Figure 3.2 Extraction Isotherm of Sr-D2EHPA System

Aqueous phase: 10ml, Initial Sr Concentration: 1040ppm, pH(see figure) is adjusted by 0.1 N HAc-NaAc Buffer or 0.1 N HNO_3 solutions.

Organic phase: 10ml, 5v % D2EHPA as extractant, 95v% Exxsol D-80 as diluent.

Experimental conditions: magnetic stirring in closed vessel for 24 hours at room temp.

3.4.2 Emulsion Liquid Membrane Removal of Strontium

Figure 3.3 gives the experimental results of strontium removal via the ELM. Strontium was quickly removed within almost 1 minute with 98% of removal efficiency. In our experiments, the external phase and internal phase volumes were 500ml and 5ml, respectively, which implied that a large volume of strontium solution could be concentrated at a ratio of 100. Highly concentrated strontium in the internal phase (at $SrSO_4$ form) would be easy for further treatment. Our experimental results were much better than the previously published work[Eroglu *et al.* (1993); Macasek *et al.* (1984)] on efficiency, removal rate and concentrated volume ratio.

The effect of buffer solution on overall performance is also given on Figure 3.3. Efficiency reached 98% or 30 % for the cases with or without the buffer solution. It could be explained when checking the pH changes on Figure 3.4. If the buffer was used, the pH in the external phase dropped slowly from 4.5 to 4.0 within 10 minutes of operation time. When pH ranged 4.0-4.5, the extraction isotherm showed very high extraction efficiency(almost 99%). However, if no buffer solution was applied, pH in the external phase dropped quickly from 4.5 to 2.5 at the first minute, and then to 2.3 within 10 minutes. Thus, from Figure 3.3, the dimensionless concentration dropped from 1.0 to 0.72 for the first minute, and then remained unchanged for the rest of the operation period, due to the bad extraction behavior at the external phase-membrane interface at the low pH surrounding.
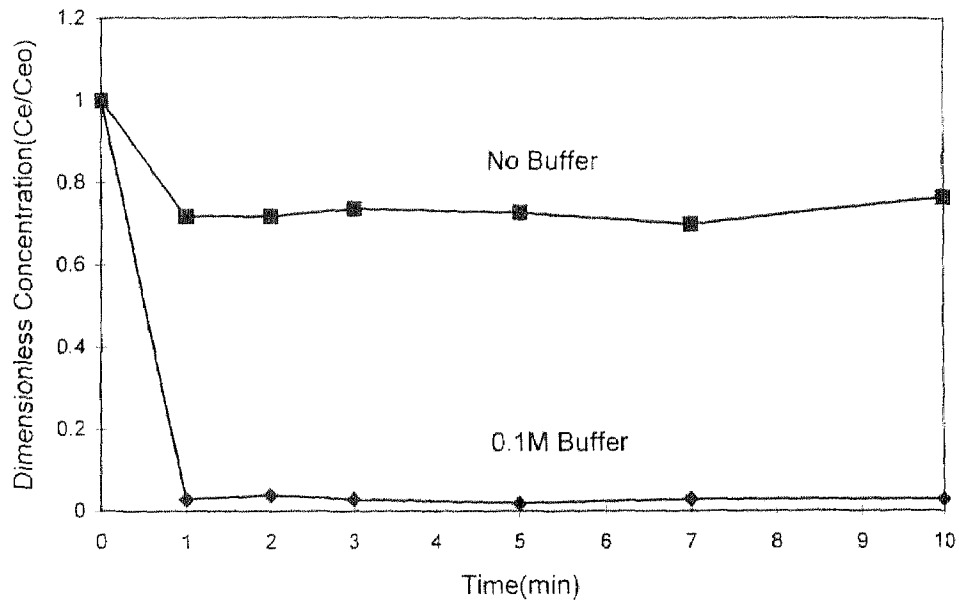
Figure 3.3 Removal of Strontium by ELM
Same conditions as below
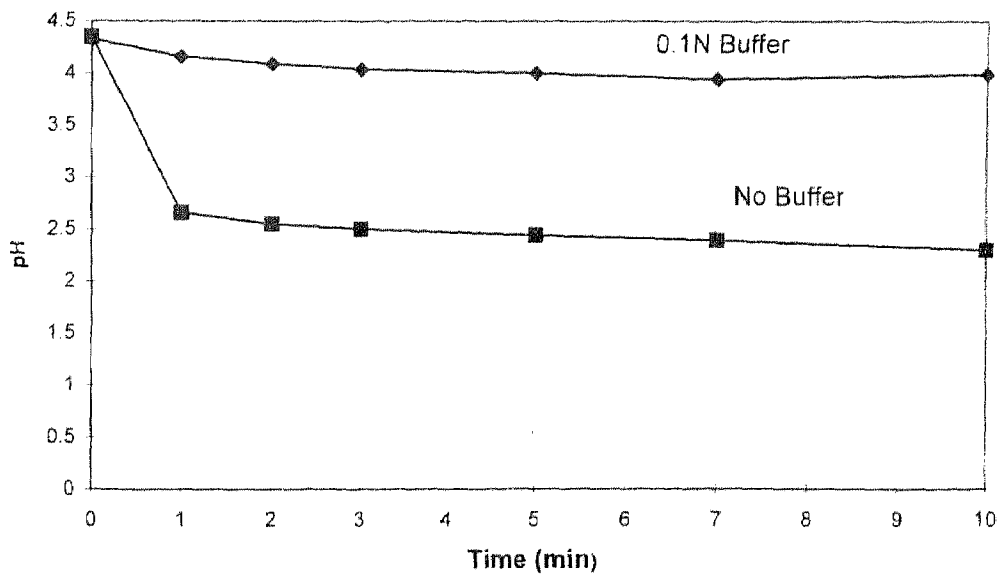
Figure 3.4 Extraction of Strontium by ELM, *pH Changes with Time*
External: 500ml, 1000ppm Sr, 300rpm; Internal: 5ml 3M H2SO4
Membrane: 20ml, 5v% D2EHPA, 3v%ECA4360, 92v% Exxsol D-80

3.4.3 Selectivity of Strontium over Sodium

The HAc-NaAC buffer solution brings a lot of sodium into the system. Meanwhile, there is a lot of sodium nitrate and sodium nitrite existing in radioactive waste. This experiment was designed to identify the competition of sodium ions to strontium ions during the mass transfer process. Figure 3.5 gives the experimental results of dimensionless Sr and Na concentrations change with time. It could be found that strontium had a quick removal with 98% efficiency, but the sodium concentration remained unchanged in the external phase, even though sodium had a bigger initial concentration than strontium. It could be explained that the extractant(D2EHPA) didn't react with alkali metal, such as sodium, but did a form complex with strontium, which is an alkali-earth metal.[Dozol and Casas, (1995)]. Thus, selectivity of strontium over sodium could be achieved.

3.4.4 Effect of Initial Strontium Concentration

Figure 3.6 shows the experimental results of two initial strontium ion concentrations, 1040 ppm and 51 ppm. They gave almost same performance. The interesting phenomena could be explained as follows: in these two experimental conditions, consumption ratios (the mole of strontium in the external phase/the mole of H_2SO_4 in the internal phase) were small, 38% and 2% respectively. H_2SO_4, as a receiving reagent in the internal phase, was large in excess so that stripping conditions were almost same for the two cases. Together with the same external buffer condition, change of initial strontium concentration had no effect on the driving force. This information technologically implied that similar strontium removal efficiency could be achieved if further lower
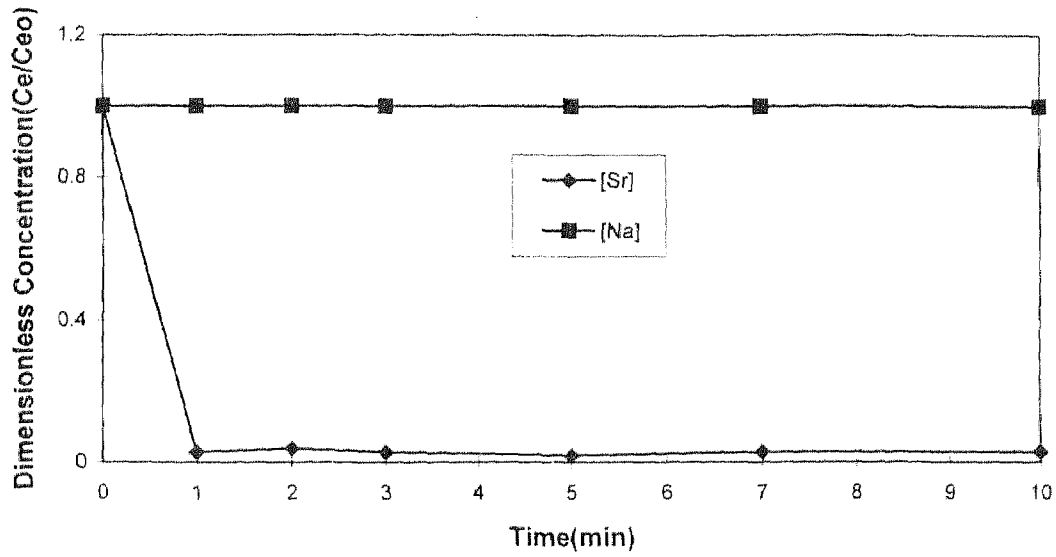
Figure 3.5 Extraction of Strontium by ELM, Selectivity of Strontium over Sodium
External: 500ml, 1000ppm Sr, 0.1 N Na, 300rpm; Internal: 5ml 3M H2SO4
Membrane: 20ml, 5v% D2EHPA, 3v%ECA4360, 92v% Exxon D-80
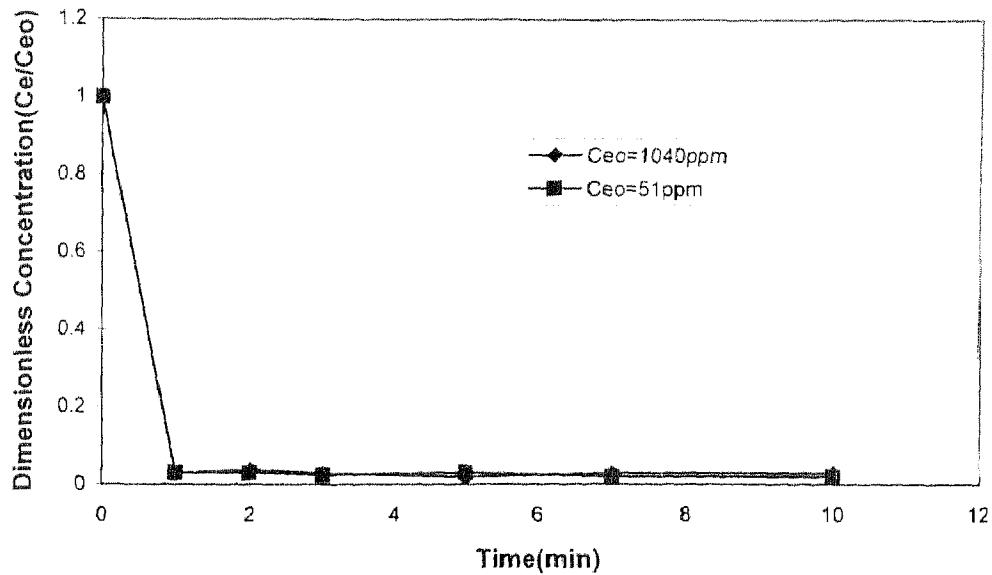
Figure 3.6 Extraction of Strontium by ELM,
Effect of Different Initial Concentrations
External: 500ml, 0.1N Buffer, 300rpm, Ceo see legand; Internal: 5ml H2SO4
Membrane:20ml,5v% D2EHPA,3v%ECA4360J,92v% Exxsol D-80

initial concentration was used, and that removal efficiency could be raised if several ELM stages were arranged in series.

3.5 Summary of the Strontium Extraction via the ELM

The emulsion liquid membrane process was successfully used for strontium extraction. In our study, 98% of removal efficiency was achieved within 1 minute at a concentrated ratio of 100. The Sr-D2EHPA extraction isotherm was found that the pH range in the external phase should be between 3-5. Selectivity of strontium over sodium was extremely high. The optimal operating conditions are listed in Table 3-1.

Table 3-1 Optimal Operating Conditions for the ELM Removal of Strontium

Initial strontium concentration	1000 ppm(Approx.)
Volume ratio of three phases	Ve:Vm:Vi=100:4:1
External phase	0.1 N HAc-NaAc buffer solution
Internal phase	3M H_2SO_4
Agitating speed	300 rpm
Membrane phase composition	5 v% D2EHPA, 2v % ECA4360J, Rest:Exxsol D-80

CHAPTER 4

MATHEMATICAL MODELING OF EMULSION LIQUID MEMBRANE SYSTEMS

4.1 Introduction and Literature Review

After Dr. Norman N. Li invented the emulsion liquid membrane in 1968, numerous mathematical models have been developed. The theory and design for emulsion liquid membranes have been reviewed recently and extensively[Ho and Li, (1992)]. Two categories have been classified for theory of ELMs, (1) diffusion-type mass transfer models for type 1 facilitation and (2) carrier facilitated transport models for type 2 facilitation. The start-of-the-art model for type 1 facilitation is the advancing front model[Ho, Hatton, Lightfoot and Li, (1982)] which assumed that the solute reacts instantaneously and irreversibly with the internal receiving reagent at a reaction surface which advances into the globule as the reagent is consumed. Resulting nonlinear partial differential equations were solved by a perturbation method and it was reported that the zero-order or pseudo-steady state solution in general adequately gave good predication of the diffusion process. Some extensions have been made by Fales and Stroeve[Fales and Strove, (1984); Strove and Varanasi, (1982)] to consider external mass transfer resistance, and it was reported that the external mass transfer resistance is negligible when Biot number is greater than 20. But, this critical Biot number only fits to that specific operating condition, the dependence of the critical Biot number to emulsion capacity hasn't been discussed. In addition, Teramoto considered reaction reversibility in the

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internal phase. Burge and Noble considered the reversibility too[Burge and Noble, (1984)]. Chan and Lee[Chan and Lee, (1987)] and Borwankar[Borwankar, *et al.*, (1988)] considered leakage of the internal phase into the external phase. However, their resulting equations were too complicated to achieve analytical solutions. The start-of-the-art model for type 2 facilitation was developed by Lorbach and Marr[Lorbach and Marr, (1987)] which took into account the diffusion of the carrier and the carrier-solute complex in emulsion globules and reversible reactions at the external and internal interfaces. Although some simplifications have been made on constant summation of free and complex carrier, constant pH in the external phase and negligible resistance for the peripheral thin membrane layer based on Teramoto[Teramoto, *et al*, (1983a)] and Kataoka's models[Kataoka, *et al.*, (1989], there were still 4 parameters dealing with extraction and stripping kinetics and equilibrium that are quite difficult to determine correctly. Actually, extraction and stripping are not the rate-limiting step in the ELM process, because of extremely huge interfacial areas on both internal and external interfaces, even though the intrinsic extraction and stripping rates are low.

Our model takes into account the following: mass transfer of solute across the film between the external phase and the membrane phase, chemical equilibrium of extraction reaction on the external phase-membrane interface, simultaneous diffusion of the solute-carrier complex inside the emulsion globule phase, stripping of the complex at the membrane-internal phase interface and the chemical equilibrium of the stripping reaction at the membrane-internal phase interface. Resulting simultaneous partial differential equations were solved analytically by the Laplace transform method. This

model is capable of predicting theoretically the effects of individual parameters on overall extraction rate. Three dimensionless groups are found with special physical meanings to characterize the emulsion liquid membrane system. This model not only predicts concentration of solute in the external phase Ce(t), but gives the concentration profile inside membrane phase Cm(r,t) and the interfacial concentration on external phase-membrane interface as well. The critical Biot number can be found so that the determination of the external mass transfer rate control or the internal globule diffusion control becomes easy. This model predicted very well the experimental data of arsenic removal and strontium removal by emulsion liquid membrane systems[Huang,Wang and Zhou, (1995)].

4.2 Physical Assumptions and Mathematical Equations

This model can fall into mass transfer model, since the extraction and stripping chemical reactions are assumed very fast so that they are not rate-limiting steps[Wang, (1984)]. Chemical reaction equilibria have been reached for both extraction at the external phase-membrane interface and stripping at the membrane-internal phase interface. This assumption is under the base of the physical structure of ELMs. The internal globules and the emulsion globules are at the radius of 1-10 μm and 0.1-2 mm, respectively, such small droplets create huge interfacial areas for two phases' contact. Thus, the extraction and stripping reactions are assumed to reach equilibria, even though the intrinsic reaction kinetics are not too fast. However, most of the extraction and stripping reactions are very fast, since they are ion-exchange reactions. Other simplifications have to be made in order

to describe the complicated ELMs, and they are similar to the assumptions of other models. (1) emulsion globule is monodisperse and spherical and Saunter mean radius is adequate for describing the globule size[Teramoto *et al.*, (1983a, 1983b)], (2) there is no internal circulation inside the globule, due to sufficient use of surfactant[Rumscheidt and Mason, (1961); Levich, (1962)] thus, mass transfer in the membrane phase is by diffusion only and effective diffusivity is constant in the membrane phase. (3) there is no coalescence and redispersion of emulsion globules[Tavlarides, *et al.*, (1970)], (4) no volume change for each phase, (5) the mass transfer resistance in the internal phase is negligible since the internal droplets are too small, (6) the permeation vessel is well mixed so that the concentration in the external phase is uniform, and (7) the leakage of the internal phase into the external phase is negligible.

Under the above physical assumptions, mathematical equations can be derived for two cases: (1) the external mass transfer resistance is neglected, (2) the external mass transfer resistance is considered.

Case 1: negligible external mass transfer film resistance

External Phase:

$$Ve\frac{dCe}{dt} = -N(4\pi R^2)De(\frac{\partial Cm}{\partial r})_{r=R} \tag{4.1}$$

Initial Condition (I.C.): Ce = Ceo, when t = 0

where: Ve: volume of the external phase (dm^3)

  Ce: concentration of solute in the external phase (mol/dm^3)

N: total number of the emulsion globules

R: radius of the globules

De: effective diffusivity of the solute-carrier complex in the emulsion

phase (m^2/sec)

Cm: concentration of the solute-carrier complex in the membrane phase(mol/dm^3)

At the external phase-membrane interface, the chemical equilibrium is reached

and the external film resistance is neglected. Thus,

$$Cm^* = mCe^* \quad \text{and} \quad Ce^* = Ce \tag{4.2}$$

where: Cm*: concentration of the solute-carrier complex at the external phase-membrane

interface(in the membrane phase), Cm*=fun(t) only

Ce*: concentration of the solute at the external phase-membrane interface(in the

external phase)

m: the extraction partition function at the external phase-membrane interface

Membrane phase:

The spherical shell material balance is taken inside globule membrane:

$$Vm*\frac{\partial Cm}{\partial t} = (Vm + Vi)*De*[\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial Cm}{\partial r})] - Vi*Rx \tag{4.3}$$

Initial Conditions (I.C.):   Cm = 0 for all r,   when t = 0

Boundary Conditions (B.C.): Cm = finite,   when r = 0;   Cm = Cm*,   when r = R

Where: Vm: volume of the membrane phase(dm^3)

Vi: volume of the internal phase(dm^3)

Vm+Vi: total volume of the emulsion

Rx: The disappearance of the solute-carrier complex in the membrane phase

into the internal phase by stripping (mol/dm^3/sec.)

Internal Phase:

$$Rx = \frac{\partial Ci(r,t)}{\partial t} \qquad (4.4)$$

I.C.:   Ci = 0,   when t = 0

where: Ci: concentration of the solute in the internal phase

At the membrane-internal phase interface, chemical equilibrium is reached. Thus,

Ci = q*Cm   (4.5)

where: q: the stripping partition function at the membrane-internal phase interface

We have three partial differential equations and two equilibrium equations, and they are all linear, so that the Laplace transform method is applied to solve three variables: Ce(t), Cm(r,t) and Ci(r.t).

Case 2: external mass transfer resistance is considered:

When the external mass transfer film resistance is considered, equation of the external phase changes to

$$Ve*\frac{dCe}{dt} = -N(4\pi R^2)k(Ce - Ce^*) \qquad (4.6)$$

$$-N(4\pi R^2)De(\frac{\partial Cm}{\partial r})|_{r=R} = -N(4\pi R^2)k(Ce - Ce^*) \qquad (4.7)$$

where: k: the external mass transfer coefficient (m/sec)

other symbols are same as previous

$k(Ce - Ce^*)$ is the flux of mass transfer outside external-membrane interface and

$De \left(\frac{\partial Cm}{\partial r}\right)|_{r=R}$ is the flux of mass diffusion inside external membrane interface. These two

flux must be equal, because there is no accumulation of the solute at the interface.

Also, the equilibrium equation changes to

$$Cm^* = mCe^* \quad Ce^* \neq Ce \tag{4.8}$$

Concentration of the solute in the external phase Ce is greater than that at the

external phase-membrane interface Ce*. The difference of these two concentrations is the

driving force to overcome the external film mass transfer resistance.

In this case, four partial differential equations together with two equilibria

equations are all linear. Thus, the Laplace transform method is applied to solve four

variables Ce(t), Ce*(t), Cm(r,t) and Ci(r,t).

Before changing the equations into their dimensionless form, some derivations

should be made for both cases. by combining equation (4.3), (4.4) and (4.5), we have

$$\left(\frac{Vm + q * Vi}{Vm + Vi}\right) \frac{\partial Cm}{\partial t} = De * \left[\frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial Cm}{\partial r}\right)\right] \tag{4.9}$$

same I.C. and B.C. as before.

Mathematically it means that concentration of the solute-carrier complex in the

membrane phase Cm is proportional to concentration of the solute in the internal phase

Ci, so that these two variables can be simply combined into one. Physically it means that

internal droplets are so small that there is no concentration difference inside it, and the

complex is fast stripped as soon as it reaches the membrane phase-internal interface.

Following are the dimensionless equations describing the ELM systems:

For case 1:

External: $$\frac{dUe}{d\tau} = -m*f*(\frac{\partial Um}{\partial v})\big|_{v=1}$$ (4.10)

Equilibrium: $Ue = Um*$ $Ue = Ue*$

I.C. $Ue = 1$, when $\tau = 0$

Membrane: $$\omega * \frac{\partial Um}{\partial \tau} = \frac{1}{v^2}\frac{\partial}{\partial v}(v^2 \frac{\partial Um}{\partial v})$$ (4.11)

I.C. $Um = 0,$ when $\tau = 0$

B.C. $Um = $ finite   when $v = 0$; $Um = Ue$ when $v = 1$

where: $Ue = \dfrac{Ce}{Ceo}$ $\tau = \dfrac{De*t}{R^2}$ $f = \dfrac{3f'}{1-f'}$ $f' = \dfrac{Vi+Vm}{Vi+Vm+Ve}$

$\omega = 1 - e + e*q$ $e = \dfrac{Vi}{Vi+Vm}$ $v = \dfrac{r}{R}$ $Um = \dfrac{Cm}{m*Ceo}$

For Case 2:

External: $$\frac{dUe}{d\tau} = -Ko*(Ue-Ue*)$$ (4.12)

$$G*(\frac{\partial Um}{\partial v})\big|_{v=1} = (Ue - Ue*)$$ (4.13)

Equilibrium: $Ue* = Um*$

I.C. $Ue = Ue* = 0$, when $\tau = 0$

Membrane: $$\omega * \frac{\partial Um}{\partial \tau} = \frac{1}{v^2}\frac{\partial}{\partial v}(v^2 \frac{\partial Um}{\partial v})$$ (4.11)

I.C. $Um = 0,$ when $\tau = 0$

B.C.   Um = finite   when v = 0;   Um = Ue*   when v = 1

where: $Ko = \dfrac{R*k*f}{De}$ $G = \dfrac{m*De}{R*k}$ $Ue* = \dfrac{Ce*}{Ceo}$ $Um* = \dfrac{Cm*}{mCeo}$

4.3 The Solutions via the Laplace Transform Method

Laplace transform and inverse Laplace transform are taken for equations (4.10) and (4.11), together with their initial and boundary conditions. The analytical solution can be found as following for case 1: external film resistance is negligible:

$$\frac{Ce}{Ceo} = \frac{3}{B+3} + \sum_{n=1}^{\infty} \frac{2B}{3B+B^2+bn^2} \exp(-\frac{bn^2}{\omega}\tau) \tag{4.14}$$

Where bn are eigen values(n=1,2,3...) solved by

$$\tan(bn) = \frac{B*bn}{B+bn^2} \tag{4.15}$$

If same method is applied to equations (4.11),(4.12) and (4.13) and their I.C. and B.C., the analytical solution can be found for case 2: external film resistance is considered:

$$\frac{Ce}{Ceo} = \frac{3}{B+3} + \sum_{n=1}^{\infty} \frac{2B}{3B+B^2+bn^2+Gbn^2(Gbn^2-2B-1)} \exp(-\frac{bn^2}{\omega}\tau) \tag{4.16}$$

$$\frac{C^*e}{Ceo} = \frac{3}{B+3} + \sum_{n=1}^{\infty} \frac{2(B-Gbn^2)}{3B+B^2+bn^2+Gbn^2(Gbn^2-2B-1)} \exp(-\frac{bn^2}{\omega}\tau) \tag{4.17}$$

$$\frac{Cm}{mCeo} = \frac{3}{B+3} + \sum_{n=1}^{\infty} \frac{2(B-Gbn^2)(\frac{\sin(bn*v)}{v*\sin(bn)})}{3B+B^2+bn^2+Gbn^2(Gbn^2-2B-1)} \exp(-\frac{bn^2}{\omega}\tau)$$ (4.18)

Where bn are eigen values(n=1,2,3...) solved by

$$\tan(bn) = \frac{bn*(B-Gbn^2)}{B+bn^2(1-G)}$$ (4.19)

Three dimensionless groups are involved in the solution equations. They are

$$B = mf\omega, \qquad G = \frac{m*De}{R*k} = \frac{1}{Biot}, \qquad \frac{\tau}{\omega} = \frac{t*De}{\omega*R^2}$$

Detailed mathematical derivations are in the appendix of this thesis.

4.4 Engineering Analysis of ELM Systems

4.4.1 The Solution Form

The solution is in summation forms involved with the series number n and the respective eigen values bn. The bn come with standard Sturm-Liouville system in the Laplace transform method, and can be determined by the eigen equations (4.15) and (4.19). Computer algorithms are designed to numerically calculate bn(n) and the summations. Three dimensionless groups appear in the model solutions. The B group can be regarded as the emulsion capability; G is the reciprocal of the Biot number, physically represents
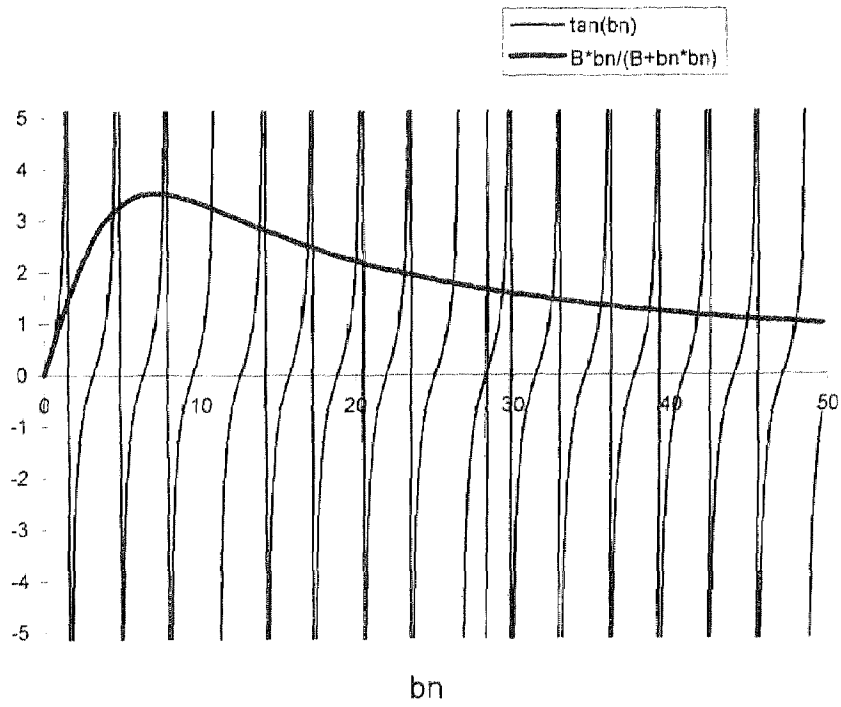
Figure 4.1 Determination of Eigen Value (Case 1, B=50)

the ratio of the external film resistance and the internal globule diffusion resistance and this number determines the importance of the external mass transfer resistance in ELM system; τ/ω is the dimensionless time. The solutions have a non-series term plus a summation of n series. The non-series term forms a base line with its specific physical meaning, and the summation at any specific time is added to the base line so as to form a dimensionless concentration form. The eigen equation is solved by the Newton-Raphson method. Details for case 1 can be seen in Figure 4.1. As soon as being found, eigen value is substitute into the summation form to calculate the concentration at that time. The bigger the eigen value, the less importance is its contribution to the summation. It also may be found that the bigger the dimensionless time, the smaller is the value of summation, because the summation is proportional to $\exp(-\tau)$.

4.4.2 Physical Significance of Time-Independent Term

The non-series term of $3/(3+B)$ is the steady state solution of the partial differential equations. For both cases, $Ce/Ceo=3/(B+3)$, when time approaches infinite. As we mentioned that the dimensionless group B could be considered as emulsion capability. Thus, the bigger the B number, the smaller is the Ce/Ceo, which implies the bigger of the removal efficiency. This steady state solution could be also solved by material balance of the an emulsion liquid membrane system. If volumes of the three phases remind unchanged and leakage is neglected, the steady state material balance is following:

$$Ceo*Ve=Ce*Ve+Cm*Vm+Ci*Vi \qquad (4.20)$$

with two equilibrium equations: $Cm=m*Ce$ and $Ci=q*Cm$

The solution is:

$$\frac{Ce}{Ceo} = \frac{Ve}{Ve + m*(Vm + q*Vi)} = \frac{3}{B+3} \qquad (4.21)$$

The consistence of two approaches implies the correctness of the model. The assumptions should be remembered that it doesn't consider the leakage and volume change of the three phases. Otherwise, the steady state term changes. The steady state term shows us that the removal efficiency increases with the B number. Therefore, a larger B value gives better performance of the ELM system. It is apparent that a good choice of the extractant and extraction conditions will give a large extraction partition function, p, and a good choice of stripping reagent and stripping conditions will give a large stripping partition function, q. Together with a large emulsion volume ratio f and a large internal volume ratio e, the B value can be increased. However, the two volume ratios cannot be selected arbitrarily because of the stability of the emulsion.

4.4.3 Effect of Biot Number on External Mass Transfer Driving Force

Equations (4.14, 4.15) and equations(4.16-4.19) are analytical solutions of the two cases. It can be found that eqns(4.16-4.19) will be simplified to eqns(4.14, 4.15) respectively when the dimensionless group G equals 0. The G is the reciprocal of the Biot number, which physically means the ratio of the external film resistance to the membrane diffusion resistance. If external film resistance is neglected, G equals 0 and the Biot number approaches infinite, so that the case 2 will be physically simplified to case 1 and
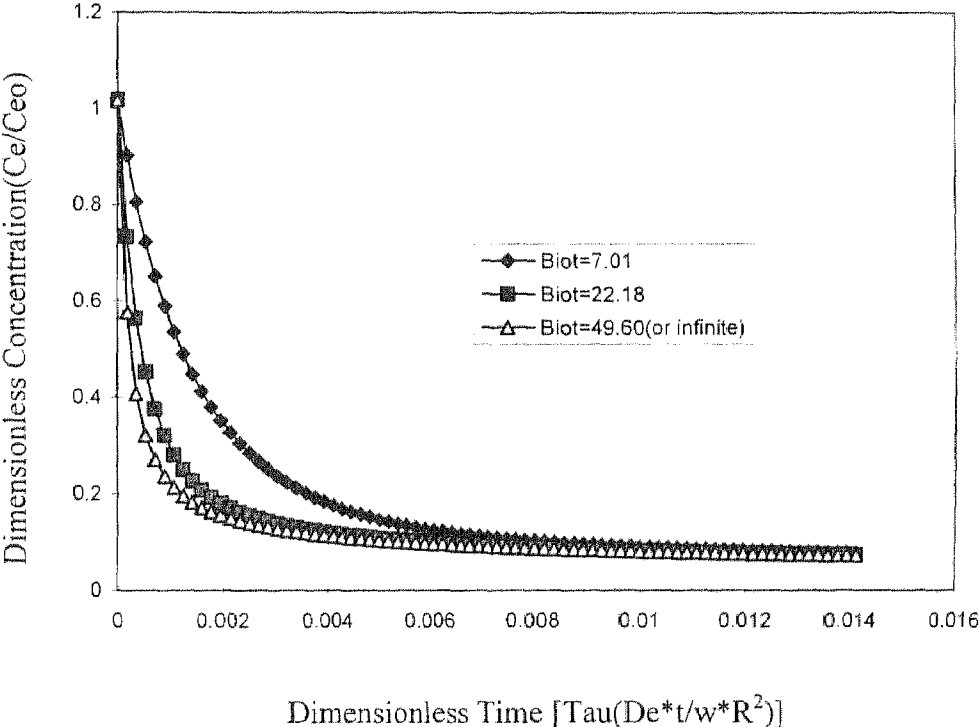
Figure 4.2 Effect of the Biot Number on ELM Performance (B=105)

Biot=7, B=105

Biot=22, B=105

Biot=50, B=105
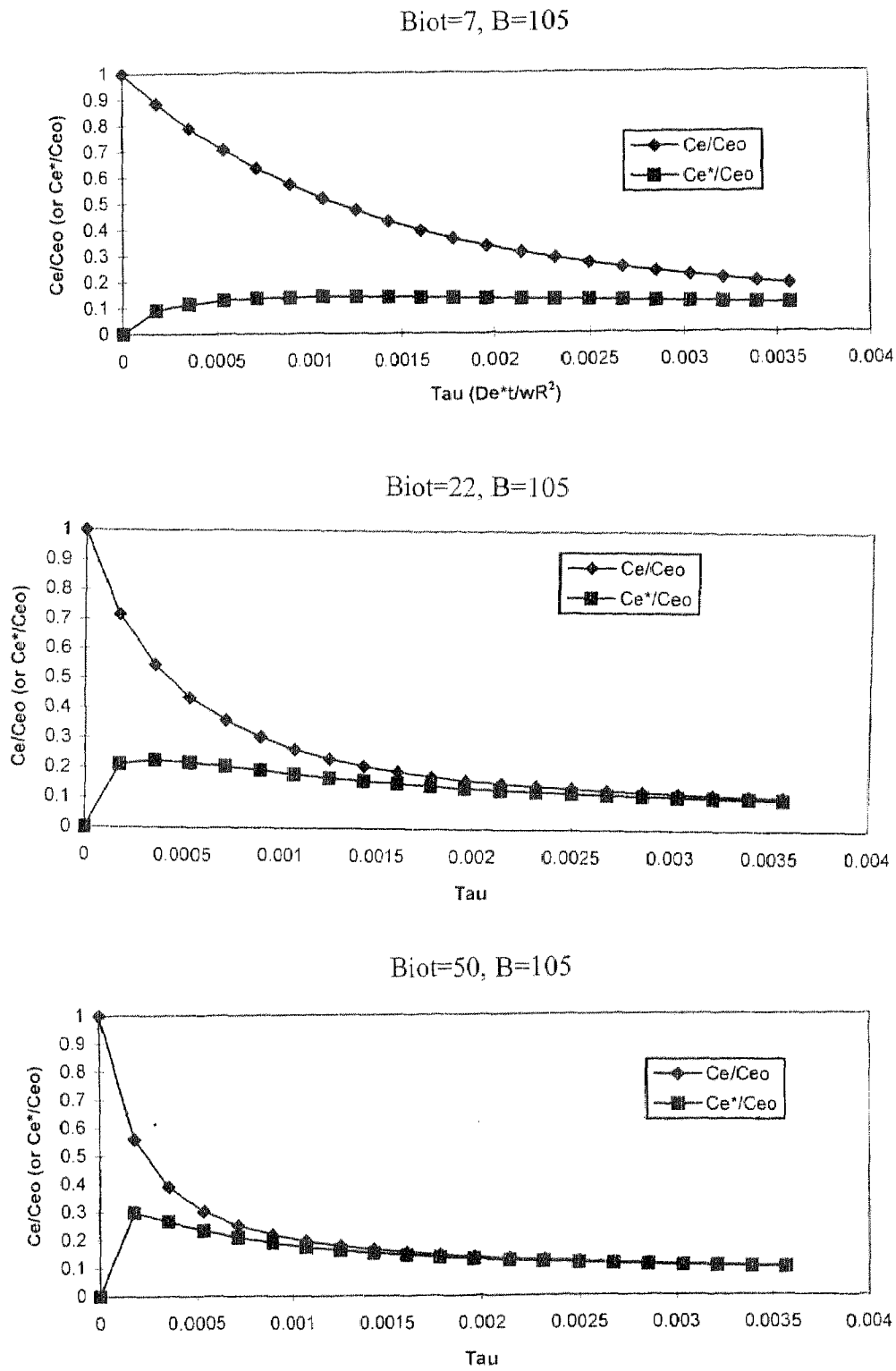
Figure 4.3 Comparison of the External and Interfacial Concentrations

also their mathematical forms are consistent. Figure 4.2 gives the comparison of the two cases and the effect of the Biot number on ELM performance.

A small Biot number implies the external mass transfer is a rate-limiting step, so that total mass transfer rate is low due to the film resistance. The effect of the film resistance is more serious at the small dimensionless time. However, at the large τ, only small difference can be seen between the different Biot curves. Film resistance becomes smaller with increasing the Biot number, so that curve falls down gradually and at last, the film resistance is too small to control the total mass transfer, so that the curve for Biot number of 49.6 and the curve for infinite Biot number are almost identical. Figure 4.3 gives the comparison of the solute concentration in the external phase Ce(t) and that at the interface C^*e(t) with different Biot numbers. It clearly shows how the Biot number affects the external film resistance. The difference of Ce(t) and C^*e(t) curve represents the driving force of the external mass transfer. The smaller the Biot number, the bigger is the driving force, because of the bigger the film resistance. When the Biot number approaches infinite, C^*e(t) curve will be the same as Ce(t) curve except Ce(t) starts as 1 and C^*e(t) curve starts at 0 when τ=0. It can also be found that driving force decreases when time increases, because system is approaching steady state in batch operation. The system can be regarded to reach steady state, when Ce(t) and C^*e(t) curve are equal.
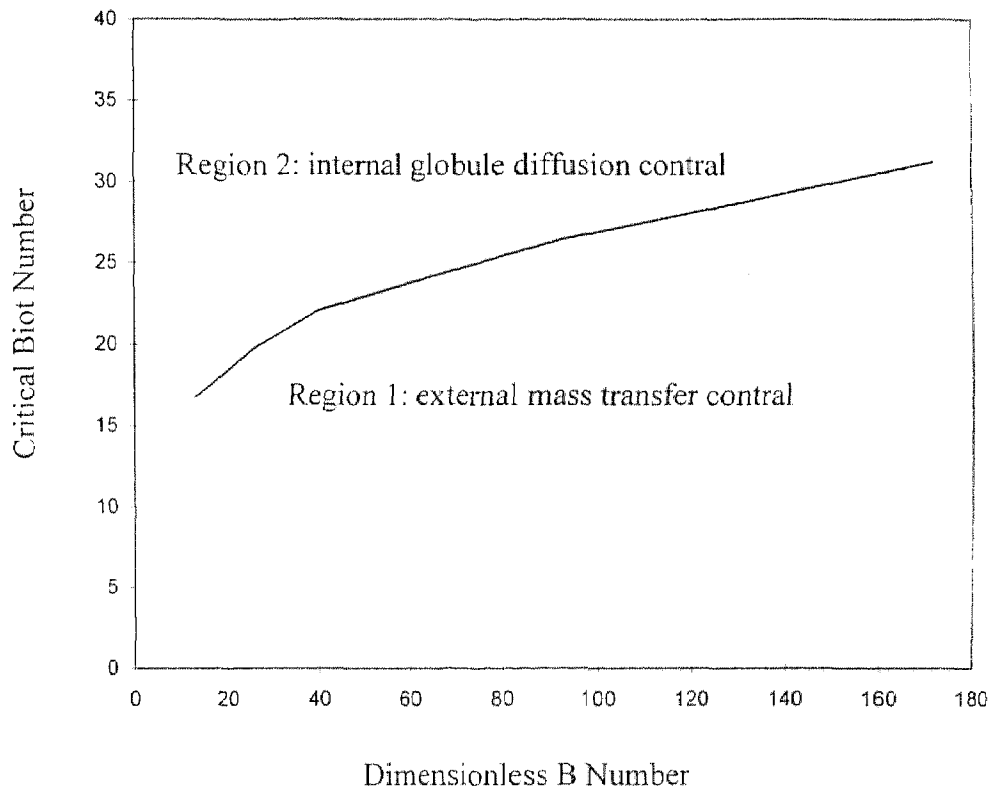
Figure 4.4 The Critical Boit Number for ELM System

4.4.4 Determination of Rate-Controlling Step for ELM

Actually, it is not necessary for the Biot number to approach infinite so that the external mass transfer resistance can be neglected. Figure 4.2 shows no difference between the curve with the Biot number of 49.6 and the curve with infinite Biot number at B=105, which means there exists a critical Biot number. The external mass transfer resistance can be neglected when the Biot number is greater than this critical Biot number. In other words, the internal membrane diffusion is the rate-controlling step. It is also reported by Ho and Li[Ho and Li, (1992)] that the critical Biot number is 20. Figure 4.4 gives the dependence of the critical Biot number of the B number. This curve is obtained by changing the B number, and then comparing the data series with a specific Biot number with data series with the infinite Biot number. If the difference of the two data series is less than 2%, the critical Biot number is found. This curve separates the Biot-B plane into two regions. The region below the curve is the external film resistance control region and the above one is the internal globule diffusion control region. It can be found the critical Biot number increases with the B number, and the typical critical Biot number is from 15 to 30, when B ranges from 20 to 250, which is the typical range for most of the emulsion liquid membrane systems.

4.4.5 Effect of B Number of Concentration Distribution Inside Globule

The effect of B, the emulsion capability dimensionless group, on the external phase concentration versus time is shown in Figure 4.5 for a fixed Biot number of 22.8. Results
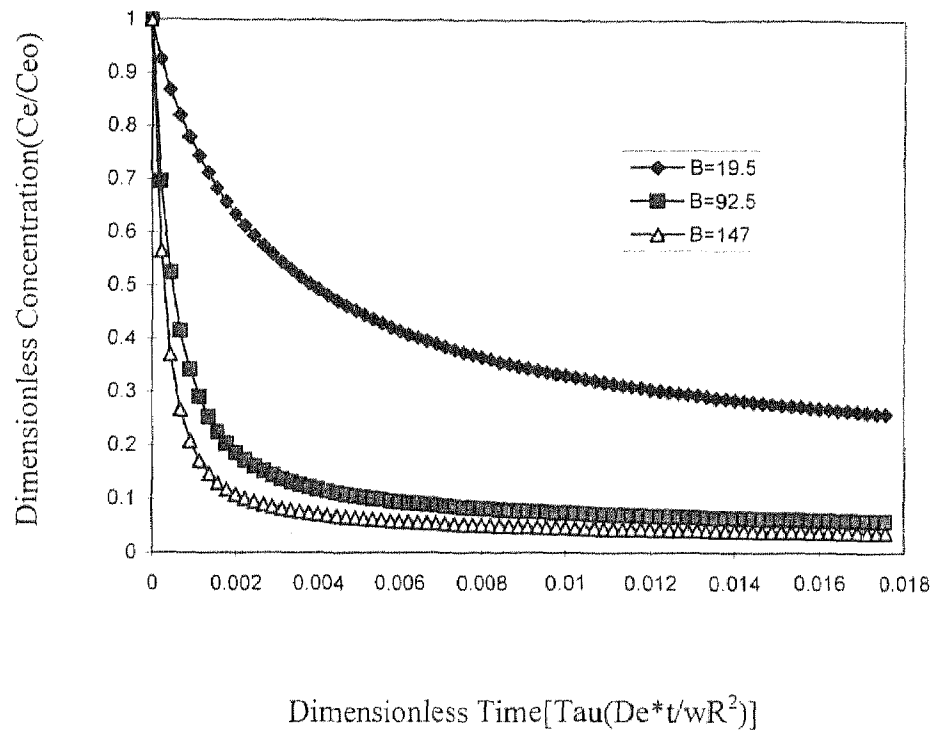
Figure 4.5 Effect of B Number on ELM Performance
(Biot=22.8)
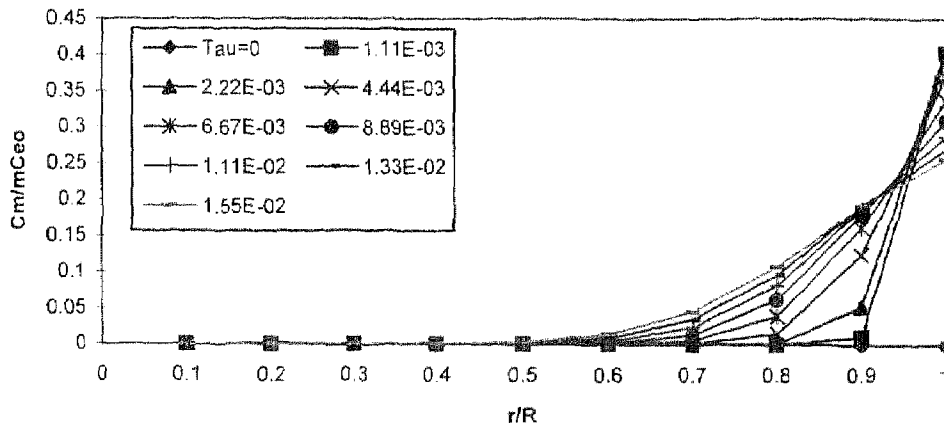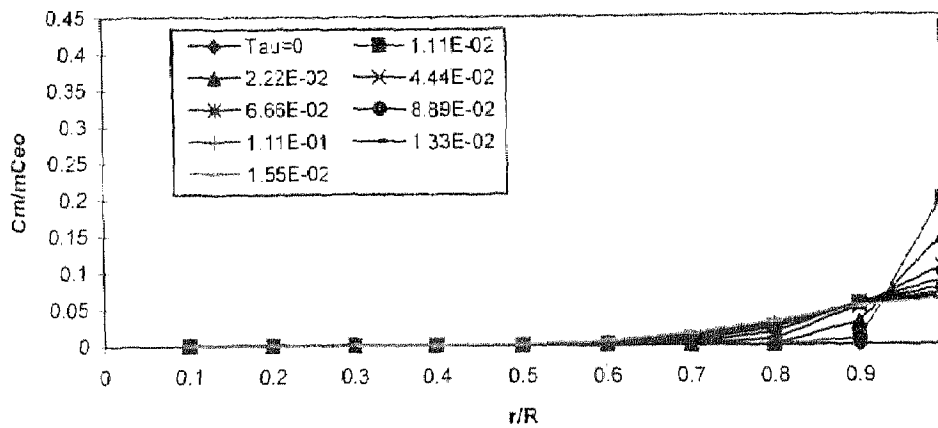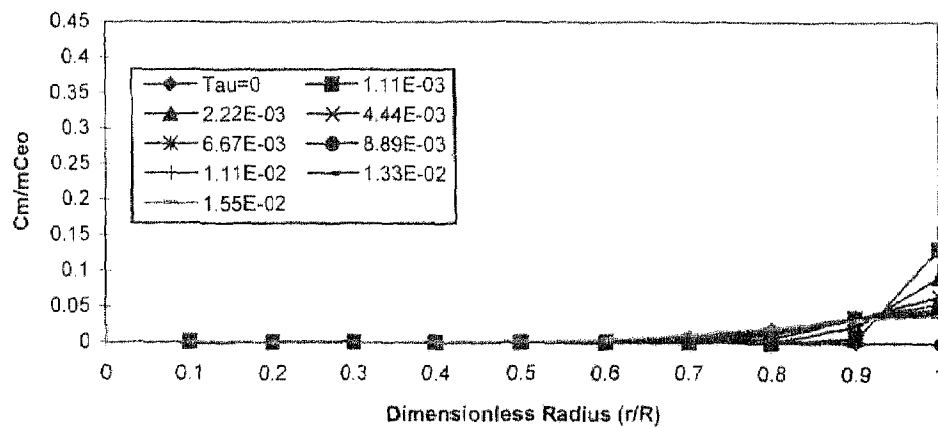
Figure 4.6 Effect of the B Number on Cm Distribution inside Emulsion Globule

for the three curves obtained with different B number shows that the curve with the largest value of B gave the best ELM performance in solute removal for this group.

It was interesting to observe theoretically the effect of B on the concentration profile in a globule at different times. In Figure 4.6, plots of the globule concentration profiles at three B values of 19.5, 92.5 and 147 are presented. The results show that at a low value of B=19.5 with a low stripping capability of the internal phase keeps the solute (in the form of the solute-carrier complex) concentration high in the membrane phase. Therefore, the solute-carrier complex in the membrane penetrates deeper toward the center of the globule. On the other hand, at the high value of B=147, most of the solute is stripped into the internal phase and which leaves a small amount in the membrane phase. Since the membrane concentration of the solute-carrier complex is a function of time, the concentration profiles for a globule are plotted at different times from tau=0 to tau=$1.55*10^{-2}$.

4.5 Summary of Mathematical Modeling of the ELM Systems

The mass transfer of an emulsion liquid membrane process has been modeled mathematically. An analytical solution which allows prediction of concentrations of solutes in the external phase, the membrane phase, and external phase-membrane interface was obtained. From the model, it was found that the ELM process was characterize by two dimensionless groups. One group governs the rate of mass transfer or the Biot number, which is the ratio of the internal diffusion resistance to the external mass transfer film resistance. The other group includes the equilibrium constants for

extraction and stripping reactions at both interfaces and expresses the limit or the capability of the separation process. Comparison of the external film resistance and the membrane diffusion resistance is discussed and the critical Biot number is found so that the determination of the rate-controlling step is easy. This model theoretically can predict any separation system via the emulsion liquid membrane.

CHAPTER 5

MATHEMATICAL MODELING OF ELMs BY CONSIDERING LEAKAGE

5.1 Introduction and Literature Review

The leakage or breakup is a very important problem in emulsion liquid membrane systems. It will affect the stability of the emulsion. Leakage in emulsion liquid membrane systems includes the rupture of the emulsion, leading to the short circuiting of the reagent and extracted solute in the internal phase to the external phase. As a result, the leakage causes a decrease of the driving force for the mass transfer and an increase of the raffinate concentration, thus lowering the extraction efficiency. The main factors governing membrane stability include the membrane formulation, the method of membrane preparation, and the conditions under which the emulsions are contacted with the feed solution.

Considerable experimental work has been done in this area[Qian, Ma, and Shi, (1989); Zhang, (1989, 1990); Goto, *et al.*, (1987, 1991); Takahashi, *et al.*,(1981); Shere and Cheung, (1988a, 1988b); Ma and Shi, (1987)]. To summarize the previous work, some conclusions may be made. The surfactant plays the dominant role for stabilizing the membrane, and the properties of the surfactant affect membrane stability considerably. Membrane with polyamine surfactants(Such as ECA4360J), which have one long alkyl chain, have been reported to be more stable than those with sorbitol oleates(such as SPAN 80)[Draxler and Marr, (1986)]. A reasonably high surfactant concentration is favorable to membrane stability. A critical surfactant concentration exists at which the

number of surfactants molecules oriented at the membrane interface is sufficient to make the membrane stable. Above this critical concentration, a further increase in surfactant concentration appears unnecessary for the membrane stability. Therefore, the suitable surfactant concentration commonly used in practice ranges from 2-5%. Membrane viscosity, determined mainly by the diluent, can also affect membrane stability. The use of a diluent with low viscosity formulates a thin but weak membrane, which offers a high initial extraction rate but shows serious leakage over long contacting time. The membrane with a high viscosity diluent is strong. Although this kind of membrane offers a lower extraction rate, it is more stable and thus has better overall extraction efficiency. Increasing the volume fraction of the internal phase will decrease the membrane thickness and thus increase the leakage rate. However, the low volume fraction of the internal phase will slow down the mass transfer process. During the mass transfer process, the emulsion is contacted generally with a large excess of the external, continuous phase. Increasing the stirring speed will increase the probability of membrane breakup. Thus, the agitating speed is always controlled ranging from 250 to 450 rpm.

From the mathematical modeling point of view, very little attention was paid to account for the leakage, while considerable efforts were directed toward the permeation mechanism. Teramoto and coworkers[Teramoto, *et al.*, (1983b)] modeled the leakage in carrier-facilitated transport, complicated equations together with a lot of kinetics data were solved numerically. Borwankar's leakage model was based on Ho's advancing front model[Borwankar, *et al.*, (1988)].

The leakage model discussed in this chapter is based on the model discussed in chapter 4 which doesn't consider the leakage. Introduction of leakage term brings a lot of difficulties while solving the differential equations. Fortunately, the leakage term can be simplified to linear, so that Laplace transform method is still capable of solving this problem. This model can evaluate the significance of the leakage on emulsion liquid membrane systems. Comparison of the models with and without the leakage is also discussed.

5.2 Mathematical Description of Leakage

The previous research work had already proven that leakage rate is proportional to the amount of extracted solute inside the internal phase[Nakashio, Goto, Matsumoto, Irir and Kondo, (1988); Teramoto, et al. (1983b); Borwankar, et al., (1988)]. All the other factors, such as formulation of the emulsion liquid membrane system, type of the permeation apparatus and the speed of the mixing will be correlated to a specific rate constant, named leakage rate constant k_b.

$$M_{leakage} = k_b \overline{V_i C_i} \tag{5.1}$$

Where k_b: leakage rate constant (1/sec)

From the total material balance at any time during the permeation process, the combination of the extracted solute in the internal phase, the solute in the membrane phase and the solute remaining in the external phase is equal to the original solute in the external phase. Thus we have

$$VeCeo = VeCe + \overline{ViCi} + \overline{VmCm} \tag{5.2}$$

Usually, the solute in the membrane phase is very small by comparing with that in the internal and external phases, thus $\overline{VmCm}$ could be neglected. The volumes of the three phases don't change.[Borwankar, *et al.* (1988)]. Thus, equation becomes

$$M_{leakage} = k_b \overline{ViCi} = k_b(VeCeo - VeCe) = k_b Ve(Ceo - Ce) \tag{5.3}$$

The k_b value was studied by Nakashio[Nakashio, *et al.*, (1988)]. There exists a critical surfactant concentration(Csc). k_b will decrease with the increase of the surfactant concentration when surfactant concentration is less than Csc, and k_b will remain unchanged when surfactant concentration is greater than Csc. Thus, for all the permeation operations, sufficient surfactant has to been used so as to keep the stability of the emulsion, and k_b value ranges from 10^{-6}-10^{-5}(1/sec). Other effects, such as the agitating condition, the diluent properties, the consumption ratio, and etc. have influence on k_b value. But, it doesn't belong to the scope of this study.

5.3 Mathematical Modeling of ELMs by Considering Leakage

The physical assumptions of this model are almost same as those of chapter 4 for second case that the external phase mass transfer resistance is considered, except the change of the last one: leakage is considered. Thus, It differs from previous model only on the consideration of the leakage. Although the leakage contributes little to the emulsion liquid membrane system, it results in more difficulties to solve the differential equations. Nevertheless, final analytical solutions are found.

Equations governing the system are follows:

Membrane phase

Spherical shell material balance is taken inside the emulsion globule:

$$Vm * \frac{\partial Cm}{\partial t} = (Vm + Vi) * De * [\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial Cm}{\partial r})] - Vi * Rx \qquad (5.4)$$

Initial Conditions(I.C.):   Cm = 0 for all r,   when t = 0

Boundary Conditions(B.C.): Cm = finite,   when r = 0;   Cm = Cm*,   when r = R

Where: Vm: volume of membrane phase (dm^3),

   Vi: volume of internal phase (dm^3),

   Vm+Vi: total volume of emulsion

   Rx: The disappearance of the solute-carrier complex in the membrane phase

   into the internal phase by stripping(mol/dm^3/sec)

Internal Phase

$$Rx = \frac{\partial Ci(r,t)}{\partial t} \qquad (5.5)$$

I.C.:   Ci = 0, when t = 0

where: Ci: concentration of the solute in the internal phase

At the membrane-internal phase interface, chemical equilibrium is reached. Thus,

   Ci = q*Cm   (5.6)

where: q: the stripping partition function at the membrane-internal phase interface

External phase

$$Ve \frac{dCe}{dt} = -N(4\pi R^2)De(\frac{\partial Cm}{\partial r})_{r=R} + M_{leakage} \qquad (5.7)$$

$$Ve * \frac{dCe}{dt} = -N(4\pi R^2)k(Ce - Ce^*) + M_{leakage} \qquad (5.8)$$

$$-N(4\pi R^2)De(\frac{\partial Cm}{\partial r})|_{r=R} = -N(4\pi R^2)k(Ce - Ce^*) \qquad (5.9)$$

Initial Condition(I.C.): $\quad$ Ce = Ceo, when t = 0

where: Ve: volume of the external phase (dm^3)

$\quad$ Ce: concentration of the solute in the external phase (mol/dm^3)

$\quad$ N: total number of the globules

$\quad$ R: radius of the globules

$\quad$ De: effective diffusivity of the solute-carrier complex in the membrane

$\qquad$ phase (m^2/sec.)

$\quad$ Cm: concentration of the solute-carrier complex in the membrane phase(mol/dm^3)

$\quad$ M$_{leakage}$: rate of the solute leaks from the emulsion globule mol/sec)

$\quad$ $k(Ce - Ce^*)$ is the flux of mass transfer outside the external-membrane interface

and $De (\frac{\partial Cm}{\partial r})|_{r=R}$ is the flux of mass diffusion inside external membrane interface. These

two fluxes must be equal, because there is no accumulation of solute at the interface.

Equilibrium equation:

$$Cm^* = mCe^* \quad Ce^* \neq Ce \qquad (5.10)$$

where: Cm*: concentration of the solute-carrier complex at interface, Cm*=fun(t) only

$\quad$ Ce*: concentration of the solute at the interface next to the external phase

$\quad$ m: the extraction partition function at the external phase-membrane interface

Equations(5.4),(5.5) differ from the previous ones on the term of $M_{leakage}$ that is the leakage term. The equation physically means that the disappearance rate of the external solute will be reduced by some raptures of the globules.

In this case, four partial differential equations together with two equilibrium equations are all linear. Thus, the Laplace transform method is also applied to solve four variables $Ce(t)$, $Ce^*(t)$, $Cm(r,t)$ and $Ci(r,t)$.

Before changing the equations into the dimensionless forms, some derivations should be made. By combining equation (5.4, 5.5, 5.6), we have

$$(\frac{Vm + q*Vi}{Vm + Vi}) \frac{\partial Cm}{\partial t} = De * [\frac{1}{r^2} \frac{\partial}{\partial r}(r^2 \frac{\partial Cm}{\partial r})] \qquad (5.11)$$

same I.C. and B.C. as before.

Dimensionless governing equations are follows:

<u>External</u>

Equation (5.5), (5.6) will become

$$\frac{dUe}{d\tau} = -Ko*(Ue - Ue^*)+I*(1-Ue) \qquad (5.12)$$

$$G*(\frac{\partial Um}{\partial v})\Big|_{v=1} = (Ue - Ue^*) \qquad (5.13)$$

Equilibrium: $Ue^* = Um^*$

I.C. $Ue = Ue^* = 0$, when $\tau = 0$

where: $Ko = \dfrac{R*k*f}{De}$ $\qquad G = \dfrac{m*De}{R*k}$ $\qquad Ue^* = \dfrac{Ce^*}{Ceo}$ $\qquad Um^* = \dfrac{Cm^*}{mCeo}$ $\qquad I = \dfrac{k_b R^2}{D_{eff}}$

$$Ue = \frac{Ce}{Ceo} \qquad \tau = \frac{Det}{R^2} \qquad f = \frac{3f'}{1-f'} \qquad f' = \frac{Vi+Vm}{Vi+Vm+Ve}$$

Membrane

Equation (5.13) will become

$$\omega \frac{\partial Um}{\partial \tau} = \frac{1}{v^2} \frac{\partial}{\partial v}(v^2 \frac{\partial Um}{\partial v}) \qquad (5.14)$$

I.C. $Um = 0$,   when $\tau = 0$

B.C. $Um = $ finite   when $v = 0$; $Um = Um^*$ when $v = 1$

where:

$$\omega = 1 - \frac{Vi}{Vi+Vm}(1+q) \qquad v = \frac{r}{R} \qquad Um = \frac{Cm}{mCeo}$$

5.4 Solution and Discussion

5.4.1 Solution Form

The Laplace transform and inverse Laplace transform are taken to Equation (5.12), (5.13) and (5.14), together with their boundary conditions and initial condition. The final analytical solutions will be found as follows:

$$Ue = 1 + \sum_{n=1}^{\infty} \frac{(-bn^2 + P)[\tan bn + G(bn - \tan bn)]Exp(-bn^2 \frac{\tau}{\omega})}{\tan bn\{[P(1-G)-B]-[2(1-G)+\frac{1}{2}(B+P)]bn^2 + \frac{G}{2}bn^4\} + \{[P(\frac{1}{2}+G)+B]bn - (\frac{1}{2}+2G)bn^3\}} \qquad (5.15)$$

Where bn are eigen values(n=1,2,3...) solved by

$$\tan(bn) = \frac{(B+GP-Gbn^2)bn}{[B-P(G+1)]-(G-1)bn^2} \qquad (5.16)$$

Four dimensionless groups shall be mentioned as follows:

$$P = \omega 1 = \frac{k_b \omega R^2}{D_{eff}}$$ which represents the leakage and physically means the ratio

of the leakage rate to the diffusion rate inside emulsion globules.

$$G = \frac{m D_{eff}}{kR}$$ which is the reciprocal of the Biot number, physically represents

the ratio of external mass transfer resistance to the internal diffusion resistance.

$$B = m\omega f$$ which represents the capability of the emulsion globule to extract

the external solute.

$$\frac{\tau}{\omega} = \frac{t * De}{\omega R^2}$$ Dimensionless time

As we see, the solution of considering the leakage is much more complicated than

the previous one that neglects the leakage. Nevertheless, the governing equations are still

linear after taking the leakage term, so that the Laplace transform method is still capable

of solving this problem.

5.4.2 Comparison of Models with and without the Leakage

The solutions of the two models seems totally different. For the model with leakage, the

first term of the solution is 1 that represents the dimensionless concentration of the

external phase when time approaches infinite It physically means that the solute

previously extracted into the internal phase returns back to the external phase due to the

total breakup of the emulsion. It differs from the case without the leakage which we

discussed before. When the leakage is neglected, the first term is $\frac{3}{3+B}$ that means the

external concentration will be reduced to a bottom line when two equilibria are finally reached at both external phase-membrane interface and membrane-internal phase interface.

The explanation of the comparisons are following:

(1). In the membrane phase, the approximation is made that is $\overline{V_m C_m}$ term is very small when comparing with Ve(Ceo-Ce) and $\overline{V_i C_i}$ so that it is neglected. Mathematically, the final time-independent term will not contain any information of membrane phase. Physically, only a very small amount of solute will retain in the membrane phase after the total breakup of the emulsion. Thus, it doesn't affect the concentration in external phase, because membrane phase in very small in volume, and so is the extractant in the membrane phase.

(2). In the internal phase, leakage is most probably because of the rapture of the emulsion, or sometimes call it breakup. Breakup happens unavoidably, but in very small amount. Breakup will cause the release of the internal aqueous volume together with its dilute. Thus, realistically, the volume of the total internal phase will decrease and the total volume of the external phase will increase due to the breakup. But, the internal phase volume is very small (one hundredth of external volume) and the breakup is very small too (1-2% during the operating time). Thus, decrease of the internal phase volume and the increase of the external phase volume are both too small to be considered. This means that we only consider the leakage of the solute from the internal phase, but didn't consider the leakage of the internal aqueous volume. Mathematically, any information related to the internal phase doesn't appear on the first time-independent term.

Based on above considerations, when total breakup happens at infinite time, the solute will return totally back to the external phase. Thus, the value of the time-independent term of the mathematical model equals to 1. This solution is consistent with the physical phenomena. It is an approximation, but is realistic.
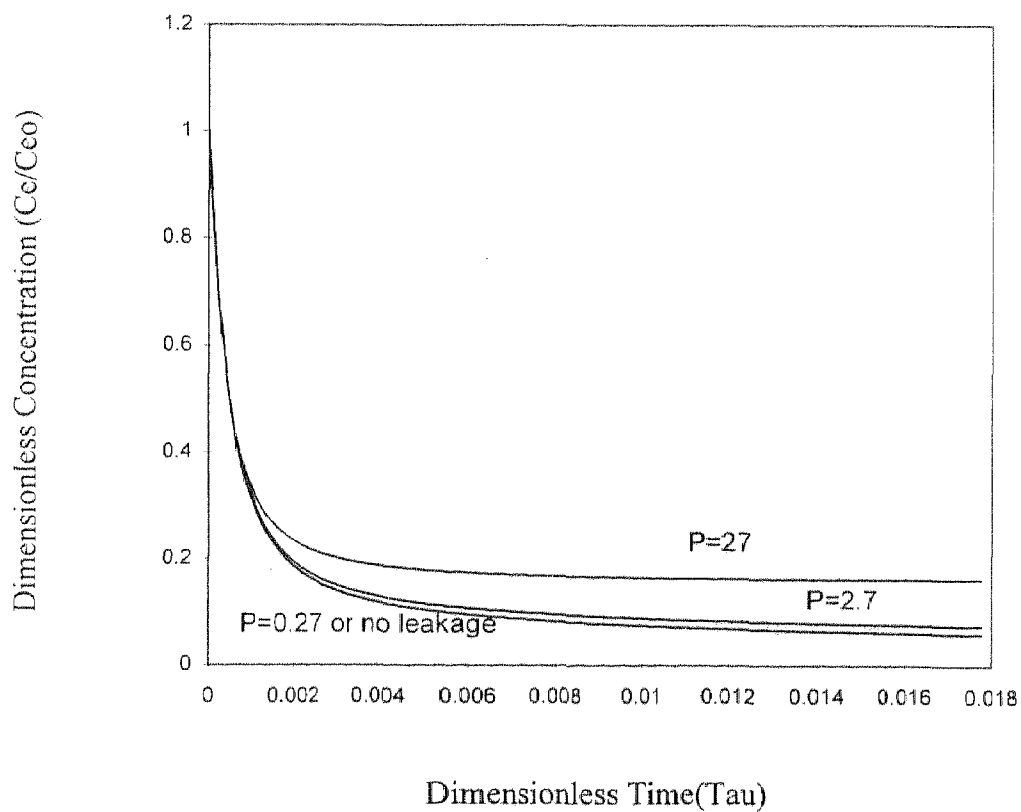
Figure 5.1 Effect of Leakage on ELM System
(B=92.5, Biot=22.7, P:see above)

5.4.3 Effect of the Leakage Dimensionless Group (P) on the ELM Performance

Figure 5.1 shows the effect of the P number on the removal efficiency, the curve rises a little when P is increasing. Since the typical k_b ranges from 10^{-5} to 10^{-6} [1/sec], the P number in this case ranges from 0.27 to 2.7. Thus it can be found that during the small permeation time, the leakage doesn't play a important role in emulsion liquid membrane systems. When time increases, dimensionless external concentration will pass a minimum value and increase gradually, which means leakage is becoming dominant gradually. For practical operations, the permeation operation is very fast (especially for Sr-D2EHPA case), so that leakage will not affect the emulsion liquid membrane process.

5.5 Summary of the Leakage Model

Leakage problem in emulsion liquid membrane process is mathematically modeled. This model has been developed by the addition of leakage term to the previous model without the leakage. Analytical solution is obtained by the Laplace transform. This model can evaluate the significance of the leakage for the emulsion liquid membrane systems. It is found that the leakage will not affect the emulsion liquid membrane process. Comparison of the models with and without the leakage is discussed.

CHAPTER 6

PREDICTION OF EXPERIMENTAL DATA BY MODELS

This chapter is predicting the experimental data by use of the mathematical models developed in chapter 4 and chapter 5. For arsenic and strontium systems, the physical and chemical parameters are determined by experiments and published correlations. These independently and individually evaluated parameters are then incorporated into our mathematical models. The results show excellent prediction.

6.1 Prediction of Arsenic Experimental Data by Mathematical Model

6.1.1 Evaluation of Diffusivities

The diffusivity of arsenic in the aqueous phase(Di) and the diffusivity of the arsenic-2EHA complex in the membrane phase are evaluated by the Wilke-Chang equation[Wilke, and Chang, (1955)].

Wilke-Chang Equation:

$$Di = \frac{7.4 * 10^{-12} (\phi * M_B)^{1/2} T}{\eta_B V_A^{0.6}} \quad (M^2/sec.) \tag{6.1}$$

where ϕ: Associate factor of solvent (2.6 for water, 1.0 for unassociated solvent);

M_B: Molecular weight of the solvent phase (g/mol);

T: Absolute temperature ($^\circ$K); η_B: Viscosity of the solvent phase (cp);

V_A: Molar volume of solute A at its normal boiling temperature (cm^3/mol)

Table 6-1 Molar Volume of Some Elements for Determination of Molar Volume of Arsenic Complex at its Normal Boiling Temperature(Le Bas Correlation)

Elements	$V_A(cm^3/mol)$
Carbon C	14.8
Hydrogen H	3.7
Oxygen O	12.0
Arsenic As	25.0

V_A is calculated by the Le Bas Correlation[Le Bas, (1915)].

Thus, for H_3AsO_3 in the aqueous phase:

Sum(V_A)=3*3.7+1*25.0+3*12.0=72.1 (cm^3/mol)

ϕ=2.6 (for aqueous phase)

η_B=1.0 (cp)

T=298.15 (K)

M_B=18.0 (molecular weight of the aqueous phase)

If plugging all above data into the Wilke-Chang equation, we have diffusivity of H_3AsO_3 in the aqueous phase:

$$Di = \frac{7.4*10^{-12}(\phi*M_B)^{1/2}T}{\eta_B V_A^{0.6}}$$

$$= \frac{7.4*10^{-12}(2.6*18)^{1/2}*298.15}{1.0*72.1^{0.6}} = 1.16*10^{-9}(m^2/sec.)$$

For the H_3AsO_3-ROH complex in heptane(membrane) phase:

Since H_3AsO_3-ROH is equivalent to $C_{18}H_{21}O_{12}As$. Thus,

Sum(V_A)=21*3.7+1*25.0+4*12.0+18*14.8=417.1 (cm3/mol)

ϕ=1.0 (for unassociate organic phase)

η_B=0.5 (cp, heptane)

T=298.15 ($^{\circ}$K)

M_B=100.0 (molecular weight of haptane phase)

If plugging all above data into the Wilke-Chang equation, the diffusivity of the

H_3AsO_3-2EHA complex in the organic phase can be calculated as follow:

$$Dm = \frac{7.4*10^{-12}(\phi*M_B)^{1/2}\,T}{\eta_B V_A^{0.6}}$$

$$= \frac{7.4*10^{-12}(1.0*100)^{1/2}*298.15}{0.5*417.1^{0.6}} = 1.18*10^{-9}(m^2 / \sec.)$$

For the effective diffusivity of complex in the membrane phase, Jefferson-Witzell-Sibbert [Jefferson, et al. (1958); Ho and Li (1992)] correlation was used.

$$D_e = D_m(\frac{4(1+2p)^2 - \pi}{4(1+2p)^2}) + \frac{\pi}{4(1+2p)^2}(\frac{(1+2p)D_A D_m}{D_m + 2pD_A})$$

where

(6.2)

$$D_A = \frac{2(D_i/m)D_m}{(D_i/m) - D_m}[\frac{D_i/m}{(D_i/m) - D_m}\ln(\frac{D_i/m}{D_m}) - 1]$$

$$p = 0.403(\frac{Vi}{Vm+Vi})^{-1/3} - 0.5$$

where Di and Dm are determined above, Vi and Vm are volume of the internal phase and

the membrane phase, m is the external partition function, π is 3.1416 and p and D_A are

intermediate variables.

If we use a set of data for example,

Di = $1.16*10^{-9}$ (m²/sec.)

Dm = $1.18*10^{-9}$ (m²/sec.)

Vi = 10 (ml)

Vm = 90 (ml)

m= 0.22 (determined by experiment)

If plugging all above data into the Jefferson-Witzell-Sibbert correlation,

De = $8.73*10^{-10}$ (m²/sec.).

Effective diffusivity represents the diffusivity of the As-2EHA complex based on the membrane phase concentration, in the emulsion. It is less than D_m, which is the diffusivity of the complex in organic phase, because of the block of the complex by internal aqueous droplets. It is also found that effective diffusivity will decrease when the internal volume ratio(Vi/(Vi+Vm)) increases.

6.1.2 Evaluation of External Mass Transfer Coefficient

The external mass transfer coefficient k is determined by the Skelland & Lee equation[Skelland and Lee, (1981); Ho and Li(1992)].

$$\frac{k}{\sqrt{ND_i}} = 2.932*10^{-7} (\frac{Vi + Vm}{Vi + Vm + Ve})^{-0.508} (\frac{d_I}{d_T})^{0.548} Re^{1.371}$$

(6.3)

$$Re = \frac{Nd_i^2 \rho}{\mu}$$

The definition of the variables and their assigned data are listed in Table 6-2.

Table 6-2 Variables and their assigned data for the Determination of the External Mass Transfer Coefficient of Arsenic System

N:	agitating speed (rps)	5
D_i:	external diffusivity (m^2/sec.)	$1.16*10^{-9}$
d_l:	diameter of the propeller (m)	0.04
d_T:	diameter of the tank (m)	0.1
V_i:	volume of internal phase (ml)	10
V_m:	volume of membrane phase (ml)	90
V_e:	volume of external phase (ml)	500
ρ:	density of the external phase (g/cm^3)	1.0
μ:	viscosity of the external phase (g/cm/sec)	0.01

If plugging above data into the Skelland & Lee Equation, we have

Reynolds Number: $\qquad$ Re=$8*10^3$

External mass transfer coefficient: $\quad$ k=$7.54*10^{-6}$ $\quad$ (m/sec.)

6.1.3 Evaluation of the Sauter Mean Globule Radius

The Sauter mean radius of the emulsion globules is determined as same method as Ohtake[Ohtake, et al., (1987); Ho and Li(1992)].

$$\frac{d_{32}}{d_I} = 0.12 We^{-0.5} \qquad \eta < 0.16 Ns/m^2$$

$$\frac{d_{32}}{d_I} = 0.50 \eta^{0.8} We^{-0.5} \qquad \eta > 0.16 Ns/m^2$$

(6.4)

where $We = \dfrac{N^2 * d_I^3 * \rho_e}{\gamma}$ is the dimensionless Weber number

The definition of the variables and their assigned data are listed in Table 6-3.

Table 6-3 Variables and their Assigned Data for Determination of Sauter Mean Diameter

N:	agitating speed (rps)	5
d_I:	diameter of the propeller (m)	0.04
ρ:	density of the external phase (g/cm^3)	1.0
γ:	Surfacial tension (dyn/cm)	72.8

Since the viscosity of emulsion is less than 160 cp for our experimental systems, the first

Ohtake equation is used. If plugging above data into the Ohtake equation, we have

Weber Number: We=21.98

Sauter mean diameter: d_{32}=0.116 (cm)

6.1.4 Prediction and Discussion

A FORTRAN algorithm is developed to calculate the dependence of the dimensionless

external concentration, the dimensionless interfacial concentration and the dimensionless

concentration profiles inside the membrane phase versus time. All the experimental data

and evaluated parameters are incorporated into the model. Experimental results and the

model predicted results are compared.

Table 6-4 : List of Model Parameters and Experimental Conditions
for Arsenic Data Prediction

Model Parameters	
Di : Diffusity of solute in the external phase(m^2/sec)	$1.16*10^{-9}$
Dm : Diff. of Complex in the membrane phase(m^2/sec)	$1.18*10^{-9}$
De : Effective Diff. of complex in the membrane phase(m^2/sec)	$8.73*10^{-10}$
f : emulsion volume fraction(Vi+Vm/Vtot)	0.16667
e : sink phase volume fraction(Vi/(Vi+Vm))	0.1
R : radius of the globule(m)	$5.8*10^{-4}$
m : external distribution coefficient	0.22
q= : internal distribution coefficient	$7.0*10^{3}$
k : external mass transfer coefficient(m/Sec.)	$7.54*10^{-6}$
B : mfw	92.5
Biot number	22.77
Experimental Conditions:	
Ceo=5.51 ppm, Ve=500ml, [H2SO4]=0.2M, 300 rpm;	
Vm=90 ml, 10 vol% 2EHA, 2 vol% ECA4360J, rest: Heptane;	
Vi=10ml, NaOH (1N)	

Figure 6.1 gives the prediction of experimental data for arsenic removal by the

ELM and Table 6-4 gives the model parameters and the experimental conditions. It can

be found that the prediction is excellent.
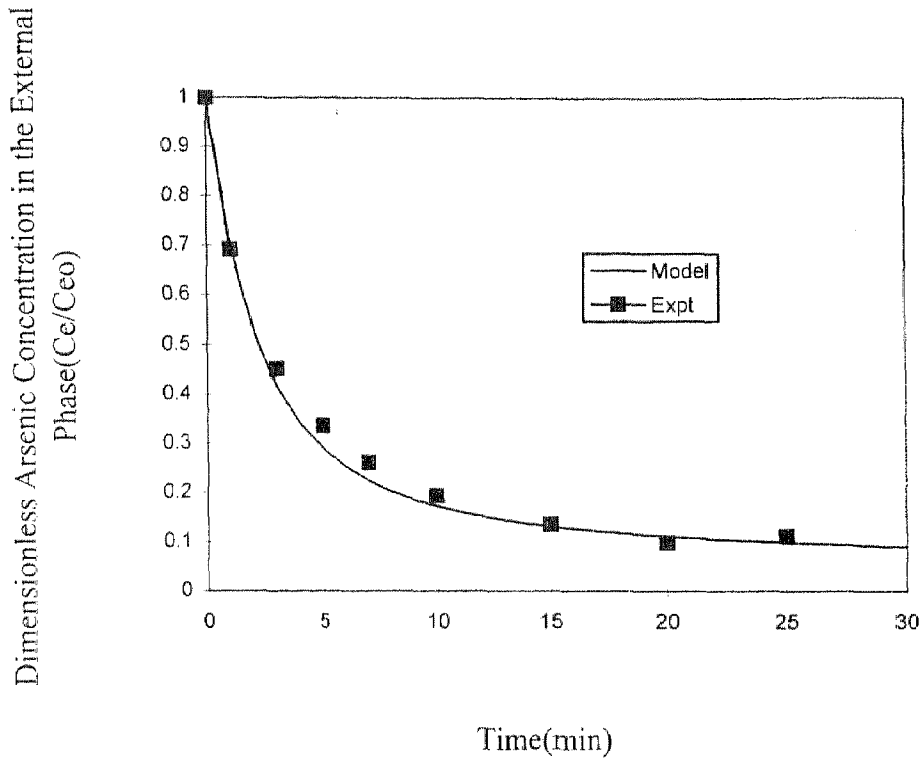
Figure 6.1 Prediction of Arsenic Experimental Data by the Model

B=92.5; Biot=22.8

Experimental Conditions:

External phase: 500ml, 5.51 ppm arsenic solution, 0.2 M H_2SO_4, 300rpm, room temp.

Emulsion phase: 100ml fresh emulsion, which contains

        90ml organic phase: 10v% 2EHA, 2v% ECA4360J, rest: heptane

        10ml internal phase: 2N NaOH solution

6.2 Prediction of Strontium Experimental Data by Mathematical Model

6.2.1 Evaluation of Diffusivities

The diffusivity of strontium in aqueous phase(Di) is determined by the Nernst-Haskell[reid, et al., (1987)] equation because it is a dilute electrolyte solution. The diffusivity of strontium-D2EHPA complex in the membrane phase are evaluated by use of the Wilke-Chang equation.

Eernst-Haskell Equation:

$$D_i = \frac{RT[(1/n^+)+(1/n^-)]}{F^2[(1/\lambda^+)+(1/\lambda^-)]} \quad (cm^2/sec.) \tag{6.5}$$

where F: Faraday Constant (96500 c/g-equiv);

n^+, n^-:   valences of the cation and the anion, respectively;

λ^+, λ^-:   limited (zero concentration) ionic conductance of cation and anion

respectively$(A/cm^2)(V/cm)(g-equiv./cm^3)$;

The data for the $SrCl_2$ aqueous solution in room temperature are listed in Table 6-5:

Table 6-5: Data for Calculation of the Diffusivity of $SrCl_2$ Solution

T: absolute temperature (^oK)	298.15
R: gas constant (J/mol/^oK)	8.314
n+: number of cation (Sr)	1
n-: number of anion (Cl)	2
λ+: of cation (Sr)	50.5
λ-: of anion(Cl,)	76.3

If plugging all above data, we have:

$$D_i = \frac{RT[(1/n^+)+(1/n^-)]}{F^2[(1/\lambda^+)+(1/\lambda^-)]}$$

$$= \frac{8,314*298.15(1/1+1/2)}{96500^2[(1/50.5)+(1/76.3)]} = 1.21*10^{-5}(cm^2/sec.)$$

The diffusivity of the Sr-D2EHPA complex in membrane phase is determined by use of the Wilke-Chang equation:

Since Sr-D2EHPA is equivalent to $C_{16}H_{34}O_4PSr$

V_A are assumed as 10.0 for P and Sr

$Sum(V_A)=34*3.7+4*12.0+16*14.8+1*10.0+1*10.0=430.6(cm3/mol)$

$\phi=1.0$(for organic phase)

$\eta_B=1.35$(cp, Exxsol D-80)

T=298.15(K)

M_B=200.0(molecular weight of Exxsol D-80)

If plugging all above data into the Wilke-Chang equation, we have diffusivity of the Sr-D2EHPA complex in the organic phase:

$$Dm = \frac{7.4*10^{-12}(\phi*M_B)^{1/2}T}{\eta_B V_A^{0.6}}$$

$$= \frac{7.4*10^{-12}(1.0*200)^{1/2}*298.15}{1.35*430.6^{0.6}} = 6.08*10^{-10}(m^2/sec.)$$

For the effective diffusivity of complex in membrane phase, the Jefferson-Witzell-Sibbert correlation has been used.

$$D_e = D_m \left(\frac{4(1+2p)^2 - \pi}{4(1+2p)^2} \right) + \frac{\pi}{4(1+2p)^2} \left(\frac{(1+2p)D_A D_m}{D_m + 2pD_A} \right)$$

where

$$(6.2)$$

$$D_A = \frac{2(D_i / m)D_m}{(D_i / m) - D_m} \left[\frac{D_i / m}{(D_i / m) - D_m} \ln \left(\frac{D_i / m}{D_m} \right) - 1 \right]$$

$$p = 0.403 \left(\frac{Vi}{Vm + Vi} \right)^{-1/3} - 0.5$$

where D_i and D_m are determined above, V_i and V_m are volumes of the internal phase and the membrane phase, m is the external partition function, π is 3.1416 and p and D_A are intermediate variables.

If we use a set of data for example,

$D_i = 1.21 * 10^{-9} (m^2/sec)$

$D_m = 6.08 * 10^{-10} (m^2/sec)$

$V_i = 5.0$ (ml)

$V_m = 20.0$ (ml)

m = 99.0 (determined by experiment)

If plugging all above data into the Jefferson-Witzell-Sibbert correlation,

$D_e = 3.65 * 10^{-10} (m^2/sec)$.

6.2.2 Evaluation of the External Mass Transfer Coefficient

The external mass transfer coefficient k is determined by the Skelland & Lee equation.

$$\frac{k}{\sqrt{ND_i}} = 2.932*10^{-7}(\frac{Vi+Vm}{Vi+Vm+Ve})^{-0.508}(\frac{d_1}{d_T})^{0.548} Re^{1.371}$$

(6.3)

$$Re = \frac{Nd_1^2\rho}{\mu}$$

The definition of the variables and their assigned data are listed in Table 6-6.

If plugging above data into the Skelland & Lee Equation, we have

Reynolds Number: $Re = 8*10^3$

external mass transfer coefficient: $k = 5.51*10^{-6}$ (M/sec.)

Table 6-6 Variables and their Assigned Data for Determination of the External Mass Transfer Coefficient of the Strontium System

N:	Agitating speed (rps)	5
Di:	external diffusivity (m^2/sec.)	$1.21*10^{-9}$
d_1:	diameter of the propeller (m)	0.04
d_T:	diameter of the tank (m)	0.1
Vi:	volume of the internal phase (ml)	5.0
Vm:	volume of the membrane phase (ml)	20.0
Ve:	volume of the external phase (ml)	500
ρ:	density of the external phase (g/cm^3)	1.0
μ:	viscosity of the external phase (g/cm/sec)	0.01

6.2.3 Evaluation of Sauter Mean Globule Radius

The prediction method and the result of the sauter mean radius of the emulsion globule is same in Chapter 6.1.3.

6.2.4 Prediction and Discussion

A FORTRAN algorithm is developed to calculate the dependence of the dimensionless external concentration, the dimensionless interfacial concentration and the dimensionless concentration profiles inside the membrane phase versus time. All the experimental data and evaluated parameters are incorporated into the model. Experimental results and the model predicted results are compared.

Figure 6.2 gives the prediction of the experimental data for arsenic removal by the ELM and Table 6-7 gives model parameters and the experimental conditions. It can be found that the prediction is excellent.

**Table 6-7:** List of the Model Parameters and the Experimental Conditions for Strontium Data Prediction

Model Parameters	
Di : Diffusity of solute in the external phase(m^2/sec)	$1.21*10^{-9}$
Dm : Diff. of Complex in the membrane phase(m^2/sec)	$6.08*10^{-10}$
De : Effective Diff. of complex in the membrane phase(m^2/sec)	$3.65*10^{-10}$
f' : emulsion volume fraction(Vi+Vm/Vtot)	0.05
e : sink phase volume fraction(Vi/(Vi+Vm))	0.2
R : radius of the globule(m)	$5.8*10^{-4}$
m : external distribution coefficient	99.0
q : internal distribution coefficient	150.0
k : external mass transfer coefficient(m/sec)	$5.51*10^{-6}$
B : mf'w	481.5
Biot number	0.09
Experimental Conditions: Ceo=1000 ppm, Ve=500ml, 0.1 NaAc-HAc Buffer, 300 rpm Vm=20 ml, 5vol% D2EHPA, 2vol% ECA4360J, rest: Exxsol D-80 Vi=5ml, H_2SO_4(3M)	
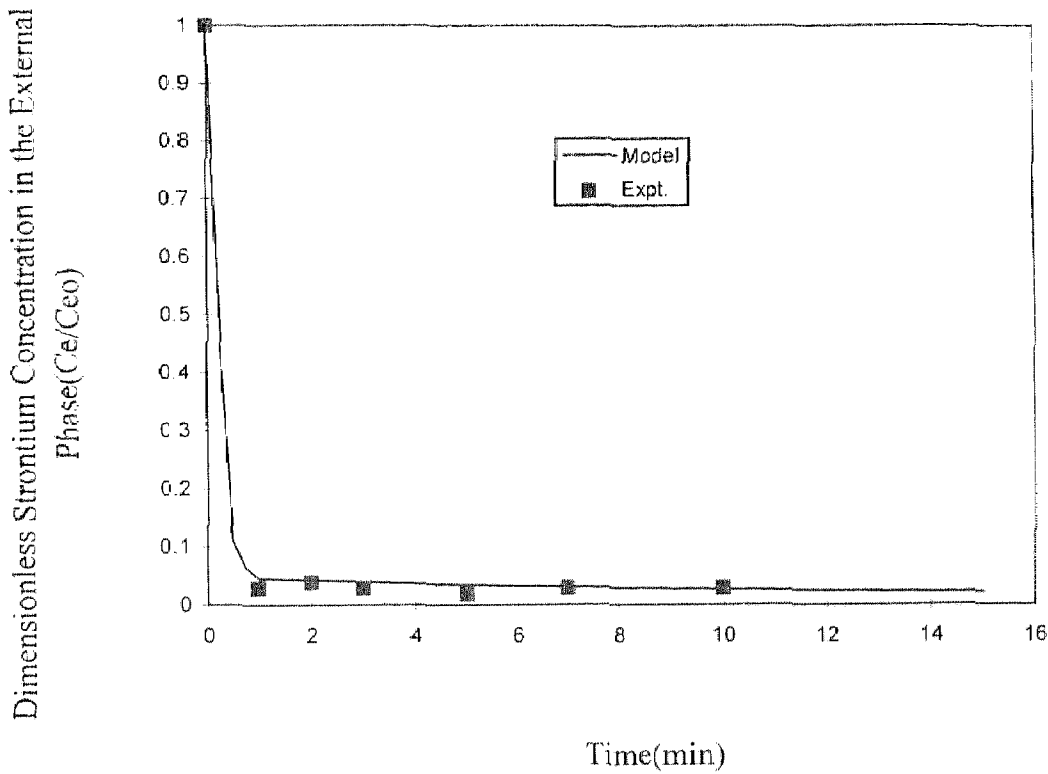
Figure 6.2 Prediction of Strontium Experimental Data by the Model
B=481.5; Biot=0.09

Experimental Conditions:
External phase: 500ml, 1040 ppm strontium solution, 0.1N HAc-NaAc buffer,
        300rpm, room temp.
Emulsion phase: 25ml fresh emulsion, which contains
        20ml organic phase: 5v% D2EHPA, 2v% ECA4360J, rest: Exxsol D-80
        10ml internal phase: 3M H_2SO_4 solution

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

From the experimental and mathematical modeling studies of extraction of arsenic ions and strontium ions, it has been found that emulsion liquid membranes are an effective tools to remove arsenic and strontium from wastewater.

Some conclusions may be made on the arsenic system:

1. 2-ethylhexyl alcohol (2EHA) was a suitable carrier for arsenic removal by the ELM system.

2. 92% removal efficiency can be achieved in one stage within 15 minutes at a concentrated ratio of 50 when 10v% 2EHA, 2v% ECA4360J and 88v% Exxsol D-80 are used as the carrier, surfactant and diluent, respectively.

3. High acidic strength in the external phase, and high alkali strength in the internal phase will accelerate arsenic transfer rate and increase arsenic removal efficiency. In this system, 0.2M H_2SO_4 and 2N NaOH solutions were selected as the external and internal phases and they gave optimal performance and keep good emulsion stability.

4. Same extraction performance was achieved for initial arsenic concentrations of 100ppm and 5ppm. This implied the removal efficiency limit of one stage can be removed by a series of stages.

5. Selectivity of arsenic ion over cupric ion was extremely high.

6. The mechanism of extraction of arsenic by 2EHA has been elucidated.

Some conclusions may be made on the strontium system:

1. Di-2-(ethylhexyl) phosphoric acid (D2EHPA) was a suitable carrier for strontium removal by the ELM system.

2. 98% removal efficiency can be achieved in one stage within 2 minutes at a concentrated ratio of 100 when 5v% 2EHA, 2v% ECA4360J and 93v% Exxsol D-80 are used as the carrier, surfactant and diluent respectively.

3. The extraction isotherm showed the pH range for the Sr-D2EHPA system ranged from 3 to 5. Therefore, the external phase pH was controlled by the use of a 0.1N HAc-NaAc buffer solution. A 3M H_2SO_4 solution as the internal phase, showed promising stripping behavior.

4. Same extraction performance was achieved for initial strontium concentrations of 1040ppm and 51ppm. This implied the removal efficiency limit of one stage can be removed by a series of stages.

5. Selectivity of strontium ion over sodium ion was extremely high.

Some conclusions may be made on mathematical modeling of ELM systems:

1. The mass transfer models have taken into account the external phase mass transfer resistance and leakage.

2. Analytical solutions have been obtained by the Laplace transform method.

3. The models can predict the time dependence of solute concentrations in the external phase, at the external-membrane phase interface and in the membrane phase.

4. Some dimensionless groups have been found to characterize the emulsion liquid membrane systems. One is Biot number, which provides the ratio of the membrane diffusion resistance to the external mass transfer film resistance. The other one is the B number, which indicates the capability of the emulsion. The large B number gives more of the percentage reduction of the solute concentration in the external phase. The third one is the P number, which indicated the significance of the leakage of the internal solute to the external phase. A theoretical study of ELMs has been conducted.

5. A relationship between the critical biot number and B number has been established so that the determination of the external mass transfer resistance as the rate-control step is straightforward.

6. The models have given excellent prediction of experimental data of arsenic and strontium systems

7.2 Recommendations

1. A feasibility study of strontium removal from radioactive wastewater via the emulsion liquid membrane includes the difference between radioactive of Sr-90 and non-radioactive Sr-87, radiation effect on organic chemical stability and effects of other non-radioactive chemicals(nitrate, nitrite, phosphate and carbonate).

2. Scale-up emulsion liquid membrane processes for treatment of arsenic and radioactive wastewaters.

APPENDIX A

CALIBRATION CURVES

A-1 Inductively Coupled Plasma-Mass Spectrometry(ICP-MS) Calibration Curve for Arsenic Concentration Measurements

A-2 Atomic Adsorption(AA) Calibration Curve for Strontium Concentration Measurements
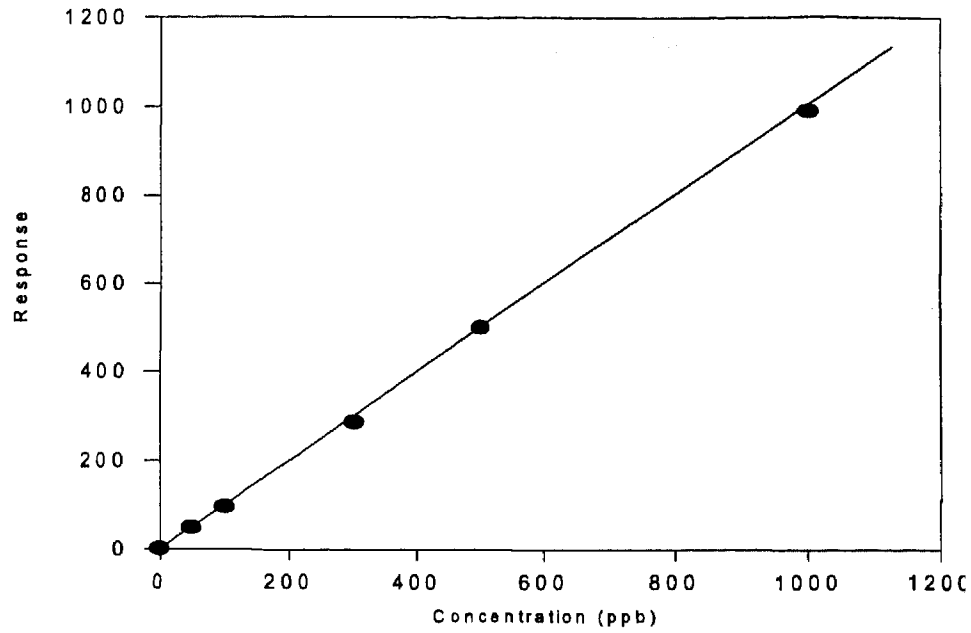
Figure A-1 Inductively Coupled Plasma- Mass Spectrometry(ICP-MS)
Calibration Curve for Arsenic Concentration Measurement
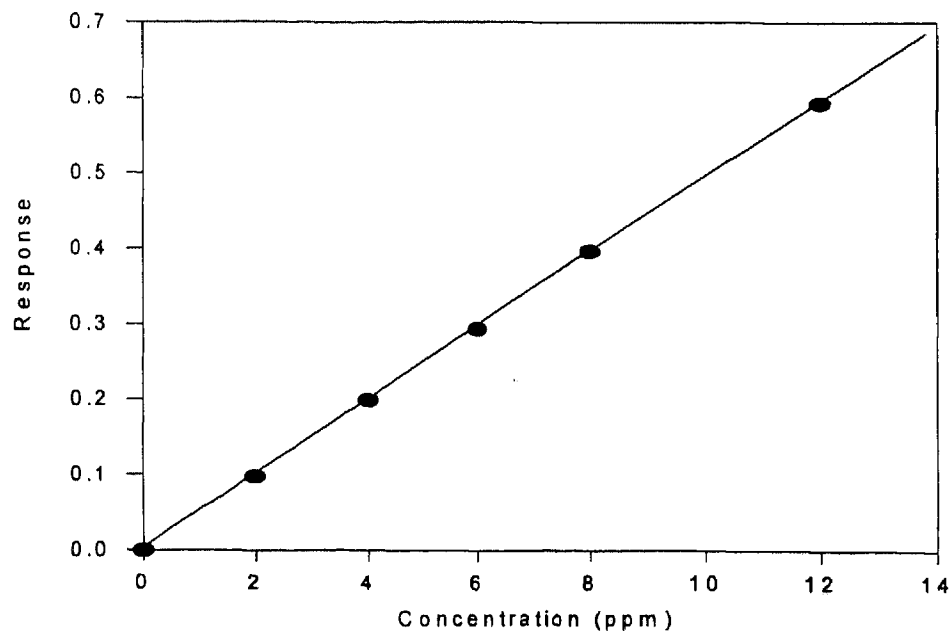
Figure A-2 Atomic Adsorption (AA) Calibration Curve for Strontium
Concentration Measurement

APPENDIX B

THE LAPLACE TRANSFORM OF ELM MATHEMATICAL MODELS

B-1   The Laplace Transform Solutions of ELM Mathematical Model With and Without External Mass Transfer Film Resistance

B-2   The Laplace Transform Solution of ELM Mathematical Model Considering the Leakage

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APPENDIX B-1

The Laplace Transform Solutions of the ELM Mathematical
Models With and Without External Mass Transfer Film Resistance

Case 1: The External Mass Transfer Resistance is Neglected

Governing equations:

External: $\qquad \dfrac{dUe}{d\tau} = -m*f*(\dfrac{\partial Um}{\partial v})|_{v=1}$ $\qquad$ (4.10)

$\qquad$ Equilibrium: $\quad Ue = Um^* \qquad Ue = Ue^*$

$\qquad$ I.C. $\qquad Ue = 1, \text{when } \tau = 0$

Membrane: $\qquad \omega*\dfrac{\partial Um}{\partial \tau} = \dfrac{1}{v^2}\dfrac{\partial}{\partial v}(v^2\dfrac{\partial Um}{\partial v})$ $\qquad$ (4.11)

$\qquad$ I.C. $\quad Um = 0, \qquad\qquad \text{when } \tau = 0$

$\qquad$ B.C. $\quad Um = \text{finite} \quad \text{when } v = 0; \quad Um = Ue \qquad \text{when } v = 1$

where: $\qquad Ue = \dfrac{Ce}{Ceo} \quad \tau = \dfrac{De*t}{R^2} \quad f = \dfrac{3f'}{1-f'} \quad f' = \dfrac{Vi+Vm}{Vi+Vm+Ve}$

$\qquad \omega = 1-e+e*q \qquad e = \dfrac{Vi}{Vi+Vm} \qquad v = \dfrac{r}{R} \quad Um = \dfrac{Cm}{m*Ceo}$

Laplace Transform

Firstly, taking the Laplace transform of equation(4.11) together with its boundary

conditions,

$$s\omega\overline{U_m} - 0 = \dfrac{1}{v^2}\dfrac{d}{dv}(v^2\dfrac{d\overline{U_m}}{dv})$$ $\qquad$ (4.20)

here s represents the Laplace domain.

Rearrange equation (4.20), we have

$$\frac{1}{v^2}\frac{d}{dv}(v^2\frac{d\overline{U_m}}{dv}) - sw\overline{U_m} = 0 \tag{4.21}$$

B.C.1 $\overline{U_m}$ is finite, when v=0;   B.C.2 $\overline{U_m} = \overline{U_e}$, when v=1

Eqn (4.21) can be solved as:

$$\overline{U_m} = C_1\frac{Sinh(Hv)}{v} + C_2\frac{Cosh(Hv)}{v} \tag{4.22}$$

here C_1 and C_2 are two constants to be determined by boundary conditions, and

$H = \sqrt{sw}$ is an intermediate variable.

apply B.C. 1 to eqn(4.22): $C_2=0$

apply B.C. 2 to eqn(4.22): $C_1 = \frac{\overline{U_e}}{Sinh(H)}$

Thus, eqn (4.22) changes to

$$\overline{U_m} = \frac{\overline{U_e}*Sinh(Hv)}{vSinh(H)} \tag{4.23}$$

Differentiate equation(4.23) and take its value at v=1:

$$(\frac{d\overline{U_m}}{dv})|_{v=1} = \frac{\overline{U_e}}{Sinh(H)}[HCosh(H) - Sinh(H)] \tag{4.24}$$

Secondly, taking the Laplace transform of eqn(4.10):

$$s\overline{U_e} - 1 = mf(\frac{d\overline{U_m}}{dv})_{v=1} \tag{4.25}$$

Plug Eqn(4.24) into Eqn(4.25), and solve for $\overline{U_e}$

$$\overline{U_e} = \frac{Sinh(H)}{s*Sinh(H) + mf[HCosh(H) - Sinh(H)]} \tag{4.26}$$

Inverse Laplace Transform

When denominator equals to zero, we may find the values of the multipoles.

1. $s=0$ (4.27)

2. $s*\text{Sinh}(H) + mf[H\text{Cosh}(H) - \text{Sinh}(H)] = 0$ (4.28)

solve for s (orH):

$$\tanh(H) = \frac{mfH}{mf - s}$$ (4.28)

since $H=(\omega s)^{1/2}$, let

$-bn^2=\omega s=H^2$, Thus H=ibn, $s=-bn^2/\omega$, tanh(H)=itan(bn)

So $i\tan(bn) = \dfrac{mf*ibn}{mf - (-\dfrac{b^2n}{\omega})}$ (4.29)

Thus, $\tan(bn) = \dfrac{B*bn}{B+b^2n}$ (4.15)

where: B=mωf which represent emulsion capability

According to Stern-Louilille theory, the inverse form should be follows:

If $\overline{U_e} = \dfrac{N(s)}{D(s)}$, then $U_e = \lim\limits_{s\to Sn} \dfrac{N(Sn)}{D'(Sn)}\exp(-Sn\tau)$ (4.30)

Here we have two solutions of Sn, they are 1. Sn=0, and 2. Sn solved by Eqn(4.15), and their related inverse solution shall be found separately.

1. Time-independent term:

When Sn=0, 1st term will be found which is time-independent, and will give the information when time approaches infinite.

$$\overline{U}e = \frac{Sinh(H)}{s*Sinh(H) + mf[HCosh(H) - Sinh(H)]} \tag{4.31}$$

Since:

$$Sinh(H) = \frac{e^H - e^{-H}}{2}$$

$$= \frac{(1 + H + \frac{H^2}{2!} + \frac{H^3}{3!} + ...) - (1 - H + \frac{H^2}{2!} - \frac{H^3}{3!} ...)}{2} = H + \frac{H^3}{3!} + ...$$

$$Cosh(H) = \frac{e^H + e^{-H}}{2}$$

$$= \frac{(1 + H + \frac{H^2}{2!} + \frac{H^3}{3!} + ...) + (1 - H + \frac{H^2}{2!} - \frac{H^3}{3!} ...)}{2} = 1 + \frac{H^2}{2} + \frac{H^4}{4!} + ...$$

Thus, Plug Sinh(H) and Cosh(H) into Eqn(4.31)

$$\overline{U}e = \frac{H + \frac{H^3}{3!} + ...}{(\frac{H^2}{\omega} - mf)(H + \frac{H^3}{3!} + ...) + mfH(1 + \frac{H^2}{2} + \frac{H^4}{4!} + ...)}$$

$$= \frac{1 + \frac{H^2}{3!} + ...}{(\frac{H^2}{\omega} - mf)(1 + \frac{H^2}{3!} + ...) + mf(1 + \frac{H^2}{2} + \frac{H^4}{4!} + ...)} = \frac{N(s)}{D(s)}$$

Thus, the first term=

$$\lim_{s \to 0} \frac{N(s)}{D'(s)} = \lim_{H \to 0} \frac{1 + \frac{2H^2}{3} + ...}{(mfH + \frac{2H}{\omega} - \frac{1}{3}mfH)\frac{\omega}{2H} + ...} \tag{4.32}$$

$$= \frac{1}{\frac{mf\omega}{3} + 1} = \frac{1}{1 + \frac{B}{3}} = \frac{3}{3 + B}$$

Remember that

$$B = mf\omega$$

$$H = (\omega s)^{1/2}, \quad s = H^2/\omega, \quad \frac{dH}{ds} = \frac{\omega}{2H}$$

2. Time-dependent terms

Time dependent term are solutions when Sn is not equal to 0. They are related to Sn that are solved from equation(4.15).

$$\text{If} \quad \overline{U_c} = \frac{N(s)}{D(s)}, \quad \text{then} \quad U_c = \lim_{s \to Sn} \frac{N(Sn)}{D'(Sn)} \exp(-Sn\tau) \tag{4.30}$$

Here,

$$\overline{U_c} = \frac{\sinh(H)}{s*Sinh(H) + mf[HCosh(H) - Sinh(H)]}$$

Thus,

$$N(s) = Sinh(H)$$
$$D(s) = s*Sinh(H) + mf[HCosh(H) - Sinh(H)]$$

Firstly, take derivative of D(s)

$$D'(s) = \frac{dD(s)}{ds} = Sinh(H) + [sCosh(H) + mfHSinh(H)]\frac{dH}{ds}$$

Secondly, substitute Hn and Sn by bn, by using of following relations:

$$Hn = ibn, \quad Sn = \frac{H^2}{\omega} = -\frac{b^2 n}{\omega}, \quad \tanh(ibn) = i*\tan(bn)$$

Thirdly, organize the complicated algebra equation

Finally, we have

$$\frac{N(Sn)}{D'(Sn)} = \frac{1}{1 + [\frac{s}{tanh(H)} + mfH]\frac{\omega}{2H}}$$

$$= \frac{2}{2 + mf\omega + \frac{\omega s}{H\,tanh(H)}}$$

$$= \frac{2B}{B^2 + 3B + b^2 n} \qquad (4.33)$$

If combine time independent and time dependent solutions together, we find the final the Laplace Transform solution of the emulsion liquid membrane system.

$$Ue = \frac{3}{B+3} + \sum_{n=1}^{\infty} \frac{2B}{B^2 + 3B + b^2 n} Exp(-bn^2 \frac{\tau}{\omega}) \qquad (4.14)$$

where bn are solved from:

$$tan(bn) = \frac{B*bn}{B + b^2 n} \qquad (4.15)$$

Case 2: External Mass Transfer Resistance is Considered

Governing equations:

External: $\qquad \frac{dUe}{d\tau} = -Ko*(Ue - Ue*) \qquad (4.12)$

$$G*(\frac{\partial Um}{\partial v})|_{v=1} = (Ue - Ue*) \qquad (4.13)$$

Equilibrium: $\quad Ue* = Um*$

I.C. $\quad Ue = Ue* = 0$, when $\tau = 0$

Membrane: $$\omega * \frac{\partial Um}{\partial \tau} = \frac{1}{v^2} \frac{\partial}{\partial v} (v^2 \frac{\partial Um}{\partial v})$$ (4.11)

I.C. $Um = 0$, when $\tau = 0$

B.C. $Um = $ finite when $v = 0$; $Um = Ue*$ when $v = 1$

where: $$Ko = \frac{R*k*f}{De} \qquad G = \frac{m*De}{R*k} \qquad Ue* = \frac{Ce*}{Ceo} \qquad Um* = \frac{Cm*}{mCeo}$$

Laplace Transform

Firstly, taking derivative of Eqn(4.11) and its boundary conditions, we can solve for

$$\overline{U_m} = C_1 \frac{Sinh(Hv)}{v} + C_2 \frac{Cosh(Hv)}{v}$$ (4.22)

here C_1 and C_2 are two constants to be determined by boundary conditions, and

$H = \sqrt{s\omega}$ is an intermediate variable.

apply B.C. 1 to eqn(4.22): $C_2 = 0$

apply B.C. 2 to eqn(4.22): $C_1 = \dfrac{\overline{U_e^*}}{Sinh(H)}$

Thus, eqn (4.22) changes to

$$\overline{U_m} = \frac{\overline{U_e^*} * Sinh(Hv)}{v Sinh(H)}$$ (4.34)

Differential equation(4.34) and give its value at $v=1$:

$$(\frac{d\overline{U_m}}{dv})|_{v=1} = \frac{\overline{U_e^*}}{Sinh(H)} [HCosh(H) - Sinh(H)]$$ (4.35)

Secondly, taking deraritive of Eqn(4.12,4.13)

$$s\overline{U}_e - 1 = -Ko*(\overline{U}e - \overline{U}e*) \tag{4.36}$$

$$G*(\frac{\partial \overline{Um}}{\partial v})\Big|_{v=1} = (\overline{U}e - \overline{U}e*) \tag{4.47}$$

Combine equation (4.35) and (4.37), the relation of $\overline{U_e^*}$ and $\overline{U_e}$ is found:

$$\overline{U_e^*} = \frac{Sinh(H)\overline{U_e}}{[GHCosh(H)-(G-1)Sinh(H)]} \tag{4.38}$$

By combining Eqn(4.34), (4.36) and (4.38), $\overline{U_e}, \overline{U_e^*}, and \overline{U_m}$ can be solved as following:

$$\overline{U_e} = \frac{Sinh(H)+G[HCosh(H)-Sinh(H)]}{sSinh(H)+G(s+Ko)[HCosh(H)-Sinh(H)]}$$

$$\overline{U_e^*} = \frac{Sinh(H)}{sSinh(H)+G(s+Ko)[HCosh(H)-Sinh(H)]} \tag{4.39}$$

$$\overline{U_m} = \frac{\dfrac{Sinh(Hv)}{v}}{sSinh(H)+G(s+Ko)[HCosh(H)-Sinh(H)]}$$

Inverse Laplace Transform

When denominator equals to zero, we may find the values of the multipoles.

1. s=0 $\hspace{6cm}$ (4.40)

2. $sSinh(H)+G(s+Ko)[HCosh(H)-Sinh(H)] = 0$ $\hspace{2cm}$ (4.41)

solve for s (orH):

$$\tanh(H) = \frac{HG(s + Ko)}{sG - s + GKo} \tag{4.42}$$

since $H = (\omega s)^{1/2}$, let

$-bn^2 = \omega s = H^2$, Thus $H = ibn$, $s = -bn^2/\omega$, $\tanh(H) = i\tan(bn)$

So $\qquad i\tan(bn) = \dfrac{ibnG(\omega Ko - b^2n)}{-b^2n(G - 1) + \omega KoG} \tag{4.43}$

Thus, $\qquad \tan(bn) = \dfrac{bn*(B - Gbn^2)}{B + bn^2(1 - G)} \tag{4.19}$

where: $\qquad B = m\omega f = \omega GKo$ which represent emulsion capability

According to Stern-Louilille theory, the inverse form should be written as following

If $\qquad \overline{U_e} = \dfrac{N(s)}{D(s)}$, then $\qquad U_e = \lim_{S \to Sn} \dfrac{N(Sn)}{D'(Sn)} \exp(-Sn\tau) \tag{4.30}$

Here we have two solutions of Sn, they are 1. Sn=0, and 2. Sn solved by Eqn(4.19), and their related inverse solution shall be found separately.

1. Time-independent term:

When Sn=0, 1st term will be found that is time-independent, and will give the information of the emulsion liquid membrane system when time approach infinite.

$$\overline{U}e = \frac{Sinh(H) + G[HCosh(H) - Sinh(H)]}{s*Sinh(H) + G(s + Ko)[HCosh(H) - Sinh(H)]} \tag{4.44}$$

$$Sinh(H) = \frac{e^{H} - e^{-H}}{2}$$

$$= \frac{(1 + H + \frac{H^2}{2!} + \frac{H^3}{3!} + ...) - (1 - H + \frac{H^2}{2!} - \frac{H^3}{3!}...)}{2} = H + \frac{H^3}{3!} + ...$$

$$Cosh(H) = \frac{e^{H} + e^{-H}}{2}$$

$$= \frac{(1 + H + \frac{H^2}{2!} + \frac{H^3}{3!} + ...) + (1 - H + \frac{H^2}{2!} - \frac{H^3}{3!}...)}{2} = 1 + \frac{H^2}{2!} + \frac{H^4}{4!} + ...$$

Thus, Plug Sinh(H) and Cosh(H) into Eqn(4.44)

$$\overline{U}e = \frac{(H + \frac{H^3}{3!} + ...) + G[(1 + \frac{H^2}{2} + ...)H - (H + \frac{H^3}{3!} + ...)]}{\frac{H^2}{\omega}(H + \frac{H^3}{3!} + ...) + G(\frac{H^2}{\omega} + Ko)[(1 + \frac{H^2}{2!} + ...)H - (H + \frac{H^3}{3!} + ...)]}$$

$$= \frac{(1 + \frac{H^2}{3!} + ...) + G(\frac{H^2}{3} + ...)}{\frac{H^2}{\omega}(1 + \frac{H^2}{3!} + ...) + G(\frac{H^2}{\omega} + Ko)(\frac{H^2}{3} + ...)} = \frac{N(s)}{D(s)}$$

Thus, the first term=

$$\lim_{s \to 0} \frac{N(s)}{D'(s)} = \lim_{H \to 0} \frac{1 + (\frac{1}{3!} + \frac{G}{3})H^2 + ...}{[\frac{2H}{\omega} + G\frac{2H}{\omega}\frac{H^3}{3} + G(\frac{H^2}{\omega} + Ko)\frac{2H}{3}]\frac{\omega}{2H} + ...} \tag{4.45}$$

$$= \frac{1}{1 + \frac{GKo\omega}{3}} = \frac{1}{1 + \frac{B}{3}} = \frac{3}{3 + B}$$

Remember that $B = mf\omega = G*Ko*\omega$ $H = (\omega s)^{1/2}, s = H^2/\omega, \frac{dH}{ds} = \frac{\omega}{2H}$

2. Time-dependent terms

Time dependent term are solutions when Sn is not equal to 0. They are related to Sn that are solved from equation(4.19).

$$\text{If} \quad \overline{U_e} = \frac{N(s)}{D(s)}, \quad \text{then} \quad U_e = \lim_{S \to Sn} \frac{N(Sn)}{D'(Sn)} \exp(-Sn\tau) \tag{4.30}$$

$$\overline{U_e} = \frac{\sinh(H) + G[H\cosh(H) - \sinh(H)]}{s*\sinh(H) + G(s + Ko)[H\cosh(H) - \sinh(H)]}$$

Thus, $\tag{4.46}$

$$N(s) = \sinh(H) + G[H\cosh(H) - \sinh(H)]$$

$$D(s) = s*\sinh(H) + G(s + Ko)[H\cosh(H) - \sinh(H)]$$

Firstly, take derivative of D(s)

$$D'(s) = \frac{dD(s)}{ds} = \sinh(H) + s\cosh(H)\frac{dH}{ds} + G[H\cosh(H) - \sinh(H)] + G(s + Ko)(H\sinh(H))\frac{dH}{ds}$$

Secondly, substitute Hn and Sn by bn, by using of following relations:

$$Hn = ibn, \quad Sn = \frac{H^2}{\omega} = -\frac{b^2n}{\omega}, \quad \tanh(ibn) = i*\tan(bn) \tag{4.47}$$

Thirdly, organize the complicated algebra equation

Finally, we have

$$\frac{N(Sn)}{D'(Sn)} == \frac{\tan(bn) + G[bn - \tan(bn)]}{\tan(bn) + \dfrac{bn}{2} + G[bn - \tan(bn)] + G(\dfrac{-b^2n}{\omega} + Ko)\dfrac{\omega}{2}\tan(bn)} \tag{4.48}$$

Subsitute

$$\tan(bn) = \frac{bn*(B - Gbn^2)}{B + bn^2(1 - G)} \tag{4.19}$$

into the above equation, and do the derivation

$$\frac{N(Sn)}{D'(Sn)} = \frac{1 + G[\dfrac{bn}{\tan(bn)} - 1]}{1 + \dfrac{bn}{2\tan(bn)} + G[\dfrac{bn}{\tan(bn)} - 1] + G(-\dfrac{bn^2}{\omega} + Ko)\dfrac{\omega}{2}}$$

$$= \frac{1 + G[\dfrac{B + b^2n(1-G)}{B - Gb^2n} - 1]}{1 + \dfrac{1}{2}\dfrac{B + b^2n(1-G)}{B - Gb^2n} + G[\dfrac{B + b^2n(1-G)}{B - Gb^2n} - 1] + G(\dfrac{-b^2n}{\omega} + Ko)\dfrac{\omega}{2}}$$ (4.48)

$$= \frac{B}{(B - Gb^2n) + \dfrac{1}{2}[B + b^2n(1-G)] + Gb^2n - \dfrac{1}{2}(B - Gb^2n)^2}$$

$$= \frac{2B}{3B + B^2 + b^2n + Gb^2n(Gb^2n - 2B - 1)}$$

If combine time independent and time dependent solutions together, we find the final Laplace Transform solution of emulsion liquid membrane system.

$$\frac{Ce}{Ceo} = Ue = \frac{3}{B+3} + \sum_{n=1}^{\infty} \frac{2B}{3B + B^2 + bn^2 + Gbn^2(Gbn^2 - 2B - 1)} \exp(-\frac{bn^2}{\omega}\tau)$$ (4.16)

where bn is solved by following equation

$$\tan(bn) = \frac{bn*(B - Gbn^2)}{B + bn^2(1-G)}$$ (4.19)

By analogy, U_e^* and U_m can be solved as following:

$$\frac{C^*e}{Ceo} = \frac{3}{B+3} + \sum_{n=1}^{\infty} \frac{2(B-Gbn^2)}{3B+B^2+bn^2+Gbn^2(Gbn^2-2B-1)} \exp(-\frac{bn^2}{\omega}\tau)$$ (4.17)

$$\frac{Cm}{mCeo} = \frac{3}{B+3} + \sum_{n=1}^{\infty} \frac{2(B-Gbn^2)(\frac{\sin(bn*v)}{v*\sin(bn)})}{3B+B^2+bn^2+Gbn^2(Gbn^2-2B-1)} \exp(-\frac{bn^2}{\omega}\tau)$$ (4.18)

where bn is solved by following equation

$$\tan(bn) = \frac{bn*(B-Gbn^2)}{B+bn^2(1-G)}$$ (4.19)

APPENDIX B-2

The Laplace Transform Solution of the ELM Mathematical Model with the Leakage

Dimensionless equations

The following three dimensionless equations, together with their equilibrium

equations and boundary conditions, can be found for the case of considering the leakage:

External Phase:

$$\frac{dUe}{d\tau} = -Ko*(Ue - Ue^*) + I*(1 - Ue) \qquad (5.12)$$

$$G*(\frac{\partial Um}{\partial v})\big|_{v=1} = (Ue - Ue^*) \qquad (5.13)$$

Equilibrium: $Ue^* = Um^*$

I.C. $Ue = Ue^* = 0$, when $\tau = 0$

where: $Ko = \dfrac{R*k*f}{De} \qquad G = \dfrac{m*De}{R*k} \qquad Ue^* = \dfrac{Ce^*}{Ceo} \qquad Um^* = \dfrac{Cm^*}{mCeo} \qquad I = \dfrac{k_b R^2}{D_{eff}}$

$$Ue = \frac{Ce}{Ceo} \qquad \tau = \frac{Det}{R^2} \qquad f = \frac{3f'}{1-f'} \qquad f' = \frac{Vi+Vm}{Vi+Vm+Ve}$$

Membrane phase:

Equation (5.11) will become

$$\omega \frac{\partial Um}{\partial \tau} = \frac{1}{v^2} \frac{\partial}{\partial v}(v^2 \frac{\partial Um}{\partial v}) \qquad (5.14)$$

I.C. $Um = 0$, when $\tau = 0$

B.C. $Um = $ finite when $v = 0$; $Um = Um^*$ when $v = 1$

where: $\omega = 1 - \dfrac{Vi}{Vi+Vm}(1+q) \qquad v = \dfrac{r}{R} \qquad Um = \dfrac{Cm}{mCeo}$

Here we may find eqn(5.12),(5.13) are describing the external phase behavior and the

eqn(5.14) is describing the membrane and internal phases.

The Laplace Transform

Firstly, taking the Laplace transform of equation(5.14) together with its boundary

conditions,

$$sw\overline{U_m} - 0 = \frac{1}{v^2}\frac{d}{dv}(v^2\frac{d\overline{U_m}}{dv})$$

rearrange it,

$$\frac{1}{v^2}\frac{d}{dv}(v^2\frac{d\overline{U_m}}{dv}) - sw\overline{U_m} = 0 \tag{5.19}$$

B.C.1 $\overline{U_m}$ is finite, when v=0; B.C.2 $\overline{U_m} = \overline{U_e^*}$, when v=1

Eqn (15) is a one type of Bessel equation and its solution is

$$\overline{U_m} = C_1\frac{Sinh(Hv)}{v} + C_2\frac{Cosh(Hv)}{v} \tag{5.20}$$

here C_1 and C_2 are two constants to be determined by boundary conditions, and

$H = \sqrt{sw}$ is an intermediate variable.

apply B.C. 1 to eqn(5.20): $C_2 = 0$

apply B.C. 2 to eqn(5.20): $C_1 = \dfrac{\overline{U_e^*}}{Sinh(H)}$

Thus, eqn (5.20) changes to

$$\overline{U_m} = \frac{\overline{U_e^*}*Sinh(Hv)}{vSinh(H)} \tag{5.21}$$

Differentiate equation(5.21) and give its value at v=1:

$$\left(\frac{d\overline{U_m}}{dv}\right)_{v=1} = \frac{\overline{U_e^*}}{Sinh(H)}\left[HCosh(H)-Sinh(H)\right]$$ (5.22)

Secondly, taking the Laplace transform of eqn(5.13):

$$\left(\frac{d\overline{U_m}}{dv}\right)_{v=1} = \frac{1}{G}(\overline{U_e} - \overline{U_e^*})$$ (5.23)

Combine equation(5.22) and (5.23), the relation of $\overline{U_e^*}$ and $\overline{U_e}$ is found:

$$\overline{U_e^*} = \frac{Sinh(H)\overline{U_e}}{\left[GHCosh(H)-(G-1)Sinh(H)\right]}$$ (5.24)

Thirdly, taking the Laplace transform of eqn(5.12):

$$s\overline{U_e} - 1 = -Ko(\overline{U_e} - \overline{U_e^*})+I(\frac{1}{s} - \overline{U_e})$$

Rearrang it:

$$\overline{U_e^*} = \frac{\overline{U_e}(s+Ko+I)-(1+\frac{I}{s})}{Ko}$$ (5.25)

We may find that Equation(5.24)&(5,25) only have $\overline{U_e}$ and $\overline{U_e^*}$, solve them, we

find

$$\overline{U_e} = \frac{(s+I)\left[(1-G)Sinh(H)+GHCosh(H)\right]}{s\left[(Ko+s+I)GHCosh(H)+((s+I)-G(Ko+s+I))Sinh(H)\right]}$$ (5.26)

This is the Laplace solution of the dimensionless external concentration. We may find

that this is a typical multipole Stern-Louilille system, and after taking the inverse

Laplace transform, final answer will be found.

If I=0, this form will reduce to

$$\overline{U_e} = \frac{s\left[(1-G)Sinh(H)+GHCosh(H)\right]}{s\left[(Ko+s)GHCosh(H)+(s-G(Ko+s))Sinh(H)\right]}$$ (5.27)

which is same as the case when leakage is not considered.

Inverse Laplace Transform

When denominator equals to zero, we may find the values of the multipoles.

1. $s=0$

2. $[(Ko+s)GHCosh(H)+(s-G(Ko+s))Sinh(H)]=0$

solve for H:

$$tanh(H)= \frac{(Ko+s+I)GH}{(Ko+s+I)G-(s+I)}$$

since $H=(\omega s)^{1/2}$, let

$-bn^2=\omega s=H^2$, Thus $H=ibn$, $s=-bn^2/\omega$, $tanh(H)=itan(bn)$

So: $\quad i\,tan(bn)= \dfrac{(Ko-\dfrac{b^2n}{\omega}+I)G*ibn}{(Ko-\dfrac{b^2n}{\omega}+I)G-(-\dfrac{b^2n}{\omega}+I)}$

Thus, $\quad tan(bn)= \dfrac{(B+GP-Gb^2n)bn}{(B-P(G+1))-(G-1)b^2n}$ $\qquad$ (5.16)

where: $\qquad P=\omega I=(1-e+eq)k_bR^2/De$ which represents leakage

$\qquad\qquad B=KoG\omega=m\omega f$ which represent emulsion capability

$\qquad\qquad G=mDe/kR$ which is inverse Biot number,

These three dimensionless groups describe the emulsion liquid membrane system.

Equation(5.16) give the value of Sn that are multipoles of the inverse Laplace transform.

According to Stern-Louilille theory, the inverse form should be written as

following

If $\quad \overline{U_e}=\dfrac{N(s)}{D(s)}$, $\quad$ then $\quad U_e = \lim_{s\to Sn} \dfrac{N(Sn)}{D'(Sn)}exp(-Sn\tau)$ $\qquad$ (5.28)

Here we have two solutions of Sn, they are 1. Sn=0, and 2. Sn solved by Eqn(5.16), and their related inverse solution shall be found separately.

1. Time-independent term:

When Sn=0, 1st term will be found that is time-independent, and will give the information when time approach infinite.

1st term

$$= \lim_{s \to 0} \frac{N(s)}{D'(s)}$$

$$= \lim_{s \to 0} \frac{(s+I)[(1-G)Sinh(H)+GHCosh(H)]}{(Ko+s+I)GHCosh(H)+[(s+I)-(Ko+s+i)G]Sinh(H)+S_{highorder}}$$

Remember that

$$Sinh(0)=0, Cosh(0)=1, H=(\omega s)^{1/2}, s=H^2/\omega$$

and

$$\lim_{H \to 0} \frac{Sinh(H)}{H} = \lim_{H \to 0} \frac{e^H - e^{-H}}{2H}$$

$$= \lim_{H \to 0} \frac{(1+H+\frac{H^2}{2!}+\frac{H^3}{3!}+...)-(1-H+\frac{H^2}{2!}-\frac{H^3}{3!}...)}{2H}$$

$$= \lim_{H \to 0} \frac{2H+2\frac{H^3}{3!}+...}{2H} = 1$$

$$\lim_{H \to 0} \frac{(s+I)[(1-G)\frac{Sinh(H)}{H}+GCosh(H)]}{(Ko+s+I)GCosh(H)+[(s+I)-(Ko+s+I)G]\frac{Sinh(H)}{H}}$$

Thus,   (5.29)

$$= \frac{I(1-G+G)}{(Ko+I)G+(I-KoG-IG)} = \frac{I}{I} = 1$$

This time-independant solution only used for the case considering the leakage ($I \neq 0$). For the case without the leakage ($I=0$), the determination of the time-independent follows the procedures described in Appendix B-1.

2. Time-dependent terms

Time dependent term are solutions when Sn is not equal to 0. They are related to Sn that are solved from equation(5.16).

$$\text{If} \quad \overline{U_e} = \frac{N(s)}{D(s)}, \quad \text{then} \quad U_e = \lim_{s \to Sn} \frac{N(Sn)}{D'(Sn)} \exp(-Sn\tau) \qquad (5.28)$$

Here,

$$\overline{U_e} = \frac{(s+I)[(1-G)Sinh(H)+GHCosh(H)]}{s[(Ko+s+I)GHCosh(H)+((s+I)-G(Ko+s+I))Sinh(H)]}$$

Thus,

$$N(s)=(s+I)[(1-G)Sinh(H)+GHCosh(H)]$$

$$D(s)= s[(Ko+s+I)GHCosh(H)+((s+I)-G(Ko+s+I))Sinh(H)]$$

Firstly, take derivative of D(s)

$$D'(s)= \frac{dD(s)}{ds} = Sinh(H)[(I-GKo-IG)+s(2-2G-0.5\omega(GKo+GI))+0.5G\omega s^2]$$

$$+ \frac{Cosh(H)}{H}[(0.5\omega I + \omega GKo + \omega GI)s + (0.5\omega + 2\omega G)s^2] \qquad (5.30)$$

Secondly, substitute Hn and Sn by bn, by using of following relations:

$$Hn=ibn, \qquad Sn = \frac{H^2}{\omega} = -\frac{b^2 n}{\omega}, \qquad \tanh(ibn)=\tan(bn)$$

Thirdly, organize the complicated algebra equation

Finally, we have

$$\frac{N(Sn)}{D'(Sn)} = \frac{(-bn^2 + P)[\tan bn + G(bn - \tan bn)]}{\tan bn\{[P(1-G)-B]-[2(1-G)+\frac{1}{2}(B+P)]bn^2 + \frac{G}{2}bn^4\} + \{[P(\frac{1}{2}+G)+B]bn -(\frac{1}{2}+2G)bn^3\}} \quad (5.31)$$

If combine time independent and time dependent solutions together, we find the final The Laplace Transform solution of emulsion liquid membrane system.

$$Ue = 1 + \sum_{n=1}^{\infty} \frac{(-bn^2 + P)[\tan bn + G(bn - \tan bn)]Exp(-bn^2\frac{\tau}{\omega})}{\tan bn\{[P(1-G)-B]-[2(1-G)+\frac{1}{2}(B+P)]bn^2 + \frac{G}{2}bn^4\} + \{[P(\frac{1}{2}+G)+B]bn -(\frac{1}{2}+2G)bn^3\}} \quad (5.15)$$

where bn are solved from:

$$\tan(bn) = \frac{(B+GP-Gb^2n)bn}{(B-P(G+1))-(G-1)b^2n} \quad (5.16)$$

The above solution is for the case considering the leakage. It can not be simplified to the case without the leakage by setting the dimensionless group P equal to 0, or I equal to 0. The reason is that the time-independent term showed in equation (5.29) will turn to be $\frac{0}{0}$, so that it is not equal to 1.

APPENDIX C

COMPUTER CODES

APPENDIX C-1

Computer Code for Numerical Calculation of Emulsion Liquid Membrane Model
Consider(or not) External Film Resistance

```
C      *****************************************************************
C      *       MATHEMATICAL MODEL OF LIQUID MEMBRANE SYSTEM       *
C      *MASS TRANSFER WITH OR WITHOUT EXTERNAL FILM RESISTANCE*
C      *****************************************************************
C
C      VARIABLES:
C      CODE: 0-WITHOUT FILM RESISTANCE, 1-WITH FILM RESISTANCE
C      DI:DIFFUSIVITY IN AQUEOUS, DM:DIFFUSITY IN MEMBRANE PHASE
C      E:SINK PHASE VOL. FRACTION  FF:EMULSION VOL. FRACTION
C      T:PRINT TIME INTERVAL         RAD:DADIUS OF GLOBULE
C      F:EIGENVALUES                 S:VALUE OF THE TERM
C      M:EXTERNAL DISTRIBUTION COEFFICIENT
C      Q:INTERNAL DISTRIBUTION COEFFICIENT
C      KO:EXTERNAL MASS TRANSFER COEFFICIENT
C      SUM: SUMMATION OF THE SERIES
C      PARA: PARAMETER=M*FV*BC
C      X:ARRAR OF CONCENTRATION
C      INPUT FILE:LT.DAT
C      OUT FILE:LT.OUT
C
       IMPLICIT DOUBLE PRECISION (A-H,O-Z)
       DIMENSION TC(100),YY(100),X(100),CE(100)
       REAL M,L,KO,CODE,P
       PARAMETER(PAI=3.14159)
       CHARACTER*13 OUT
       OPEN(9,FILE='LT.DAT', STATUS='OLD')
c      OPEN(3,FILE='CHECK.OUT',STATUS='NEW')
       READ(9,'(F12.5)') CODE,DI,DM,FF,E,RAD,T,M,Q,
     &      RS,DIA,DENSITY,VIS,DP
       READ(9,'(A13)') OUT
C
C   HERE TO CALCULATE EXTERNAL MASS TRANSFER COEFFICIENT
C      SKELLAND AND LEE EQUATION
C   DATE FROM UNIT=9, FILE=LT.DAT
C
       RS1=RS/60.
```

```
      Re=1.0E6*RS1*(DP**2.0)*DENSITY/VIS
      FUN=2.932E-7*FF**(-0.508)*(DP/DIA)**0.548*Re**1.371
      KO=FUN*SQRT(RS1*DI)
C
C   END OF KO CALCULATION
C
C   START TO CALCULATE EFFECTIVE DIFUSIVITY
C
      PP=0.403*E**-0.333333-0.5
      DA=2.0*(DI/Q)*DM/(DI/Q-DM)*((DI/Q)*DLOG(DI/Q/DM)/(DI/Q-DM)-1.)
      DEX=DM*((4.0*(1+2.0*PP)**2.0-PAI)/4.0/(1+2.0*PP)**2.)+
    &    PAI/4./(1+2.*PP)**2.*((1.0+2.*PP)*DA*DM)/(DM+2.*PP*DA)
c     DEX=DM*(1.0-E)
      WRITE(*,*) DEX
      L=M*DEX/(RAD*KO)
      BIOT=1.0/L
      FV=3.0*FF/(1.0-FF)
      BC=1.0-E*(1.0-Q)
      PARA=M*FV*BC
C     X(1)=1.0
C     YY(1)=0.0
      TIME=0.0
      DO 100 I=1,80
      TC(I)=DEX*TIME/(BC*RAD**2.0)
      J=0
      SUM=3.0/(3.0+PARA)
  60  J=J+1
      CALL EIGN (CODE,PARA,J,F,L)
      CALL SERIES (CODE,PARA,TC(I),F,S,J,L)
      write(*,*) i,j,s
      SUM=SUM+S
C     WRITE(3,20) TIME,J,F,S
  20  FORMAT(2X,'TIME',F15.5,2X,'SERIES',I4,2X,
    &      'EIGEN VALUE',F15.6,2X,'S',F15.6)
      IF(J.GT.3000) THEN
            GO TO 70
      ELSE IF (S.GT.1.0E-5) THEN
            GO TO 60
            ELSE
      ENDIF
  70  X(I)=SUM
      YY(I)=TIME/60.0
      TIME=TIME+T
      CE(I)=X(I)-(X(1)-1.0)
 100  CONTINUE
```

```
C
      OPEN(2,FILE=OUT,STATUS='NEW')
      IF(CODE .EQ. 0.0) THEN
      WRITE(2,111)
      ELSE IF (CODE .EQ. 1.0) THEN
      WRITE(2, 110)
      ENDIF
110   FORMAT(/,15X,'MASS TRANSFER WITH FILM RESISTANCE',/)
111   FORMAT(/,15X,'MASS TRANSFER WITHOUT FILM RESISTANCE',/)
      WRITE(2,31) CODE
31    FORMAT(4X,'CODE:0-NO RESISTANCE, 1-WITH RESISTANCE',10X,F3.1)
      WRITE(2,32) DI
32    FORMAT(4X,'DI=DIFF. OF SOLUTE IN AQUEOUS(M2/SEC)',12X,F15.12)
      WRITE(2,42) DM
42    FORMAT(4X,'DM=DIFF. OF COMPLEX IN MEMBR.(M2/SEC)',10X,F15.12)
      WRITE(2,43) DEX
43    FORMAT(4X,'DEX=EFF. DIFF. OF COMPLEX IN
MEM(M2/SEC)',10X,F15.12)
      WRITE(2,33) FF
33    FORMAT(4X,'FF=VOL. FRACTION OF EMULSION(Vi+Vm/Vtot)',7X,F6.4)
      WRITE(2,34) E
34    FORMAT(4X,'E=SINK PHASE VOLUME FRACTION(Vi/(Vi+Vm))',9X,F3.1)
      WRITE(2,35) RAD
35    FORMAT(4X,'RAD=RADIUS OF GLOBULES(M)', 24X,F8.6)
      WRITE(2,36) T
36    FORMAT(4X,'T=PRINT TIME INTERVAL(SEC.)',22X,F4.1)
      WRITE(2,37) M
37    FORMAT(4X,'M=EXTERNAL DISTRIBUTION COEFF.',18X,F6.3)
      WRITE(2,38) Q
38    FORMAT(4X,'Q=INTERNAL DISTRIBUTION COEFF.',18X,F8.1)
      WRITE(2,39) KO
39    FORMAT(4X,'KO=EXTERNAL MASS TRANSFER COEFF.',17X,F10.8)
      WRITE(2,40) PARA
40    FORMAT(4X,'B=M*F*W',30X,F6.1)
      WRITE(2,41) BIOT
41    FORMAT(4X,'BIOT NUMBER', 30X, F10.2)
      WRITE(2,112)
112   FORMAT(10X,'TOU',5X,'TIME(MIN)',5X,'CONCENTRATION%',/)
      DO 200 I=1,80
      WRITE(2,113) TC(I),YY(I),CE(I)
113   FORMAT(5X,F12.8,4X,F10.2,12X,F10.4)
200   CONTINUE
      STOP
      END
C
```

```
C       'EIGN' IS THE SUBROUTINE TO CALCULATE EIGEN VALUE
C              BY SOLVING THE THE CHARACTERISTIC EQUATION
C       FOR FILM RESISTANCE
C              TAN(B)=B*(PARA-L*B**2)/(PARA-(L-1)*B**2)
C       FOR NO FILM RESISTANCE
C.             TAN(B)=B*PARA/(PARA+B**2)_
C       H==PARA
C       N==NTH TERM
C       B==CALCULATED EIGENVALUES
C       CODE=0: WITHOUY FILM RESISTANCE,
C       CODE=1: WITH FILM RESISTANCE
C
        SUBROUTINE EIGN(CODE,H,N,B,L)
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        REAL H,B,Q1,L,CODE
        PARAMETER(PAI=3.1415926536)
        IF (CODE.EQ.0) THEN
        Y=4.0+(N-1)*PAI
  11    Q1=H*Y/(H+Y**2)
        QQ=ATAN(Q1)+N*PAI
        DIF=Y-QQ
               IF(ABS(DIF).GT.1.0E-3) THEN
               Y=QQ
               GO TO 11
               ENDIF
        B=Y
        ELSE IF (CODE.EQ.1.) THEN
        Y=0.2+(N-1)*PAI
  10    Q1=Y*(H-L*Y**2)/(H-(L-1.0)*Y**2)
        QQ=ATAN(Q1)+(N-1.0)*PAI
        DIF=Y-QQ
               IF(ABS(DIF).GT.1.0E-3) THEN
               Y=QQ
               GO TO 10
               ENDIF
        B=Y
        ENDIF
        RETURN
        END
C
C
C       'SERIES' IS THE SUBROUTINE FOR CALCULATION THE VALUE
C              OF THE TERM IN SERIES
C       G==PARA
C       W=TC
```

```
C      Y==B(EIGEN VALUES CALCULATED FROM 'EIGN'
C      Z==VALUE OF THE TERM BEING CALCULATED
C      N==NTH TERM
C      CODE=0: WITHOUT FILM RESISTANCE
C      CODE=1: WITH FILM RESISTANCE
C
       SUBROUTINE SERIES(CODE,G,W,Y,Z,N,L)
       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
       REAL L,CODE
       PARAMETER(PAI=3.1415926536)
       IF(CODE.EQ.0.) THEN
       U=Y-N*PAI
       A1=-(W*Y**2)
            IF(ABS(A1) .GT. 30.0) THEN
            A2=0.0
            ELSE
            A2=EXP(A1)
            ENDIF
       A3=3.0*G+G**2+Y**2
       A4=2.0*G/A3
       Z=A2*A4
C
       ELSE IF(CODE.EQ.1.) THEN
       U=Y-N*PAI
       A1=-(W*Y**2)
            IF(ABS(A1).GT.30.0) THEN
                 A2=0.0
            ELSE
            A2=EXP(A1)
            ENDIF
       A3=(Y**2.0)*(1.0+L*(L*Y**2.0-(2.0*G+1.0)))
       A4=2.0*G/(A3+G*(3.0+G))
       Z=A2*A4
       ENDIF
       RETURN
       END
```

APPENDIX C-2

Computer Code for Numerical Calculation of Emulsion Liquid Membrane Model
Critical Biot Number Calculation

```
C      **************************************************************
C      *      MATHEMATICAL MODEL OF LIQUID MEMBRANE SYSTEM      *
C      *   CALCULATE THE CRITICAL BIOT NUMBER FOR ELM SYSTEM    *
C      **************************************************************
C
C      VARIABLES:
C      CODE: 0-WITHOUT FILM RESISTANCE, 1-WITH FILM RESISTANCE
C      DI:DIFFUSIVITY IN AQUEOUS, DM:DIFFUSITY IN MEMBRANE PHASE
C      E:SINK PHASE VOL. FRACTION  FF:EMULSION VOL. FRACTION
C      T:PRINT TIME INTERVAL       RAD:DADIUS OF GLOBULE
C      F:EIGENVALUES               S:VALUE OF THE TERM
C      M:EXTERNAL DISTRIBUTION COEFFICIENT
C      Q:INTERNAL DISTRIBUTION COEFFICIENT
C      KO:EXTERNAL MASS TRANSFER COEFFICIENT
C      SUM: SUMMATION OF THE SERIES
C      PARA: PARAMETER=M*FV*BC
C      X:ARRAR OF CONCENTRATION
C      INPUT FILE:LT.DAT
C      OUT FILE:BIOT.DAT
C      CE1(100) SERIES IS INPUT DATA SERIES( NO FILM RESISTANCE)
C      CE(100) SERIES IS OUTPUT DATA SERIES( WITH FILM RESISTANCE)
C      TEMP: SUMMATION OF DIFFERENCE OF TWO DATA SERIES
C
       IMPLICIT DOUBLE PRECISION (A-H,O-Z)
       DIMENSION TC(100),YY(100),X(100),CE(100),CE1(100)
       REAL M,L,KO,CODE,P,TEMP
       PARAMETER(PAI=3.14159)
       CHARACTER*13 OUT
       OPEN(9,FILE='LT.DAT', STATUS='OLD')
c      OPEN(3,FILE='CHECK.OUT',STATUS='NEW')
       READ(9,'(F12.5)') CODE,DI,DM,FF,E,RAD,T,M,Q,
     &      RS,DIA,DENSITY,VIS,DP
       READ(9,'(A13)') OUT
       OPEN(6,FILE='CE1.DAT', STATUS='OLD')
       DO 151 I=1,80
 151   READ(6,'(F10.8)') CE1(I)
C
C  HERE TO CALCULATE EXTERNAL MASS TRANSFER COEFFICIENT
```

```
C       SKELLAND AND LEE EQUATION
C    DATE FROM UNIT=9, FILE=LT.DAT
C
  2     RS=RS+5.0
        TEMP=0.0
        RS1=RS/60.
        Re=1.0E6*RS1*(DP**2.0)*DENSITY/VIS
        FUN=2.932E-7*FF**(-0.508)*(DP/DIA)**0.548*Re**1.371
        KO=FUN*SQRT(RS1*DI)
C
C    END OF KO CALCULATION
C
C    START TO CALCULATE EFFECTIVE DIFUSIVITY
C
        PP=0.403*E**-0.333333-0.5
        DA=2.0*(DI/Q)*DM/(DI/Q-DM)*((DI/Q)*DLOG(DI/Q/DM)/(DI/Q-DM)-1.)
        DEX=DM*((4.0*(1+2.0*PP)**2.0-PAI)/4.0/(1+2.0*PP)**2.)+
     &     PAI/4./(1+2.*PP)**2.*((1.0+2.*PP)*DA*DM)/(DM+2.*PP*DA)
c       DEX=DM*(1.0-E)
        L=M*DEX/(RAD*KO)
        BIOT=1.0/L
        FV=3.0*FF/(1.0-FF)
        BC=1.0-E*(1.0-Q)
        PARA=M*FV*BC
C
        TIME=0.0
        DO 100 I=1,80
        TC(I)=DEX*TIME/(BC*RAD**2.0)
        J=0
        SUM=3.0/(3.0+PARA)
 60     J=J+1
        CALL EIGN (CODE,PARA,J,F,L)
        CALL SERIES (CODE,PARA,TC(I),F,S,J,L)
        SUM=SUM+S
C       WRITE(3,20) TIME,J,F,S
 20     FORMAT(2X,'TIME',F15.5,2X,'SERIES',I4,2X,
     &        'EIGEN VALUE',F15.6,2X,'S',F15.6)
        IF(J.GT.3000) THEN
              GO TO 70
        ELSE IF (S.GT.1.0E-5) THEN
              GO TO 60
              ELSE
        ENDIF
 70     X(I)=SUM
        YY(I)=TIME/60.0
```

```
        TIME=TIME+T
        CE(I)=X(I)-(X(1)-1.0)
        TEMP=TEMP+ABS(CE(I)-CE1(I))
100     CONTINUE
        WRITE(*,*) TEMP
        IF (TEMP.GT.1.5) GO TO 2
C
        OPEN(2,FILE=OUT,STATUS='NEW')
        IF(CODE .EQ. 0.0) THEN
        WRITE(2,111)
        ELSE IF (CODE .EQ. 1.0) THEN
        WRITE(2, 110)
        ENDIF
110     FORMAT(/,15X,'MASS TRANSFER WITH FILM RESISTANCE',/)
111     FORMAT(/,15X,'MASS TRANSFER WITHOUT FILM RESISTANCE',/)
        WRITE(2,31) CODE
31      FORMAT(4X,'CODE:0-NO RESISTANCE, 1-WITH RESISTANCE',10X,F3.1)
        WRITE(2,32) DI
32      FORMAT(4X,'DI=DIFF. OF SOLUTE IN AQUEOUS(M2/SEC)',12X,F15.12)
        WRITE(2,42) DM
42      FORMAT(4X,'DM=DIFF. OF COMPLEX IN MEMBR.(M2/SEC)',10X,F15.12)
        WRITE(2,43) DEX
43      FORMAT(4X,'DEX=EFF. DIFF. OF COMPLEX IN
MEM(M2/SEC)',10X,F15.12)
        WRITE(2,33) FF
33      FORMAT(4X,'FF=VOL. FRACTION OF EMULSION(Vi+Vm/Vtot)',7X,F6.4)
        WRITE(2,34) E
34      FORMAT(4X,'E=SINK PHASE VOLUME FRACTION(Vi/(Vi+Vm))',9X,F3.1)
        WRITE(2,35) RAD
35      FORMAT(4X,'RAD=RADIUS OF GLOBULES(M)', 24X,F8.6)
        WRITE(2,36) T
36      FORMAT(4X,'T=PRINT TIME INTERVAL(SEC.)',22X,F4.1)
        WRITE(2,37) M
37      FORMAT(4X,'M=EXTERNAL DISTRIBUTION COEFF.',18X,F6.3)
        WRITE(2,38) Q
38      FORMAT(4X,'Q=INTERNAL DISTRIBUTION COEFF.',18X,F8.1)
        WRITE(2,39) KO
39      FORMAT(4X,'KO=EXTERNAL MASS TRANSFER COEFF.',17X,F10.8)
        WRITE(2,40) PARA
40      FORMAT(4X,'B=M*F*W',30X,F6.1)
        WRITE(2,41) BIOT
41      FORMAT(4X,'BIOT NUMBER', 30X, F10.2)
        WRITE(2,112)
112     FORMAT(10X,'TOU',5X,'TIME(MIN)',5X,'CONCENTRATION%',/)
        DO 200 I=1,80
```

```fortran
      WRITE(2,113) TC(I),YY(I),CE(I)
113   FORMAT(5X,F12.8,4X,F10.2,12X,F10.4)
200   CONTINUE
      STOP
      END
C
C     'EIGN' IS THE SUBROUTINE TO CALCULATE EIGEN VALUE
C           BY SOLVING THE THE CHARACTERISTIC EQUATION
C     FOR FILM RESISTANCE
C           TAN(B)=B*(PARA-L*B**2)/(PARA-(L-1)*B**2)
C     FOR NO FILM RESISTANCE
C           TAN(B)=B*PARA/(PARA+B**2)
C     H==PARA
C     N==NTH TERM
C     B==CALCULATED EIGENVALUES
C     CODE=0: WITHOUY FILM RESISTANCE,
C     CODE=1: WITH FILM RESISTANCE
C
      SUBROUTINE EIGN(CODE,H,N,B,L)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      REAL H,B,Q1,L,CODE
      PARAMETER(PAI=3.1415926536)
      IF (CODE.EQ.0) THEN
      Y=4.0+(N-1)*PAI
11    Q1=H*Y/(H+Y**2)
      QQ=ATAN(Q1)+N*PAI
      DIF=Y-QQ
           IF(ABS(DIF).GT.1.0E-3) THEN
           Y=QQ
           GO TO 11
           ENDIF
      B=Y
      ELSE IF (CODE.EQ.1.) THEN
      Y=0.2+(N-1)*PAI
10    Q1=Y*(H-L*Y**2)/(H-(L-1.0)*Y**2)
      QQ=ATAN(Q1)+(N-1.0)*PAI
      DIF=Y-QQ
           IF(ABS(DIF).GT.1.0E-3) THEN
           Y=QQ
           GO TO 10
           ENDIF
      B=Y
      ENDIF
      RETURN
      END
```

```
C
C
C
C      'SERIES' IS THE SUBROUTINE FOR CALCULATION THE VALUE
C            OF THE TERM IN SERIES
C      G==PARA
C      W=TC
C      Y==B(EIGEN VALUES CALCULATED FROM 'EIGN'
C      Z==VALUE OF THE TERM BEING CALCULATED
C      N==NTH TERM
C      CODE=0: WITHOUT FILM RESISTANCE
C      CODE=1: WITH FILM RESISTANCE
C
       SUBROUTINE SERIES(CODE,G,W,Y,Z,N,L)
       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
       REAL L,CODE
       PARAMETER(PAI=3.1415926536)
       IF(CODE.EQ.0.) THEN
       U=Y-N*PAI
       A1=-(W*Y**2)
             IF(ABS(A1) .GT. 30.0) THEN
             A2=0.0
             ELSE
             A2=EXP(A1)
             ENDIF
       A3=3.0*G+G**2+Y**2
       A4=2.0*G/A3
       Z=A2*A4
C
       ELSE IF(CODE.EQ.1.) THEN
       U=Y-N*PAI
       A1=-(W*Y**2)
             IF(ABS(A1).GT.30.0) THEN
                   A2=0.0
             ELSE
             A2=EXP(A1)
             ENDIF
       A3=(Y**2.0)*(1.0+L*(L*Y**2.0-(2.0*G+1.0)))
       A4=2.0*G/(A3+G*(3.0+G))
       Z=A2*A4
       ENDIF
       RETURN
       END
```

APPENDIX C-3

Procedures for Calculation of the Critical Biot Number
of Emulsion Liquid Membrane Systems

METHOD:

A: PRODUCE DATA SIRIES FOR NO FILM RESISTANCE
1. SET LT.DAT FILE
  RPM=10000; MEANS NO FILM RESISTANCE(R REMAINS UNCHANGED)
  OUT=CE1: PRODUCE CE1 DATA FILE FOR COMPARISON
2. RUN LT.FOR
  PRODUCE CE1 FILE FOR COMPARISON

B: COMPARE DATA SERIES WITH FILM RESISTANCE TO CE1.DAT

3. SET LT.DAT FILE
  DO LOOP AT DIFFERENT AGITATING SPEED
  INITIAL RPM=100, 5 RPM FOR INCREMENT(R REMAIN UNCHANGED)
  OUT=ZHOU: OUTPUT FILE
4. RUN BIOT.FOR
  DO THE COMPARISON OF TWO DATA FILE
  BASE ON SUMMATION OF (CE(I)-CE1(I))<1.5
  MEAN TOTAL 80 DATA WITH 1.5 DIFFERENCE, 0.02 FOR EACH POINT

5. THE PROGRAM WILL TERMINATE WHEN (CE(I)-CE1(I))<1.5, WHICH MEANS
THE RESULTS AT THIS SPECIFIC AGITATING RATE IS SIMILAR TO THE
RESULTS AT NO EXTERNAL FILM RESISTANCE(10000RPM). IT WILL
AUTOMATICALLY CALCULATE THE EXTERNAL MASS TRANSFER
COEFFICIENT AT SPECIFIC RPM, THEN GIVE THE CRITICAL BIOT NUMBER.

APPNDIX C-4

Computer Code for Numerical Calculation of Emulsion Liquid Membrane Model
Considering Leakage

```
C      ***************************************************************
C      *       MATHEMATICAL MODEL OF LIQUID MEMBRANE SYSTEM       *
C      *     MASS TRANSFER WITH EXTERNAL FILM RESISTANCE          *
C      *        CONSIDER LEAKAGE(Kb=LEAKAGE RATE)                 *
C      ***************************************************************
C
C      VARIABLES:
C      CODE: 0-WITHOUT FILM RESISTANCE, 1-WITH FILM RESISTANCE
C      DI:DIFFUSIVITY IN AQUEOUS, DM:DIFFUSITY IN MEMBRANE PHASE
C      E:SINK PHASE VOL. FRACTION  FF:EMULSION VOL. FRACTION
C      T:PRINT TIME INTERVAL        RAD:DADIUS OF GLOBULE
C      F:EIGENVALUES                S:VALUE OF THE TERM
C      M:EXTERNAL DISTRIBUTION COEFFICIENT
C      Q:INTERNAL DISTRIBUTION COEFFICIENT
C      KO:EXTERNAL MASS TRANSFER COEFFICIENT
C      KB:LEAKAGE RATE (1/MIN)
C      SUM: SUMMATION OF THE SERIES
C      PARA: PARAMETER=M*FV*BC
C      X:ARRAR OF CONCENTRATION
C       KB=LEAKAGE RATE
C      INPUT FILE:LT.DAT -
C      OUT FILE:LT.OUT
C
       IMPLICIT DOUBLE PRECISION (A-H,O-Z)
       DIMENSION TC(200),YY(200),X(200),CS(200)
       REAL M,L,KO,CODE,KB,P
       CHARACTER*13 OUT
       PARAMETER(PAI=3.14159)
       OPEN(9,FILE='LEAK.DAT', STATUS='OLD')
       OPEN(3,FILE='CHECK.OUT',STATUS='NEW')
       READ(9,'(F12.5)') CODE,DI,DM,FF,E,RAD,T,M,Q,
     &      RS,DIA,DENSITY,VIS,DP,KB
       READ(9,'(A13)') OUT
C
C   HERE TO CALCULATE EXTERNAL MASS TRANSFER COEFFICIENT
C
C   DATE FROM UNIT=9, FILE=LT.DAT
```

```
C
      RS1=RS/60.
      Re=1.0E6*RS1*(DP**2.0)*DENSITY/VIS
      FUN=2.932E-7*FF**(-0.508)*(DP/DIA)**0.548*RE**1.371
      KO=FUN*SQRT(RS1*DI)
C
C    END OF KO CALCULATION
C    START TO CALCULATE EFF. DIFFUSIVITY
C
      PP=0.403*E**-0.33333333-0.5
      DA=2.0*(DI/Q)*DM/(DI/Q-DM)*((DI/Q)*DLOG(DI/Q/DM)/(DI/Q-DM)-1.0)
      DEX=DM*((4.0*(1.+2.0*PP)**2.0-PAI)/4.0/(1+2.0*PP)**2.0)+
    &    PAI/4.0/(1.+2.*PP)**2.0*((1.0+2.*PP)*DA*DM)/(DM+2.*PP*DA)
      WRITE(*,*) DEX
      L=M*DEX/(RAD*KO)
      BIOT=1.0/L
      FV=3.0*FF/(1.0-FF)
      BC=1.0-E*(1.0-Q)
      PARA=M*FV*BC
      P=BC*KB*(RAD**2.0)/DEX
C
      TIME=0.0
C
      DO 100 I=1,200
      TC(I)=DEX*TIME/(BC*RAD**2.0)
      J=0
      SUM=1.0
 60   J=J+1
      CALL EIGN (CODE,PARA,J,F,L,P)
      CALL SERIES (CODE,PARA,TC(I),F,S,J,L,P)
      SUM=SUM+S
      WRITE(3,20) TIME,J,F,S
 20   FORMAT(2X,'TIME',F15.5,2X,'SERIES',I4,2X,
    &        'EIGEN VALUE',F15.6,2X,'S',F15.6)
C
      IF(J.GT.3000) THEN
              GO TO 70
      ENDIF
C
      IF(ABS(S).GT.1.0D-5) THEN
              GO TO 60
      ENDIF
C
 70   X(I)=SUM
      YY(I)=TIME/60.0
```

```fortran
      TIME=TIME+T
      CS(I)=X(I)-(X(1)-1.0)
100   CONTINUE
C
      OPEN(2,FILE=OUT,STATUS='NEW')
      IF(CODE .EQ. 0.0) THEN
      WRITE(2,111)
      ELSE IF (CODE .EQ. 1.0) THEN
      WRITE(2, 110)
      ENDIF
110   FORMAT(/,15X,'MODEL WITH FILM RESISTANCE + LEAKAGE',/)
111   FORMAT(/,15X,'MASS TRANSFER WITHOUT FILM RESISTANCE',/)
      WRITE(2,31) CODE
31    FORMAT(4X,'CODE:0-NO RESISTANCE, 1-WITH RESISTANCE',10X,F3.1)
      WRITE(2,32) DI
32    FORMAT(4X,'DI=DIFF. OF SOLUTE IN AQUEOUS(M2/SEC)',12X,F15.12)
      WRITE(2,42) DM
42    FORMAT(4X,'DM=DIFF. OF COMPLEX IN MEMBR.(M2/SEC)',10X,F15.12)
      WRITE(2,44) DEX
44    FORMAT(4X,'DEX=EFF. DIFF. OF COMPLEX (M2/SEC)',10X,F15.12)
      WRITE(2,33) FF
33    FORMAT(4X,'FF=VOL. FRACTION OF EMULSION(Vi+Vm/Vtot',7X,F6.4)
      WRITE(2,34) E
34    FORMAT(4X,'E=SINK PHASE VOLUME FRACTION(Vi/(Vi+Vm))',9X,F3.1)
      WRITE(2,35) RAD
35    FORMAT(4X,'RAD=RADIUS OF GLOBULES(M)', 24X,F8.6)
      WRITE(2,36) T
36    FORMAT(4X,'T=PRINT TIME INTERVAL(SEC.)',22X,F4.1)
      WRITE(2,37) M
37    FORMAT(4X,'M=EXTERNAL DISTRIBUTION COEFF.',18X,F6.3)
      WRITE(2,38) Q
38    FORMAT(4X,'Q=INTERNAL DISTRIBUTION COEFF.',18X,F8.1)
      WRITE(2,39) KO
39    FORMAT(4X,'KO=EXTERNAL MASS TRANSFER COEFF.',17X,F10.8)
      WRITE(2,40) PARA
40    FORMAT(4X,'B=M*F*W',40X,F6.1)
      WRITE(2,41) BIOT
41    FORMAT(4X,'BIOT NUMBER', 33X, F10.2)
      WRITE(2,43) P
43    FORMAT(4X, 'LEAKAGE NUMBER=W*KB*R**2/DEX ', 11X, F18.6)
      WRITE(2,112)
112   FORMAT(10X,'TOU',5X,'TIME(MIN)',5X,'CONCENTRATION%',/)
      DO 200 I=1,200
      WRITE(2,113) TC(I),YY(I),CS(I)
113   FORMAT(5X,F12.8,4X,F10.2,12X,F10.4)
```

```
  200   CONTINUE
        STOP
        END
C
C       'EIGN' IS THE SUBROUTINE TO CALCULATE EIGEN VALUE
C              BY SOLVING THE THE CHARACTERISTIC EQUATION
C       FOR FILM RESISTANCE
C              TAN(B)=B*(PARA-L*B**2)/(PARA-(L-1)*B**2)
C       FOR NO FILM RESISTANCE
C              TAN(B)=B*PARA/(PARA+B**2)
C       G==PARA
C       N==NTH TERM
C       B==CALCULATED EIGENVALUES
C       CODE=0: WITHOUY FILM RESISTANCE,
C       CODE=1: WITH FILM RESISTANCE
C
        SUBROUTINE EIGN(CODE,G,N,B,L,P)
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        REAL G,B,Q1,L,CODE
        PARAMETER(PAI=3.1415926536)
        IF (CODE.EQ.0) THEN
        Y=4.0+(N-1)*PAI
   11   Q1=G*Y/(G-P+Y**2)
        QQ=ATAN(Q1)+N*PAI
        DIF=Y-QQ
              IF(ABS(DIF).GT.1.0E-3) THEN
              Y=QQ
              GO TO 11
              ENDIF
        B=Y
C
        ELSE IF (CODE.EQ.1.) THEN
        Y=1.0+(N-1)*PAI
   10   Q1=Y*(G+L*P-L*Y**2)/(G-(L+1)*P-(L-1.0)*Y**2)
        QQ=ATAN(Q1)+(N-1.0)*PAI
        DIF=Y-QQ
              IF(ABS(DIF).GT.1.0E-3) THEN
              Y=QQ
              GO TO 10
              ENDIF
        B=Y
        ENDIF
        RETURN
        END
C
```

```
C      'SERIES' IS THE SUBROUTINE FOR CALCULATION THE VALUE
C            OF THE TERM IN SERIES
C      G==PARA
C      W=TC
C      L=EXTERNAL MASS TRANSFER TERM
C      P=LEAKAGE TERM
C      Y==bn(EIGEN VALUES CALCULATED FROM 'EIGN'
C      Z==VALUE OF THE TERM BEING CALCULATED
C      N==NTH TERM
C      CODE=0: WITHOUT FILM RESISTANCE
C      CODE=1: WITH FILM RESISTANCE
C

       SUBROUTINE SERIES(CODE,G,W,Y,Z,N,L,P)
       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
       REAL L,CODE,P
       PARAMETER(PAI=3.1415926536)
       IF(CODE.EQ.0.) THEN
       U=Y-N*PAI
       A1=-(W*Y**2)
            IF(ABS(A1) .GT. 30.0) THEN
            A2=0.0
            ELSE
            A2=EXP(A1)
            ENDIF
       A3=(-Y**2.0+P)*TAN(Y)
       A4=TAN(Y)*((P-G)-2.0+0.5*(G+P)*Y**2.0)+(0.5*P+G)*Y-0.5*Y**3.0
       Z=A2*A3/A4
C

       ELSE IF(CODE.EQ.1.) THEN
       A1=-(W*Y**2)
            IF(ABS(A1).GT.30.0) THEN
                  A2=0.0
            ELSE
            A2=EXP(A1)
            ENDIF
       A3=(-Y**2.0+P)*(TAN(Y)+L*(Y-TAN(Y)))
       A4=TAN(Y)*((P*(1-L)-G)-(2.0-2.0*L+0.5*(G+P))*Y**2.0+0.5*L*Y**4.0)
       A5=(P*(0.5+L)+G)*Y-(0.5+2.0*L)*Y**3.0
       Z=A2*A3/(A4+A5)
       ENDIF
       RETURN
       END
```

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