การสกัดแอล-ไลซีนจากสารละลายที่เหลือจากการตกผลึก โดยกระบวนการเยื่อแผ่นเหลวแบบอิมัลชัน

นางสาววันวิสา ทวีแสง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2542

ISBN 974-334-457-8

L-LYSINE EXTRACTION FROM MOTHER LIQUOR BY EMULSION LIQUID MEMBRANE

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 1999

ISBN 974-334-457-8

Thesis title	L-lysine Extraction from Mother Liquor by Emulsion Liquid Membrane
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วันวิสา ทวีแสง : การสกัดแอล-ไลซีนจากสารละลายที่เหลือจากการตกผลึกโดยกระบวนการเยื่อแผ่นเหลวแบบอิมัลชัน (L-LYSINE EXTRACTION FROM MOTHER LIQUOR BY EMULSION LIQUID MEMBRANE) อ. ที่ปรึกษา : รศ. ดร. จิรกานต์ เมืองนาโพธิ์, อ. ที่ปรึกษาร่วม : คุณสุนทร สถาพรกุล; 118 หน้า. ISBN 974-334-457-8

ทำการศึกษาสมดุลการสกัดของสารละลายแอล-ไลซีนสังเคราะห์และสารละลายแอล-ไลซีนจากสารละลายที่เหลือจากการตกผลึก ในภาวะที่มีความเข้มข้นของสารตัวพา (D2EHPA) แตกต่างกันที่อุณหภูมิห้องและความเร็วรอบในการกวน 420 รอบต่อนาทีเป็นเวลา 48 ชั่วโมง จากผลการทดลองพบว่าค่าสัมประสิทธิ์การกระจายตัวของสารละลายแอล-ไลซีนสังเคราะห์มีค่าสูงกว่าของสารละลายที่เหลือจากการตกผลึกและค่าทั้งสองยังแปรผันตามความเข้มข้นของสารตัวพาด้วย ค่าคงที่ในการสกัด (K_{ex}) ของสารละลายแอล-ไลซีนสังเคราะห์และของสารละลายที่เหลือจากการตกผลึกมีค่าเท่ากับ 5.26 $x10^{-4}$ และ 4.72 $x10^{-5}$ ดม^3/โมล ตามลำดับ นอกจากนี้ยังพบว่าแอล-ไลซีน (Lys^+) 1 โมลจะรวมกับ 1.2 โมล และ 2 โมลของกรดไดเอทีล-เฮกซิลฟอสฟอริกซึ่งอยู่ในรูปของโมโนเมอร์เกิดเป็นสารที่มีโมเลกุลซับซ้อนสำหรับสารละลายแอล-ไลซีนสังเคราะห์และสารละลายที่เหลือจากการตกผลึกตามลำดับ

ได้ทำการศึกษาการสกัดแอล-ไลซีนจากสารละลายที่เหลือจากการตกผลึกโดยกระบวนการเยื่อแผ่นเหลวแบบอิมัลชันชนิดอาศัยสารตัวพาแบบไม่ต่อเนื่อง โดยวัฏภาคเยื่อประกอบด้วยกรดไดเอทีล-เฮกซิลฟอสฟอริกเป็นสารตัวพา, สแปน 80 เป็นสารลดแรงตึงผิวซึ่งละลายในตัวทำละลายโดเดเคน และมีสารละลายกรดไฮโดรคลอริกเป็นวัฏภาคภายใน ได้ทำการศึกษาผลกระทบของภาวะต่างๆ จากผลการทดลองพบว่าภาวะที่เหมาะสมในการสกัดคือความเป็นกรดด่างของวัฏภาคภายนอกเท่ากับ 5, ความเข้มข้นของวัฏภาคภายในเท่ากับ 2 นอร์มัล, ความเข้มข้นของสารลดแรงตึงผิวเท่ากับ 1 เปอร์เซนต์โดยปริมาตร, ความเข้มข้นของสารตัวพาเท่ากับ 10 เปอร์เซนต์โดยปริมาตร , อัตราส่วนระหว่างวัฏภาคเยื่อและวัฏภาคภายนอกเท่ากับ 1:2 และความเร็วในการกวนเท่ากับ 360 รอบต่อนาที ที่สภาวะนี้มีค่าเปอร์เซนต์ในการสกัดเริ่มต้นภายในเวลา 1 นาทีเท่ากับ 20 เปอร์เซ็นต์ นอกจากนี้แบบจำลองที่ใช้ทำนายอิทธิพลของความเข้มข้นของสารตัวพาต่ออัตราการสกัดยังได้แสดงไว้ในงานวิจัยนี้ด้วย

ภาควิชา.....วิศวกรรมเคมี..... ลายมือชื่อนิสิต.....วันวิสา ทวีแสง.....

สาขาวิชา.....วิศวกรรมเคมี..... ลายมือชื่ออาจารย์ที่ปรึกษา.....

ปีการศึกษา.....2542..... ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....สุนทร สถาพรกุล.....

3971543921 : MAJOR CHEMICAL ENGINEERING DEPARTMENT

KEYWORD: EMULSION LIQUID MEMBRANE / L-LYSINE / FACILITATED TRANSPORT

WANWISA THAWISAENG : L-LYSINE EXTRACTION FROM MOTHER LIQUOR BY EMULSION LIQUID MEMBRANE. THESIS ADVISOR : ASSOC.PROF. CHIRAKARN MUANGNAPOH, Dr. Ing. THESIS COADVISOR : MR. SOONTORN STAPORNKUL, page 118 pp. ISBN 974-334-457-8

The extraction equilibrium of synthetic L-lysine and L-lysine from mother liquor were studied at various carriers, D2EHPA, concentration. Each experiment was carried out at room temperature for 48 hours with a stirred speed of 420 rpm. It was found that the distribution coefficient of synthetic L-lysine was greater than that of L-lysine from mother liquor and both values vary with the carrier concentration. The extraction equilibrium constant (K_{ex}) are 5.26 x10^{-4} and 4.72 x10^{-5} dm^3/mol for L-lysine in synthetic solution and in mother liquor, respectively. It was also found that 1 mole of lys^+ reacted with 1.2 and 2 moles of monomeric form of D2EHPA to form complex for L-lysine in synthetic solution and mother liquor, respectively.

L-lysine extraction from mother liquor was carried out in batch type facilitated ELM stirred extractor. W/O membrane extraction phase was D2EHPA as carrier, Span 80 as surfactant in n-dodecane and HCl solution as stripping phase. The effects of various conditions were investigated. The experimental results showed the optimum conditions for this process to be at pH5, 2N HCl, 1%span 80 (v/v), 10%D2EHPA (v/v), volume ratio 1: 2, and 360 rpm. And by these optimum conditions, 20% initial extraction of L-lysine from mother liquor was obtained in the first minute. The influence of carrier concentration on the permeation rate can be predicted by the model presented in this study.

ภาควิชา.....วิศวกรรมเคมี..... ลายมือชื่อนิสิต.....

สาขาวิชา.....วิศวกรรมเคมี..... ลายมือชื่ออาจารย์ที่ปรึกษา.....

ปีการศึกษา.....2542..... ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

ACKNOWLEDGEMENTS

The author would like to express her sincere gratitude to her advisor Assoc Prof. Chirakarn Muangnapoh for her encouragement and guidance and co-advisor Mr. Soontorn Stapornkul, Plant manager of Ajinomoto Co., (Thailand) Ltd., Pathumthani Plant, for his extreme assistance throughout her research work.

The author also thanks Assoc Prof. Kroekchai Sukanjanajtee, who serves as the chairman, and Assoc Prof. Noppaporn Panich and Mr. Tomoya Yoshizumi who serve as committee members.

To all her friends in the Department of Chemical Engineering, thank you for making it a happy environment in which to work, particularly to Chawlid for his support and encouragement.

Most of all, the author would like to express the highest gratitude to her father, mother, and sisters for their every helps in her life.

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NOMENCLATURES

a	:	Area of liquid membrane (m^2)
A^+	:	Amino acid in cationic form
$A^{\pm}$	:	Amino acid in zwitterion form
A^-	:	Amino acid in anionic form
$[A_T]$	:	Total amino acid concentration
Ci	:	L-lysine concentration in the external phase (g/l)
Co	:	Initial L-lysine concentration in the external phase (g/l)
D^+	:	Distribution coefficient of amino acid in the cationic form
D_A	:	Diffusivity of amino acid (m^2/sec)
D_C	:	Diffusivity of amino acid/carrier complex phase (m^2/sec)
D_i	:	Diameter of inner sphere (m)
D_o	:	Diameter of outer sphere (m)
$[H^+]_{eq}$	:	Equilibrium hydrogen ion concentration in the external phase (mol/dm^3)
(HR)	:	Monomer of carrier molecule in the membrane phase
$AR(HR)_{m-1}$	:	Carrier/amino acid complex in the membrane phase
J_A	:	Permeation rate of amino acid ($mol/m^2.sec$)
k_1, k_2	:	Interfacial area reaction rate constant
K_1	:	Dissociation constant of Lys^{2+} (mol/dm^3)
K_2	:	Dissociation constant of Lys^- (mol/dm^3)
K_3	:	Dissociation constant of $Lys^{\pm}$ (mol/dm^3)
Kex	:	Extraction equilibrium constant (dm^3/mol)
l	:	Thickness of the membrane phase (m)
m	:	Stoichiometric coefficient
δ	:	Thickness of aqueous layer for extraction (m)
τ	:	Membrane constant

CHAPTER 1

INTRODUCTION

1.1 General

Emulsion liquid membranes (ELMs) have been successfully utilized to treat aqueous streams contaminated with heavy metal ions such as copper, zinc, cadmium, nickel, mercury, lead and chromium. ELMs, first reported by N.N. Li (1968), are made by forming an emulsion between two immiscible phases. His work showed that some of limitations of traditional solvent extraction could be removed by using liquid emulsion membrane. At present, the applications of ELMs in bioseparations and biomedicals have become active. ELMs have great potential for applications in biotechnology and for recovery bioproducts from fermentation products such as amino acid. The main advantages of the emulsion liquid membrane process are

1. Separation and concentration can be achieved in a single step.
2. The specific interfacial areas for extraction are large and give rise to very fast extraction rates.
3. The efficient recovery of solutes from low concentration streams.
4. Low energy consumption and minimal downstream unit operation.

One disadvantage of the system is swelling due to water transport from the external to the internal phase, resulting in a decrease in the degree of concentration of the solute achieved the inside membrane.

From advantages and disadvantages of emulsion liquid membrane processes, it is interesting for using this process to apply for extraction of L-lysine. L-lysine is one of the most important amino acids for livestock feed additive. At present, L-lysine is manufactured by a fermentation method at Ajinomoto Co., (Thailand) Ltd. in Pathumthani Province. In 1991, Boyadzhiev and co-worker studied kinetics of liquid membrane recovery of L-lysine from dilute aqueous solutions in a two compartment glass cell by using 5%(vol) di(2-ethylhexyl) phosphoric acid (D2EHPA) as carrier in n-Dodecane. The results proved the feasibility of the

pertraction process for recovery and concentration of L-lysine from dilute aqueous solution. After that, Apirak Suetrong (1995) studied the extraction of L-lysine from aqueous solution by emulsion liquid membrane process. At optimum conditions, 50% of L-lysine from aqueous solution in external phase have been extracted within 5 minutes. In this research, emulsion liquid membrane may improve in L-Lysine separation from mother liquor, which is residue solution in crystallizer. Mother liquor usually contains high L-lysine concentration with impurities residue. Therefore, we only focus on the possibility of separation rather than concentration.

1.2 Objectives of the Study

The objectives of this research are the following:

1. To study the equilibrium extraction of L-lysine from mother liquor by emulsion liquid membrane process.
2. To determine the optimum conditions for the extraction of L-lysine from mother liquor by emulsion liquid membrane process.
3. To describe the transport mechanism of L-lysine from mother liquor by emulsion liquid membrane.
4. To compare L-lysine permeation flux from mother liquor with synthetic L-lysine solution.

1.3 Scopes of the Study

1. L-lysine extraction from mother liquor by emulsion liquid membrane process covers the following scope:
   - 1.1 The concentration of mother liquor from L-lysine production plant, as external phase, was about 350-400 g/l.
   - 1.2 The acidities (pH) of the external phase were 3, 4, 5, 6 and 8.
   - 1.3 The concentrations of Hydrochloric acid in the internal phase were 1, 2, 4, and 6 N.

1.4 The concentrations of surfactant (Span 80) in membrane phase were 0.5, 1, 2,and 3 %(v/v) in n-Dodecane.

1.5 The concentrations of carrier (D2EHPA) in membrane phase were 5, 10, 20, and 30 %(v/v) in n-Dodecane.

1.6 The W-O Phase and external phase volume ratio were 1:0.5, 1:1, and 1:2

1.7 The characteristics of mother liquor were filtration and no-filtration.

1.8 The speeds of agitation for extraction were 300, 360, 420, and 480 rpm.

1.9 The sources of L-lysine were synthetic solution and L-lysine from mother liquor.

1.10 Temperature of extraction used was at room temperature.

2. Study the extraction performance in term of % initial extraction and L-lysine concentration in the external phase.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Liquid membrane

Membranes have been a source of interest for separation process for biotechnology. Membrane processes have the properties that they are technically simple, have high efficiency, and in the case of solid membrane, the component to be separated are not altered chemically or thermally (Marr and Kopp,1982).

A liquid membrane is an insoluble liquid, usually an organic solvent which is selective for a solute, which separates two aqueous: a feed phase, initially containing the desired solute, and a recovery or striping phase into which the solute is extracted. Liquid membranes are particularly suitable for recovery from dilute feeds, and have been proposed as an alternative in the separation of biomolecules with low molecular weight.

Some of the economic advantages of liquid membranes are apparent (Aharton and Bressler , 1993) :

1. Only liquids are treatd, avoiding costs related to solid separation and product dilution through solid washing.

2. Liquid membrane operate at about ambient temperature, decreasing costs of energy and of heat exchange, decreasing product decomposition, and providing for the use of low-cost construction materials.

3. Polymeric membrane-based liquid membranes allow a simple single-operation process (in contrast to liquid-liquid extraction).

Liquid membranes can be divided into two types according to the configurations: polymer-supported liquid membrane and emulsion liquid membrane (liquid surfactant membrane).

Polymer-supported liquid membranes are made up of two forms. The first consists of a porous polymeric film with the liquid membrane materials held strongly in the pores. The membrane geometry can be either of plate or of hollow fiber type. The problem with supported liquid membranes is the insufficient area for mass transfer (100-200 m^2/m^3 of

equipment volume) (Marr and Kopp, 1982). The emulsion liquid membranes concept, which are a three-phase system: a water-oil-water (w-o-w) system or an oil-water-oil (o-w-o) system, overcomes this problem by generating the necessary large surface area byway creating numerous emulsion-size spheres (1,000-3,000 m^2/m^3) (Marr and Kopp, 1982).

Since their discovery by N. Li in 1968, emulsion liquid membrane have been considered as effective equipment for a wide variety of separation such as heavy metal, biochemical processing application such as phospholipids, antibiotics, organic acids and amino acids from fermentation broth.

2.2 Emulsion liquid membrane Applications

2.2.1 Metal Applications

Frankenfeld and Li (1987) reviewed the applications of liquid membrane includes the use of emulsion liquid membrane for the removal of toxic substances such as Cr^{6+}, Hg^{2+}, Cd^{2+} and Cu^{2+} from waste water, separations in hydrometallurgy and as heterogenous catalysts. A typical formula of the membrane phase was 0.1% Span 8o (Sorbitan Monooleate), 3% of a nonionic polyamine acts as a membrane strengthening additive, and 86% of an isoparaffinic solvent. The internal phase is Sodium hydroxide solution. Emulsion was stirred at 1,000-2,000 rpm. for 10-20 minutes at ambient temperatures to ensure complete encapsulation. The result was shown in Table 2.1.

Table 2.1 Separation of metal ions by ELM Frankenfeld and Li (1987)

Element	Extractant	Initial concentration (ppm)	Final concentration (ppm)	Time (min)
Cr^{6+}	Alamine 336	390	12	15
Hg^{2+}	Alamine 336	1100	0.2	10
Cu^{2+}	LIX 64N	40	0.38	10
Cd^{2+}	Aliquat 336	40	0.45	10

Draxler, Furst and Marr (1986) reviewed the applications of emulsion liquid membrane for the separation of metal ions in a pilot plant. As can be seen in Table 2.2, zinc, copper, cadmium and lead easily be separated down to concentrations which are below the limits of the most environment protection agencies. This is not true for nickle. The result for this is the residence time in the column used was not long enough for nickle separation. Under the same conditions nickle could be separated in a two-stage counter current mixer-settler with sufficient residence time down to 2 ppm. Addition, they also concluded that problem in the application of emulsion liquid membrane in all membrane processes is the co-transport of water, which causes the concentration of the effluent and the dilute of the concentrate inner phase.

Table 2.2 Separation of various metals in pilot plant. Draxler, Furst and Marr (1986)

Element	Throughput (l/hr)	Initial concentration (mg/l)	Final concentration (mg/l)
zinc	30	4500	4
zinc	30	500	0.8
zinc	70	150	0.5
copper	20	8000	27
copper	40	800	3
nickel	20	2200	360
cadmium	60	14	0.01
lead	60	8	0.01
chromium	40	1500	4

K. Yamashita et al. (1998) studied synergistic extraction of Ni(II) by a mixture of the active component in the commercial extractants LIX63, 5,8-dimethyl-7-hydroxydodecane-6-oxime, and di-oleylphosphoric acid (DOLPA) has been investigated by emulsion liquid membrane containing a commercial surfactants, Span 80. Solvent extraction of Ni(II) with the mixture of LIX63 and ordinary extractant, di(2-ethylhexyl)-phosphoric acid (D2EHPA) was carried out. The results show that the LIX63-DOLPA mixture has a high synergistic

effect on the extraction of Ni(II) in the ELM system compared with the LIX63-D2EHPA mixture. And the effects of several operation factors in the ELMs were investigated: permeation of Ni(II), pH of external aqueous phase, and concentrations of extractant and surfactant. It was found that under a low surfactant concentration of less than 10 mol/m^3 good recovery of nickel ions by ELMs did not occur due to the low stability of the emulsions. On the other hand, the emulsion stability increased with an increase in the concentration of surfactant, and a stable emulsion was formed with a surfactant concentration of more than 30 mol/m^3.

2.2.2 Bioproduct Application

M.P. Thien and T.A. Hatton (1986) discussed the potential for emulsion liquid membrane system in biochemical application and their advantages over conventional systems. Examples are cited where emulsion liquid membrane has been uesd to sucessfully separate organic acids, amino acids, and other bioproducts.

2.2.2.1 Organic Acids

Terry et al. (1982) reported the extraction of acetic and propionic acids using unfacilitated transport emulsion liquid membrane (simple diffusion). The studies indicated that emulsion liquid membranes were particularly good at separating acetic acid from dilute solutions and fermentation broths.

Boey et.al. (1987) studied the recovery of citric acid from aqueous solution and unfiltered broth. The emulsion liquid membrane consist of Alamine 336 and Span 80 dissolved in Shellol A. Sodium carbornate was used as the internal phase reagent. The results show that very fast extraction of citric acid can be achieved : over 80% of a 10% (w/v) citric acid solution was removed in under 5 minutes in stirred vessel. Experiment of 4.5% citric acid from unfiltered broth showned the similar extraction profile. Significant emulsion swelling was also observed in this study, the volume of the internal phase was more than doubled.

C.C., Wang et al. (1990) studied the multiple solute extraction for two binary solute systems (m-cresol/benzoic acid and phenol/phenylacetic acid) and single solute batch extractions for five organic acids : m-cresol, phenol, benzoic acid, phenylacetic acid, and acetic acid. The membrane phase contains 3 wt% surfactant (Paranox 106) in Solvent 100 Neutral (S100N). The internal phase is LiOH solution. The result is when multiple extracable solutes are present, competition for the avaiable reagent arised, slowing extraction rates and reducing emulsion capacity for each solute.

2.2.2.2 Amino Acids

The first study of amino acid transport in emulsion liquid membrane was carried out by M.P.Thien et al. (1986). They studied the separation and concentration L-phenylalanine using a facilitated system. The membrane phase consist of Paranox 100, an emulsion-stabilizing nonionic surfactant, tri-capryl quaternary ammonium salt (Aliquat 336), anion carrier, Decyl alcohol, cosurfactant and Solvent 100N, solvent. The stripping agent is Potassiumchloride solution. The facilitated transport system investigated here features a concentrated chloride salt solution in the internal phase as the driving force for the separation. Changes in the carrier concentration are shown to result in higher initial fluxs and higher swell rates. Experiments indicate that osmotically induced water transport ("swelling") in the emulsion liquid membrane system is mediatd by both the carrier and the emulsion-stabilizing surfactant. And the specificity of the carrier is examined and is found to be directly related to the hydrophobicity of the solute.

Itoh et al. (1990) studied the effect of various parameters on the separation L-phenylalanine (Phe) by using cationic carrier (D2EHPA, Di(2-ethylhexyl) phosphoric acid). The internal phase is Hydrochloric acid solution. It was demonstrated that 80% of Phe could separated from the external phase to the internal phase with one batch operation and thus the final Phe concentration of the internal phase was eight times as high as the initial concentration of the external phase. The selectivity of this process was examined and it is concluded that this process is relatively unaffected by the presence of impurities. In this system, removal of cells from fermentation broth might not be necessary, since the surface

of microorganisms are usually negatively charged so it could not result in the fouling of the membrane interface.

Seong-Ahn Hong et al. (1992) studied the concentration of L-Phe in an emulsion liquid membrane system. The effect of two different types, D2EHPA when L-Phe is transported as cation and Adogen 464 when it is transported as an anion, were examined. For the given experimental conditions, which were presumed to be optimum, D2EHPA led to much faster extraction than Adogen 464. In addition, with the use of D2EHPA there is room to further increase the transport rate by adjusting the pH of the external phase. While the accumulation of chloride ions makes the continuous multistage process impossible for the Adogen 464 system, the increase in hydrogen ion concentration resulting from the transfer from the internal phase may be easily adjusted for the D2EHPA system. It was found that a liquid emulsion membrane obtained by demulsification of the emulsion by an electrostatic coalescer could be reused without any efficiency decline, and also that consisting of aliphatic hydrocarbons rather than aromatics is more stable and its stability increases with the increasing carbon number.

Noppaporn Panich (1994) studied the extraction of two essencial amino acids, L-Phenylalanine (Phe) and L-tryptophan (Trp), by emulsion liquid membrane from dilute solution. In this case, it has been studied the equilibrium extraction of mixtures and batch extraction of single dilute Phe, dilute Trp and mixture of both amino acids. The membrane phase consist of cation carrier D2EHPA and the surfactant Span 80 dissolved in n-dodecane. The internal phase was 1N. HCl solution. It was found that Trp had a higher flux than Phe. The extraction rate at pH 5 and 3 was higher than at pH 2. In the extractiion of binary mixtures solution of Trp and Phe, Trp did not significant effect on the transport rate of Phe.

Apiruk Suetrong (1995) studied experiment on batch extraction of L-lysine from aqueous solution by emulsion liquid membrane process. The composition of membrane and internal phase is as same as Noppaporn 's study. It was found that at optimum condition for the external phase was 1 mM of L-lysine at pH 5, 50% of L-lysine from aqueous solution have been extracted within 5 minutes. At the final of extraction, the concentration of L-lysine in the internal phase was double from the external phase.

2.2.3 Other bioproducts

Kwi Ho Lee et al. (1994) studied Penicillin G extraction from media by an emulsion liquid membrane. The effects of surfactants, diluents, and carrier mixtures, together with their combined effect on the initial extraction rate and emulsion stability were examined. Surfactants, diluents, and carriers used were Span 80 (Sorbitan Monooleate)/ECA4360J (Nonoionic Polyamine), n-butyl acetate/kerosene, and DOA (Dioctylamin)/Amberlite LA-2 (Secondary Amine), respectively. The optimum extraction conditions were found to be 20% (v/v) of Span 80 in ECA4360J as a surfactant, kerosene as adiluent and Amberlite LA-2 as a carrier.

2.2.3 Kinetic mechanism and swelling studies

Ho W.S. et al. (1982) developed model of diffusion controlled mass transfer in liquid surfactant membranes for uniform emulsion globules having no internal circulation. The solute is assumed to react instantaneously and irreversibly with the internal reagent at a reaction surface, which advances into the globule as the reagent is consumed. A perturbation solution to the resulting non-linear equations is presented. In general, the zero-order, or pseudo-steady state solution alone often gives an adequate representation of the process. Experimental data on the batch extraction of phenol from wastewater are in good agreement with the model predication.

Itoh. H et al. (1990) reported water transport mechanism in emulsion liquid membrane process for the separation amino acid. The membrane consist of D2EHPA, Paranox 100 dissolved in Terula 619. They concluded that two possible mechanism occured for swelling in this process. The first mechanism suggested that swelling is mediated by hydrated sufactant then diffuses to the internal phase. This phenomenon is driven by the difference in osmotic pressure between the external phase and the internal phase. The other proposed mechanism states that water is transported by reversed micelles. Addition,

the swelling increased linearly with increase in the initial concentration of hydrochloric acid in the internal phase.

Boyadzhiev et al. (1991) studied kinetics of liquid membrane (pertraction) recovery of L-lysine from dilute aqueous solutions in a two compartment glass cell. A 5% (vol) solution of the cation exchange carrier di (2-ethylhexyl) phosphoric acid in n-decane was used as intermediate, membrane liquid. The third stripping phase was 1N hydrochloric acid. It was found that overall transfer rate is controlled by the eddy diffusion of transported species in the donor and membrane liquids. The results proved the feasibility of the pertraction process for recovery and concentration of L-lysine from its dilute aqueous solutions.

J.B. Chaudhuri et al. (1992) reported and proposed model for the experiment of the batch of lactic acid using emulsion liquid membrane system in which effects of the surfactant Span 80, and tertiary amine carrier Alamine 336 in n-heptane, on the system stability, kinetics and swelling. It was found that at the onset of extraction solute transport was dominated by external phase mass transfer. However, after a short contact time, as the diffusion distance into the globule increased the membrane phase mass transfer become rate-limiting. A comparison of facilitated extraction between with and without swelling showed that swelling had little effect on the rate of decrease of the external phase lactic acid concentration.

Young Sum Mok et al. (1996) studied control of swelling of two different emulsion liquid membrane systems for separation of lactic acid. One system was composed of Kerosene, Span 80 and tri-octylamine (TOA) and the other composed of Kerosene, Paranox 100, Amberlite LA2. The internal phase of two systems is sodium carbonate solution. Several additives including liquid paraffin, cyclohexanone and n-decanol were investigated with respect to both emulsion swelling and lactic acid separation rate. The results showed that the extent of swelling depended strongly on membrane viscosity by increasing concentration of Span 80 and membrane composition by the addition of cyclohexanone. While the addition of liquid paraffin was very effective for reducing swelling, the solute transport rate also greatly decreased. And the swelling increase with the quantity of hydrophillic in the surfactant.

Qing-Hong Shi et al. (1997) studied on the distribution equilibrium of L-tryptophan (L-Trp) by extraction with di(2-ethylhexyl) phosphoric aicd (D2EHPA) dissolved in n-hexane. Also the effects of L-Trp and D2EHPA concentrations, pH, and ionic strength, particularly of L-Trp loading in the organic phase, on extraction equilibrium were examined. The results showed that when the amino acid loading ratio (the molar concentration ratio of the equilibrium amino acid in the organic phase to the initial dimeric D2EHPA) was less than $3*10^{-3}$, one L-Trp molecule was extracted by forming a complex with four monomeric D2EHPA molecules, and the extraction equilibrium constant (K_e) was determined to be 0.045 dm^3/mol. Above this loading ratio the equilibrium formula did not hold, and the apparent equilibrium constant (K_a) increased significantly with increasing loading ratio. The phenomenon was explained by taking into account two parallel reactions in which fewer D2EHPA molecules, two and one respectively, were needed to extract one L-Trp molecule.

CHAPTER 3

THEORY

3.1 Supported liquid membrane (SLM)

Supported liquid membrane (SLM) is made by soaking the pores of a solid support, usually a microfiltration membrane, with an organic phase which is stabilized by capillary or surface forces (see Figure 3.1); transport takes place across this place. Extraction occurs because of the difference in concentration that exist between the two aqueous phases. When an extracting agent or carrier is added, the process is called facilitated. The advantages of SLM is no emulsion to be prepared and only an extremely small quantity of membrane liquid is required for "filling" the pores. However, one of the main disadvantages is that supported liquid membranes have a much thickener than emulsion liquid membrane.

The application of SLM has mainly been considered follow:

a. Wastewater treatment,

b. Metal extraction and,

c. Fermentation product recovery.

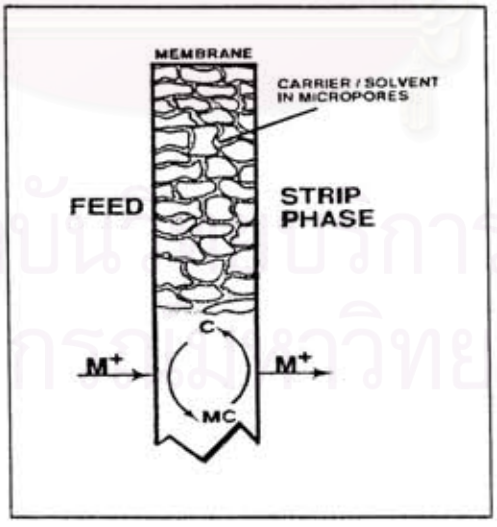


Figure 3.1 Schematic Diagram of a Supported Liquid Membrane

3.2 Emulsion liquid membrane (ELM)

Emulsion liquid membrane (ELM, see Figure 3.2 where A is interested solute, C is carrier, and H is counter ion) also called surfactant membrane or liquid surfactant membranes was first proposed by Li in 1968. The principle of separation in this type of liquid membrane is that solute is transported from the continuous phase (Feed phase, external phase) into the emulsions (Microdrop). The emulsion is subsequently broken up by various means to release the substance transported and the emulsion components are then transport to the inlet of the system to be re-emulsified and mixed with the continuous phase once more. Usually, the emulsion components and the continuous phase must be immiscible with either phase. Therefore, the emulsion is of o-w type if the continuous phase is oil and of w-o type if the continuous is water. To maintain the integrity of the emulsion during the separation process, the membrane phase usually contains certain surfactants, additives as stabilizing agents, and a base material which is a solvent for all the ingredients.

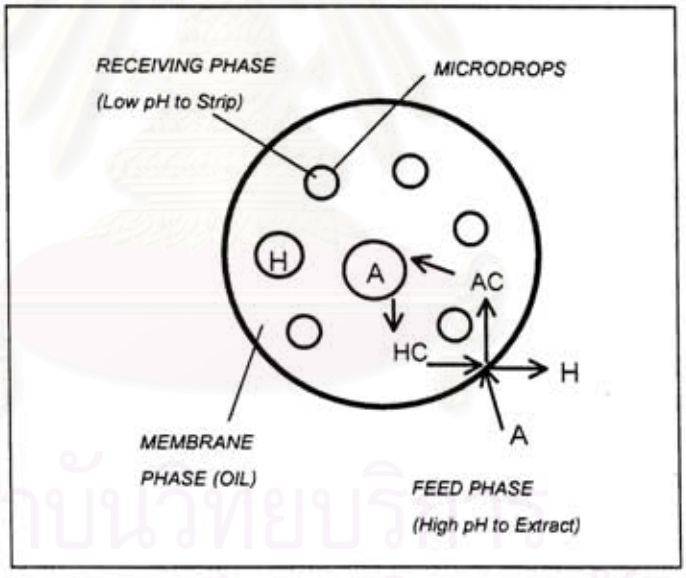


Figure 3.2 Schematic of Emulsion Liquid Membrane

Their main application is for the case where the concentration of the permeating components in the feed stream is low. The driving force for the solute transport from the continuous phase to the reception phase is the concentration difference across the

membrane and selectivity is achieved because of the different solubility of the feed species in the membrane.

When the emulsion is dispersed by agitation in a continuous phase (Third phase), many small globules of emulsion are formed. Their sizes depend on the nature and concentration of the surfactants in the emulsion, the emulsion viscosity, and the mode and intensity of mixing. In general, the globule size is controlled in the range 0.1 to 1 mm in diameter. Thus a large number of globules of emulsion can easily be formed to produce a large member surface are for rapid mass transfer from either the continuous phase to the encapsulated phase, or vice versa. It should be noted that many such smaller droplets, typically 1 μm in diameter, are encapsulated with each globule.

Separation of mixtures can readily be achieved by selective diffusion of one component through the liquid membrane phase into the liquid of lower concentration. Once separation is effected, the three phases can be separated by first settling the emulsion and continuous phase and the breaking the used emulsion. It has many ways of breaking the emulsion such as heating, centrifuge, ultrasonic, solvent dissolution, high shear and the use of high-volume electrostatic fields (Martin and Davies, 1977 and Yan and Wang, 1988).

As discussed above, a flow pattern of a continuous ELM process is illustrated in Figure 3.3. The four steps in the process are as follows:

1. Emulsification,
2. Dispersion of the emulsion in contact with the continuous phase (the external phase) for extraction,
3. Settling to separate the emulsion from the continuous phase which is the raffinate if the internal phase becomes the extract, and
4. Breaking of the emulsion (Demulsification) to recover the internal phase as the extract and the membrane phase for recycle.

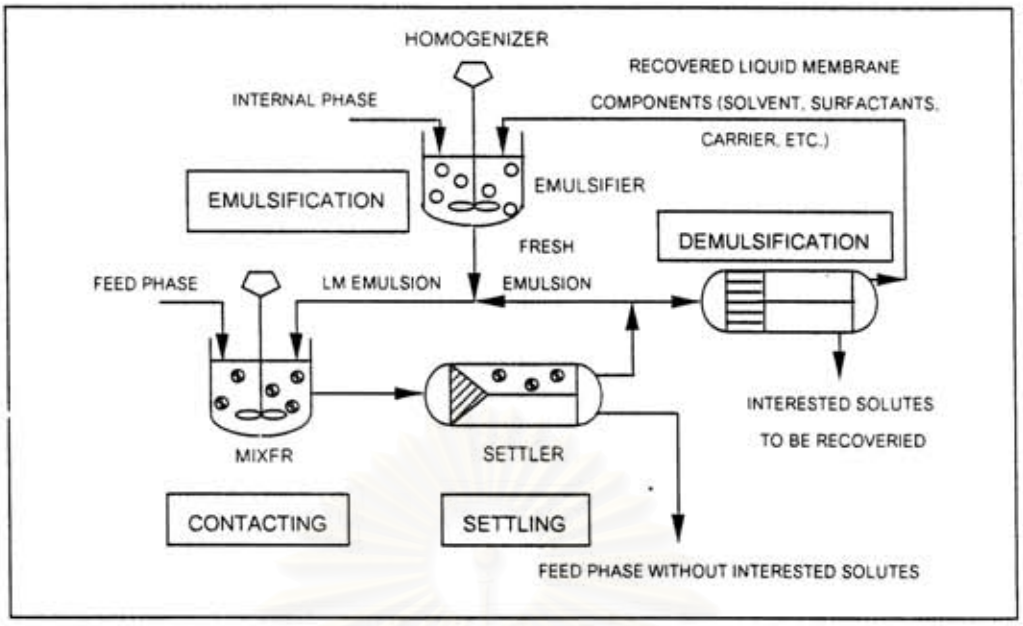


Figure 3.3 Diagram of conceptual emulsion liquid membrane process.

3.3 Facilitated Mechanism and Driving Force

In a liquid-membrane separation system, there may be two types of facilitation to improve the mass transfer rate.

3.3.1 Unfacilitated Transport

This is the simplest case of solute transport through the membrane phase and is a diffusion process. This type uses a stripping agent in the internal phase to entrap the solute and maximize the mass transfer rate. No carrier is contained in the membrane phase. The selectivity of solute separation depends solely on the partition coefficient of the solute.

The solute is initially in the bulk of the external phase and diffuses to the interface with the membrane phase. Here it partitions into the membrane and diffuse across to the interface with the internal phase into which it partition, the driving force for transport is concentration difference in the solute across the membrane phase.

The driving force can be manipulated by the inclusion in the internal phase a chemical reagent which reacts with the solute. This has a two-fold effect first the solute is now in a different chemical form and cannot back diffuse if it is insoluble in the organic solvent. Second, because the solute is now in a different form, the concentration of the

transportable species in the internal phase, is effectively zero and hence the concentration gradient is maximized, thus enhancing mass transfer.

Examples of this type separation systems are extraction of weak acids (e.g. phenol, chlorophenol, cresol) or weak bases (e.g. ammonia, aniline, toluidine) from waste treatment.

3.3.2. Facilitated Transport

This form of transport is of great importance in any potential liquid membrane separation. Three points demonstrate the benefits of using carriers in liquid membrane (Richard and Koval, 1989).

1. High fluxes are possible. By combining the advantages of high-diffusion coefficients in liquids with the added carrying capacity of the carrier, larger fluxes will be obtained than those in unfacilitated transport.

2. Very selective separations are possible. The selective nature of the complexion reaction provides much better separations than those that can be obtained based solely on relative solubility and diffusion.

3. Solutes, especially ions, can be concentrated. Coupled transport allows one to pump ions against their concentration gradient.

The application of this type is for membrane-insoluble material, such as charged species, e.g. metal ions, organic acids and zwitterions. By introducing a 'carrier' molecules into the membrane phase, the carrier used in the membrane not only facilitates the mass transfer but also enhances the separation selectivity. The solute solubility is increased the reversible of a membrane-solute carrier-solute complex. The facilitated transport can be divided into categories, depending on the type of reaction occurring between complexing agent and permeant.

3.3.2.1 Counter Transport

The key feature of counter transport is that the fluxes of the two permeating ions move counter to each other across the membrane. The solute is transport across the membrane by the formation of complex as follow (Figure 3.4)

1. At the interface between the external phase and membrane phase

the solute A, reacts with the carrier complex BC, to form the complex AC, and liberates B in the external phase.

2. The carrier-solute complex, AC, diffuses across the membrane to the interface between the membrane and internal phase.

3. At this interface with the internal phase the reverse reaction occurs, brought about by a shift in the reaction equilibrium due to the higher concentration of a counter-ion B, in the internal phase. Hence the solute A is released into the internal phase reagent.

4. The carrier reacts with the counter-ion to form the carrier-counter-ion complex, BC, which then diffused back through the membrane to the exterior interface.

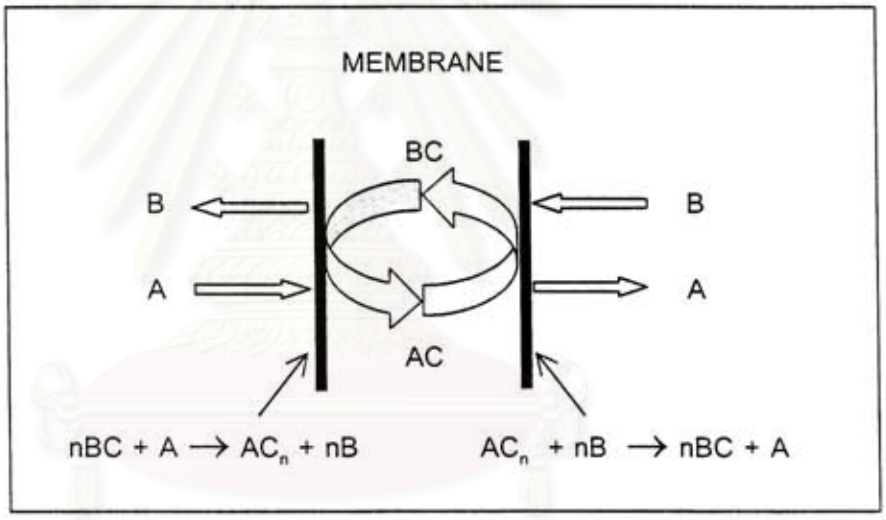


Figure 3.4 Schematic of Counter Transport of Solute A and B by Carrier C

3.3.2.2 Co-Transport

The second type of coupled transport is co-transport, illustrated in Figure 3.5. The key feature of co-transport is that the fluxes of the two permeating ions move in the same direction across the membrane.

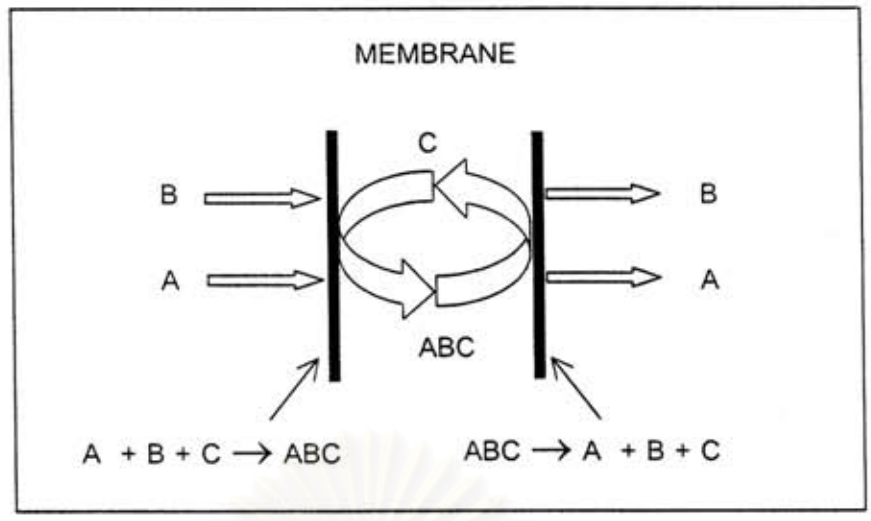


Figure 3.5 Schematic of Co-Transport of Solute A and B by Carrier C

Because of the importance of membrane phase for mass transfer mechanism we have to study the composition of membrane phase.

3.4 Advantages and Disadvantages of Emulsion Liquid Membrane

The main advantages of emulsion liquid membranes are summarized below:

1. The specific surface area of emulsion liquid membranes is very high, giving rise to very fast extraction rates, because of the small droplet sizes.

2. Liquid membrane extraction is ideal for the separation of products, which are in low concentration in fermentation broth, because the concentration difference is always maximized.

3. The solute can be simultaneously separation and concentrated at one stage.

4. Emulsion liquid membrane systems are based on liquid-liquid extraction technology. This technology has been shown to easily scaled up industrial scale operation and for continuous use.

5. Emulsion liquid membrane separations are little effected by solids that suggest application of this process as a primary separation step without the requirement of filtration.

Two disadvantages of emulsion liquid membranes are emulsion formation and breaking. There are two other phenomena associated with the operation of emulsion

systems, which can have a detrimental effect on the overall separation. There are leakage and swelling.

1. Leakage

The degree of membrane leakage or breakdown is an important parameter in assessing the stability of the liquid membranes. Membrane leakage in emulsion liquid membrane systems means the rupture of the emulsion, leading to releasing solute and internal reagents in the internal phase to the external phase. As a result, the leakage causes a decrease of the driving force for 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 emulsion preparation, and the condition under which the emulsion are contacted with the feed solution.

2. Swelling

Emulsion swelling that increase the internal phase volume is a troublesome problem associated with the use of emulsion liquid membrane. It is a process by which water is transfer from the external phase into the internal phase. The water transfer will

a. Dilute the solute that has been concentrated in the internal droplets, thus preventing a highly concentrated solute solution from being obtained.
b. Reduce the driving force for solute extraction
c. Make the membrane thinner, thereby leading to a less stable emulsion
d. Change the rheological properties in emulsion transport and phase separation.

Where swelling in ELMs is significant this may effect on extraction in two ways. Firstly, it is possible that dissolved species in the external phase will be transported across the membrane solute transport may be occur by a combination of facilitated extraction and convection transport. Secondly, the increase in the emulsion volume may give rise to significant changes in the globule and internal phase droplet sizes and their distribution, thus affecting the rate of solute extraction.

3.5 Membrane Phase Components

For Unfacilitated Transport, the membrane phase consists only of a membrane solvent and a surfactant to stabilize the primary emulsion. No carrier needed for this type because the solute transport across the membrane is accomplished through its physical solubility and then diffuses in this membrane. However for Facilitated Transport, a carrier associated stripping agent must be incorporated into internal phase, respectively, in order to achieve a couple extracting/stripping processes.

3.5.1. Surfactant

The surfactant is the key component for formulating a stable emulsion. Surfactant is characterized on the basis of the hydrophilic/lipophilic balance of the molecule or HLB scale. On this scale, species with high hydrophilic character and which is good oil in water emulsifier are assigned high HLB values. In order to get water in oil emulsion surfactants with a low HLB are generally chosen. In addition to be membranes have become commercialized, their applications have required more of surfactant than their major contribution to membrane stability such as chemical resistance, bacterial resistance, etc.

Span 80 (Sorbitan monooleate) is a nonionic surfactant with a molecular weight of 428. Its structure is shown below.

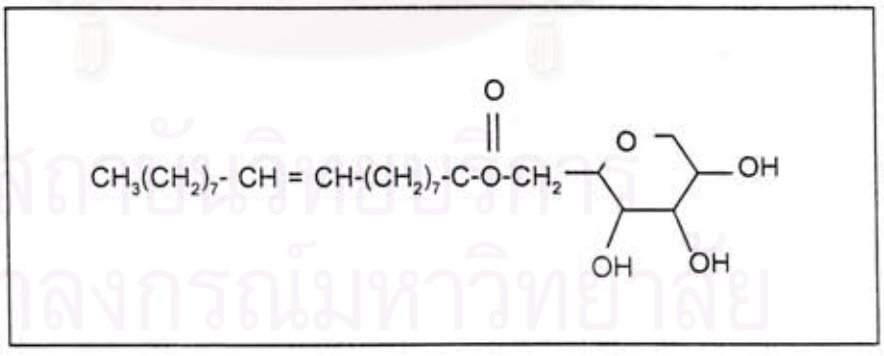


Figure 3.6 Schematic of Span 80 Structure

Span 80, which has a HLB value of 4.3, is a fairly good emulsifier, so it is widely used to form water in oil in emulsion in liquid membrane studies. During extraction

operation, the membrane incorporated with Span 80 show less resistance for mass transfer than those with other surfactants. Span 80, however suffers from some drawbacks. It is good carrier for water molecules and therefore favors the osmotic swelling of emulsion. Another disadvantage of Span 80 as an emulsifier lies in its poor chemical stability especially when the NaOH is incorporated into the internal phase. (Hirato et al., 1990)

3.5.2. Membrane Solvent

The membrane solvent is the main membrane component in which both extractant and surfactant are dissolved. Although the membrane solvent is normally regarded as an 'inert' component it does effect the membrane properties, such as distribution coefficient and diffusion coefficient, and can have significant impact on the effectiveness of the membrane system.

Seong A. H et al. (1992) reported that aliphatic solvent is generally preferred to aromatic solvent because the aliphatic solvent usually can meet of the above-mentioned requirement.

3.5.3 Carrier Species (Extractant)

A carrier species is used to enhance solute solubility and selectivity in Facilitated Transport. There are two classes of carrier molecules, charged and uncharged, but common criteria for both are that carrier and its complexes must be insoluble in the aqueous phase.

D2EHPA (Di(2-ethylhexyl) phosphoric acid) is one of the most preferable cationic exchanger which is solubilized in the membrane phase (its aqueous solubility is extremely low). It has both a hydrophilic and hydrophobic group. Its structure is shown below.

From the result of Itoh et al. (1990) 's experiment, although it seems to be similar to a surfactant, it was not effected on swelling. So it is commonly used for metal ions, organic acid and amino acid separation.

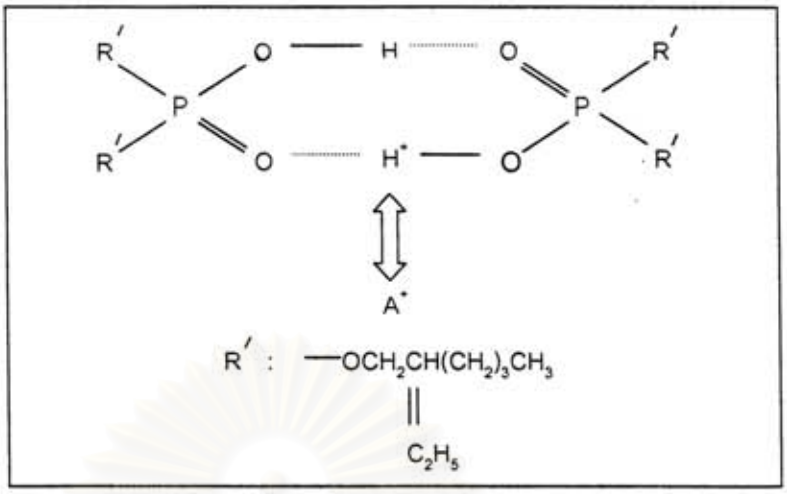


Figure 3.7 Schematic of Di(2-ethylhexyl) phosphoric acid (D2EHPA)

3.6 Internal Phase Reagent (Stripping Agent)

An acidic solution (Hydrochloric acid solution) usually is used as the internal phase reagent. The capacity of the internal phase for the solutes to be extracted depends on the initial concentration of such reagent.

3.7 Interested Solute

The model solute in this study is L-lysine HCl (Feed-grade) with chemical structure is shown in Figure 3.8.

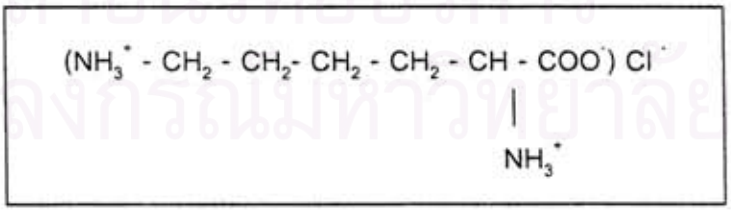


Figure 3.8 Schematic of L-lysine monohydrochlorate structure

L-lysine is the first-limiting amino acid in corn-soybean diets for swine and second limiting, after methionine, in poultry. The dissociation character of amino acid has shown in

Figure 3.9.

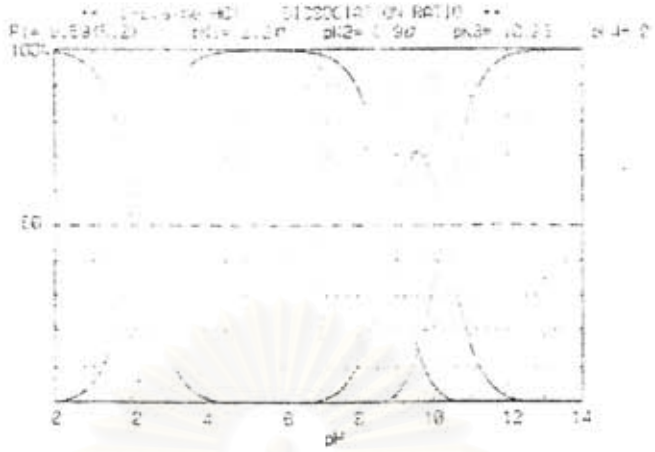
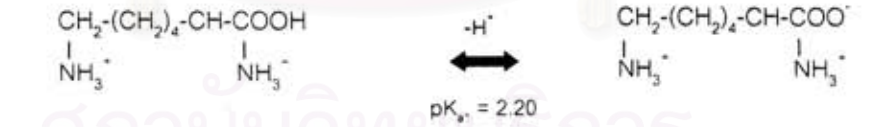
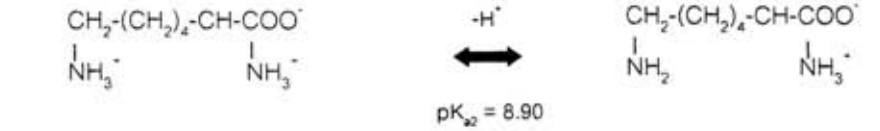


Figure 3.9 Dissociation of L-lysine at different pH

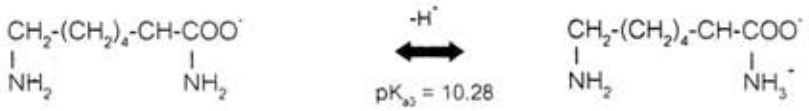
L-lysine is an amino acid that has an extra-NH_2 group on it ε carbon. In strongly acidic solution, L-lysine will be present as a dication because both amino groups will be protonated. The first proton to be lost as the pH is raised is a proton of the carboxyl group (pK_{a1}=2.20), the next is form the α-ammonium group (pK_{a2}=8.90), and the last is from the ε-amomonium group. The isoelectric point of L-lysine, which is the average of pK_{a2} (the monocation), and pK_{a3} (the dipolar ion), is 9.57. The equation for dissociation of L-lysine can be explained:



Dicationic form of L-lysine, A^{2+} Monocationic form, A^{+}



Monocationic form, A^{+} Dipolar ion, $A^{\pm}$



Dipolar ion, $A^{\pm}$ Anioic form. A^{-}

Where A^{2+} is dicationic form, A^{+} is monocatioic form, $A^{\pm}$ is aniionic form of L-lysine. K_1, K_2 and K_3 are the dissociation constant of amino acid which are $10^{-2.20}$,$10^{-8.90}$ and $10^{-10.28}$ mol/dm^3 respectively.

3.8 Transport Mechanism of L-lysine

Since amino acid is insoluble in the oil phase, an ion exchange carrier must be added to the membrane phase in order to solubilize amino acid into oil and transport it to the internal phase. Carrier in this study is D2EHPA, first exists as a carrier/proton complex. When the carrier reaches the interfacial between the external and the membrane phase, an ion exchanger take place and the carrier make a complex with an amino acid. Although the actual structure of complex is complicated, a simplified structure is shown in figure 3.10. The carrier/amino acid complex then diffuses through the membrane phase to the interface between the internal and membrane phase. Another ion exchange reaction takes place. The carrier/amino acid complex must release the Lys^{+} and the carrier immediately protonated. These processes are repeated and the amino acids thus are separated and are concentrated in the internal phase.

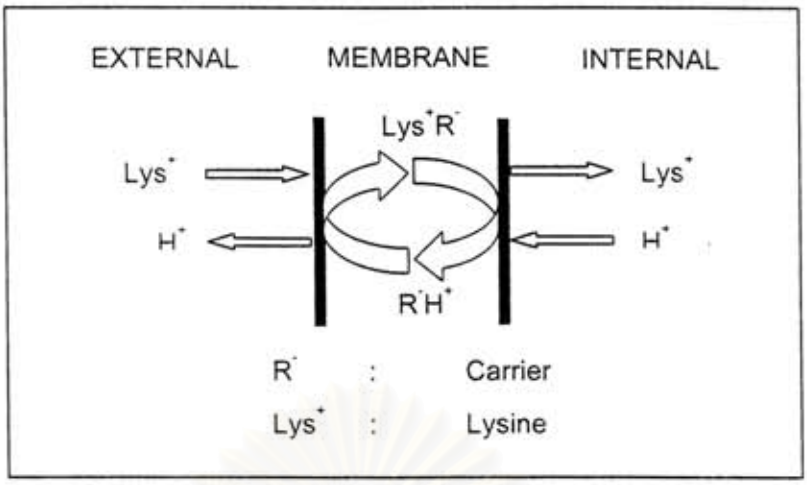


Figure 3.10 Schematic diagram of the transport mechanism for L-lysine

CHAPTER 4

EXTRACTION EQUILIBRIUM

This chapter presents the study of the extraction equilibrium of L-lysine from synthetic solution and mother liquor by using D2EHPA as a carrier, Span 80 as a surfactant and n-Dodecane as organic solvent. The extraction equilibrium constant (K_{ex}) and distribution coefficient (D^*) were determined from this study.

4.1 Experimental Materials

All chemical used in this study are of analytical grade unless otherwise stated. L-lysine monohydrochloride ($C_6H_{24}N_2O_2.HCl$, Analysis grade) purchased from Sigma Chemical Co. was used as standard tester for L-lysine determination.

4.1.1 Organic Phase

a. Surfactant: Span 80, Sorbitan monooleate (Analysis grade) from Fluka Chemika Co.

b. Carrier: di(2-ethylhexyl) phosphoric acid (D2EHPA, $C_{16}H_{35}O_4P$, Laboratory grade) from Sigma Chemical Co.

c. Solvent: n-Dodecane ($C_{12}H_{26}$, laboratory grade) from Fluka Chemika Co.

4.1.2 Aqueous Phase

Synthetic solution and mother liquor were used as aqueous phase in this experiment. Mother liquor given from Ajinomoto Co., (Thailand) Ltd. has specification as follow; L-lysine content: 350-400 g/l, pH: 6.0-6.5. Before running each experiment, aqueous phase were adjusted to pH 5.0 with concentrated sulphuric acid.

4.2 Experimental Equipment

The equipment used in these experiments consisted of

a. Homogenizer (Model T25, IKA Labortechnik) used to prepare w-o emulsion.

b. pH meter (MP 220 Metler Toledo) used to measure pH of solution.

c. Particle size analyzer (Coulter LS 230) used to analyze the particle sizes of the internal droplets.

d. Standard baffle stirred contactor with two impellers as shown in Figure 4.1.

e. Spectrophotometer (Model 4001/4, Spectronic 20 Genesys).

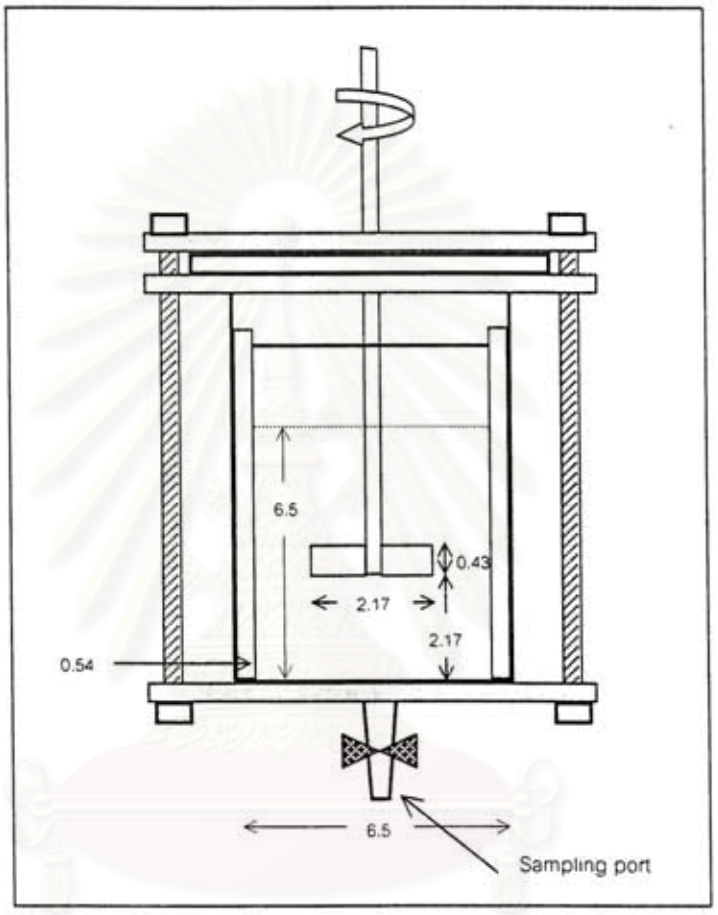


Figure 4.1 Drawing of the stirred contactor. The dimensions shown are in cm.

4.3 Experimental Methods

The extraction of L-lysine was carried out in stirred contactor by pouring 40 ml of aqueous phase to 40 ml of organic phase to make an aqueous mixture solution to organic ratio of 1 : 1 by volume. And then agitating at 420 rpm at room temperature (about 25 °C) for a period of 48 hours. The aqueous phase was mother liquor adjusted to pH 5.0 with concentrated sulphuric acid and the organic phase was prepared by dissolved 1%(vol)

span 80 and 5, 10, 20, and 30 %(vol) (0.15, 0.30, 0.61, and 0.92 mol/dm^3) of D2EHPA in n-dodecane. After extraction, the two phases were allowed to settle. The samples were collected at the end of the extraction. The aqueous phase was separated and then analyzed for L-lysine and pH was then measured. The concentration of L-lysine in the organic solution was determined by the difference of L-lysine concentrations in the aqueous phase between the initial and final stage. The L-lysine concentration in the aqueous phase was analyzed by Ninhydrin method as that used by Ajinomoto (Thailand) Co.,Ltd. using a Spectrophotometer (Model 4001/4, Spectronic 20 Genesys) at wavelength of 475 nm.

4.4 Equilibrium Extraction of L-lysine

4.4.1 Calculation Distribution Coefficient (D^*) and Equilibrium Constant (K_{ex}) for L-lysine in Synthetic solution.

Experimental Conditions:

Aqueous phase : 369.18 g/dm^3 (2.52 mol/dm^3) of L-lysine in synthetic solution adjusted pH to 5.0

Organic phase : 1% Span 80 and D2EHPA at various concentration dissolved in n-Dodecane

Agitation speed : 420 rpm

Temperature : room temperature

The extraction of L-lysine with D2EHPA started from D2EHPA at the interface between the aqueous and organic phase reacts with the cationic L-lysine (lys^*) then forming a complex and releasing H^*. Then complex diffuses into the organic phase. The extraction equilibrium can be described by the following:

$$A^* + m\,\overline{(HR)} \overset{K_{ex}}{\Longleftrightarrow} \overline{AR(HR)_{m-1}} + H^* \qquad (4.1)$$

Where a component under a bar indicates the organic phase and A^* is cationic form of L-lysine, (HR) is the monomer of D2EHPA, m is the stoichiometric coefficient and $AR(HR)_{m-1}$ is

the Lysine and carrier complex. The extraction equilibrium constant for this equation is expressed as

$$K_{ex} = \frac{\overline{[AR(HR)_{m-1}]}_{eq}[H^+]_{eq}}{[A^+]_{eq}[\overline{(HR)}]^m_{eq}} \tag{4.2}$$

Where [ ] represents the molar concentration of each components. The distribution coefficient of L-lysine between the organic and aqueous phase is defined as

$$D^+ = \frac{\overline{[AR(HR)_{m-1}]}_{eq}}{[A^+]_{eq}} \tag{4.3}$$

Combining Eqs.(4.2) and (4.3) give

$$D^+ = \frac{K_{ex}\overline{[(HR)]}^m_{eq}}{[H^+]_{eq}} \tag{4.4}$$

$$\log D^+ = \log K_{ex}[\overline{(HR)}]^m_{eq} - \log[H^+]_{eq} \tag{4.5}$$

$$\log D^+ + \log[H^+]_{eq} = \log K_{ex} + m\log[\overline{(HR)}]_{eq}$$

$$\log(D^+[H^+]_{eq}) = \log K_{ex} + m\log[\overline{(HR)}]_{eq} \tag{4.6}$$

In this work, from Table A.1 in Appendix A, the initial and equilibrium pH of synthetic L-lysine solution is less than 8.90. Therefore, the concentration of the anionic L-lysine (A^-) and dipolar ion ($A^{\pm}$) are negligible. Then the total L-lysine (A_T) is expressed by:

$$[A_T] = [A^+] \tag{4.7}$$

Because the concentration of reacted D2EHPA equal to the concentration of reacted Lys^{+}, the following mass balance equation of equilibrium D2EHPA can be obtained:

$$\overline{[(HR)]}_{eq} = \overline{[(HR)]}_{i} - m([A^{+}]_{i} - [A^{+}]_{eq}) \quad (4.8)$$

$$\overline{[AR(HR)_{m-1}]}_{eq} = [A^{+}]_{i} - [A^{+}]_{eq} \quad (4.9)$$

The values of K_{ex}, D^{*}, and $\overline{[(HR)]}_{eq}$ can be calculated from the above equations. Then we plotted the experimental data of log $(D^{*}[H^{+}])$ vs log $\overline{[(HR)]}_{eq}$ as shown in Figure 4.2, the value of *m* can be obtained. For synthetic L–lysine solution case, the value of slope or *m* is equal to 1.23 and from the intercept, extraction equilibrium constant or K_{ex} obtained is 5.26 $x10^{-4}$ dm^{3}/mol. The experimental results showed that Distribution coefficient (D^{*}) varied directly with D2EHPA concentration (Figure 4.3). Figure 4.4 showed the calculated value of K_{ex} from the individual experimental data point from Eqs (4.4). Average calculated K_{ex} from individual data point similarly to K_{ex} from experimental data. The data of these experiments were shown in Table 4.1.

4.4.2 Calculation Distribution Coefficient (D^{*}) and Equilibrium Constant (K_{ex}) for L-lysine in Mother Liquor

Experimental Conditions:

Aqueous phase : mother liquor adjusted pH to 5.0

Organic phase : 1% Span 80 and D2EHPA at various concentration dissolved in n-Dodecane

Agitation speed : 420 rpm

Temperature : room temperature

From Figure 4.5 and the same calculation, the value of *m* for equilibrium extraction of L-lysine in mother liquor is 2.02 and the extraction equilibrium constant or K_{ex} is 4.72 $x10^{-5}$ dm^{3}/mol. The effect of carrier concentration on D^{*} shown in Figure 4.6 and the calculated value of K_{ex} from the individual experimental data points from Eqs (4.4) are shown in Figure 4.7. The data of these experiments were shown in Table 4.1.

Table 4.1 Comparison of K_{ex} and D^* of L-lysine in synthetic solution and mother liquor at various D2EHPA Concentration

$[D2EHPA]_{initial}$ mol/dm^3	L-lysine in Mother Liquor		Synthetic L-lysine	
	D^*	K_{ex}	D^*	K_{ex}
0.15	7.33E-03	4.25E-05	3.70E-02	5.99E-04
0.30	1.58E-02	5.07E-05	5.48E-02	3.85E-04
0.61	2.12E-02	4.05E-05	1.11E-01	6.44E-04
0.92	2.89E-02	5.00E-05	-	-

The comparisons of D^* and K_{ex} from synthetic solution and mother liquor were illustrated in Figure 4.8 and 4.9. At the same L-lysine concentration, as carrier concentration increases the distribution coefficient (D^*) is also increased but not effects on equilibrium constant (K_{ex}). Moreover, it can be seen that D^* of L-lysine in synthetic solution is higher than of mother liquor. Because it is possible that there are impurities in mother liquor that could competed with L-lysine to form complex with D2EHPA as the same of Wang's experiment (1990). In addition, when we considered the value of D^* of L-lysine in mother liquor, it was found that D^* increased slowly proportional to carrier concentration. This behavior can be explained that there are impurities or other amino acids that could formed complex with D2EHPA faster than L-lysine, therefore D^* were not much increased.

When we compare our D^* of synthetic solution at 10% of D2EHPA, $5.48*10^{-2}$, with Boyadzhiev' s (1991), 14.7, We found that our D^* was much less than. It could be explained by Eqs (4.3) and Eqs (4.4) that we used L-lysine concentration, (2.85 M) which was about 285 times higher than that of his experiment (0.01 M), thus D^* and K_{ex} from of our experiment were very small.

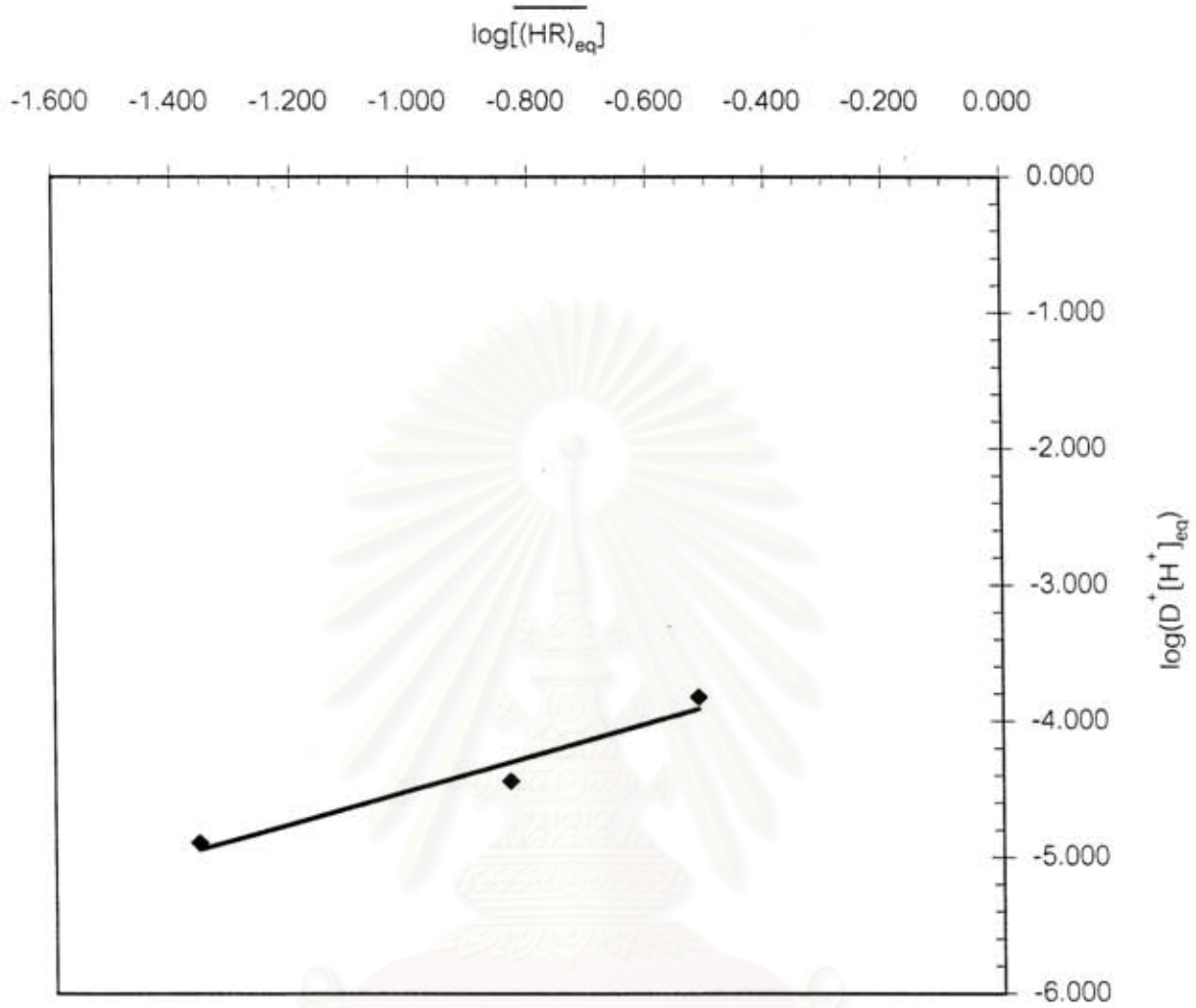


Figure 4.2 log ($D^+[H^+]$) vs log $[\overline{(HR)}]_{eq}$ of synthetic L-lysine solution

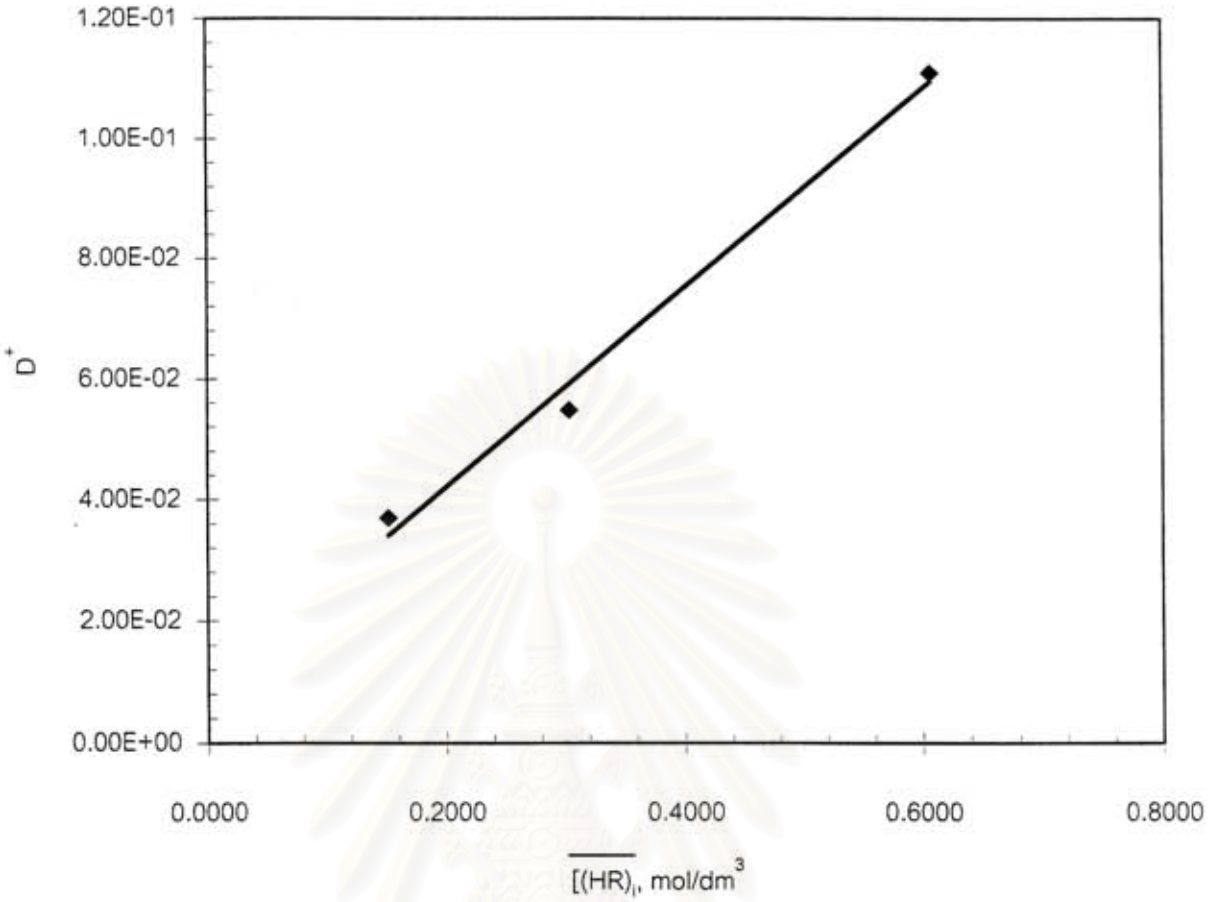


Figure 4.3 D^+ vs $[\overline{(HR)}]_i$ of synthetic L-lysine solution

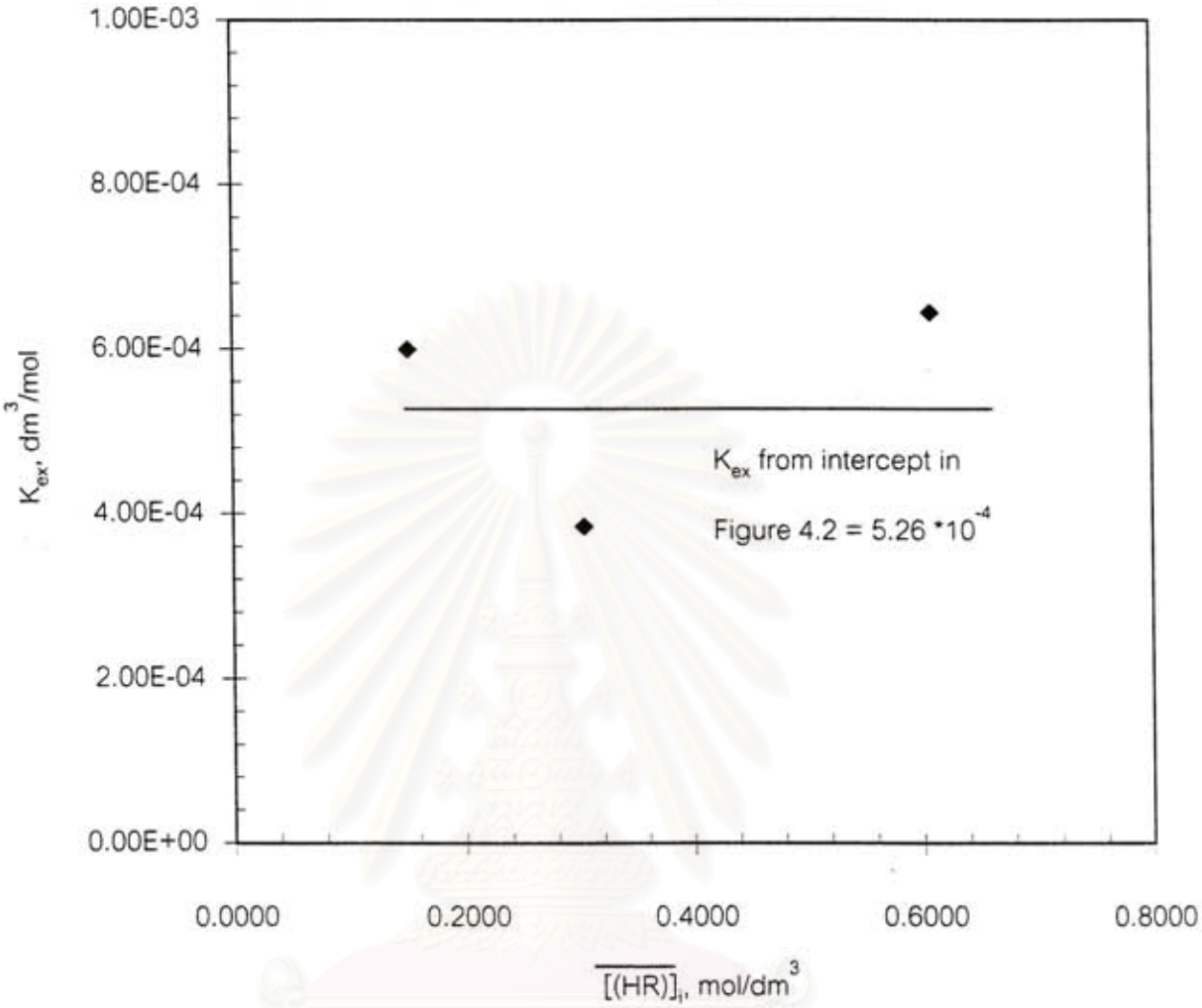


Figure 4.4 K_{ex} of Synthetic L-lysine vs $\overline{[(HR)]_i}$

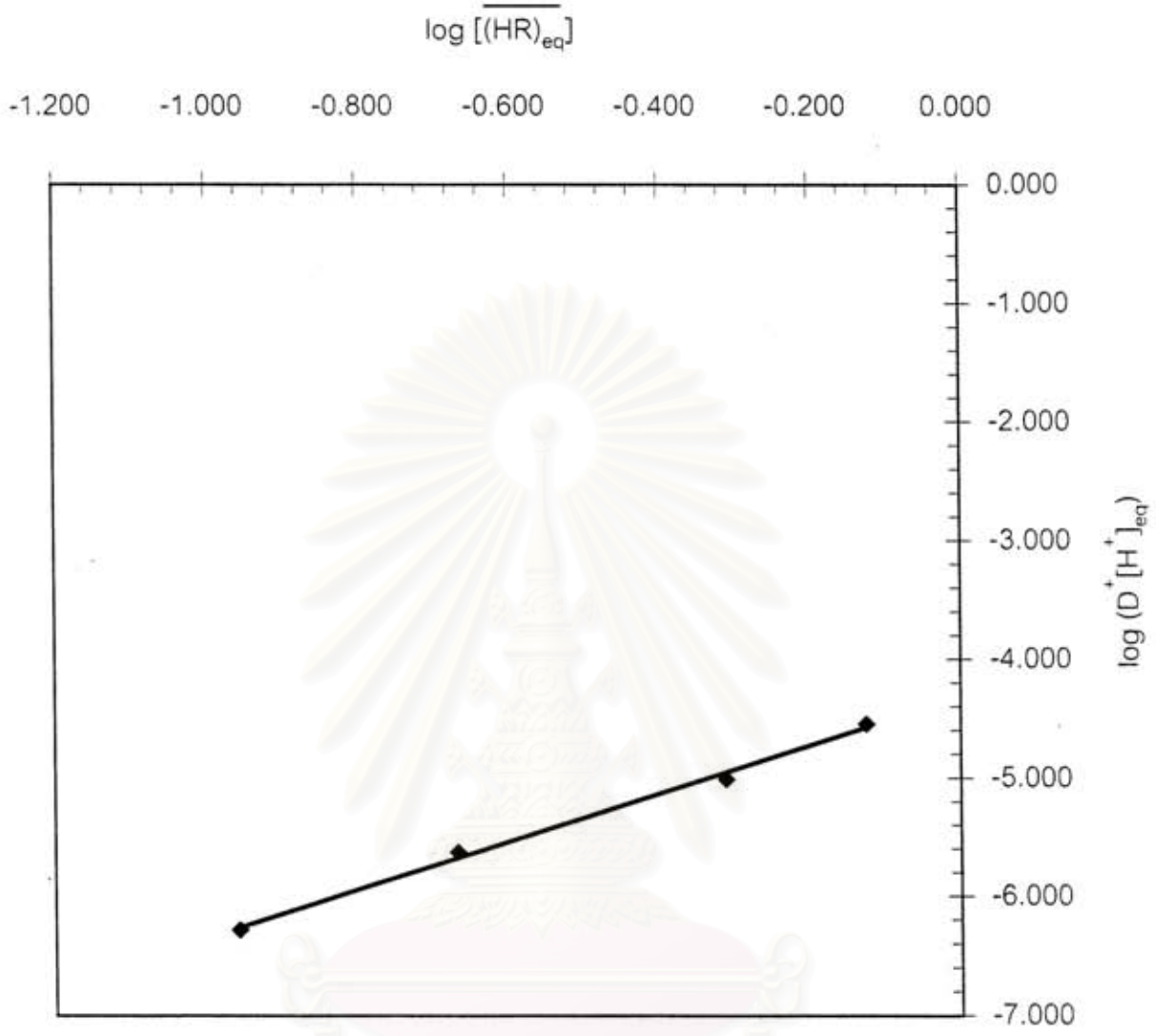


Figure 4.5 $\log(D^{+}\,[H^{+}]_{eq})$ vs $\log[\overline{(HR)}]_{eq}$ of L-lysine in Mother Liquor solution

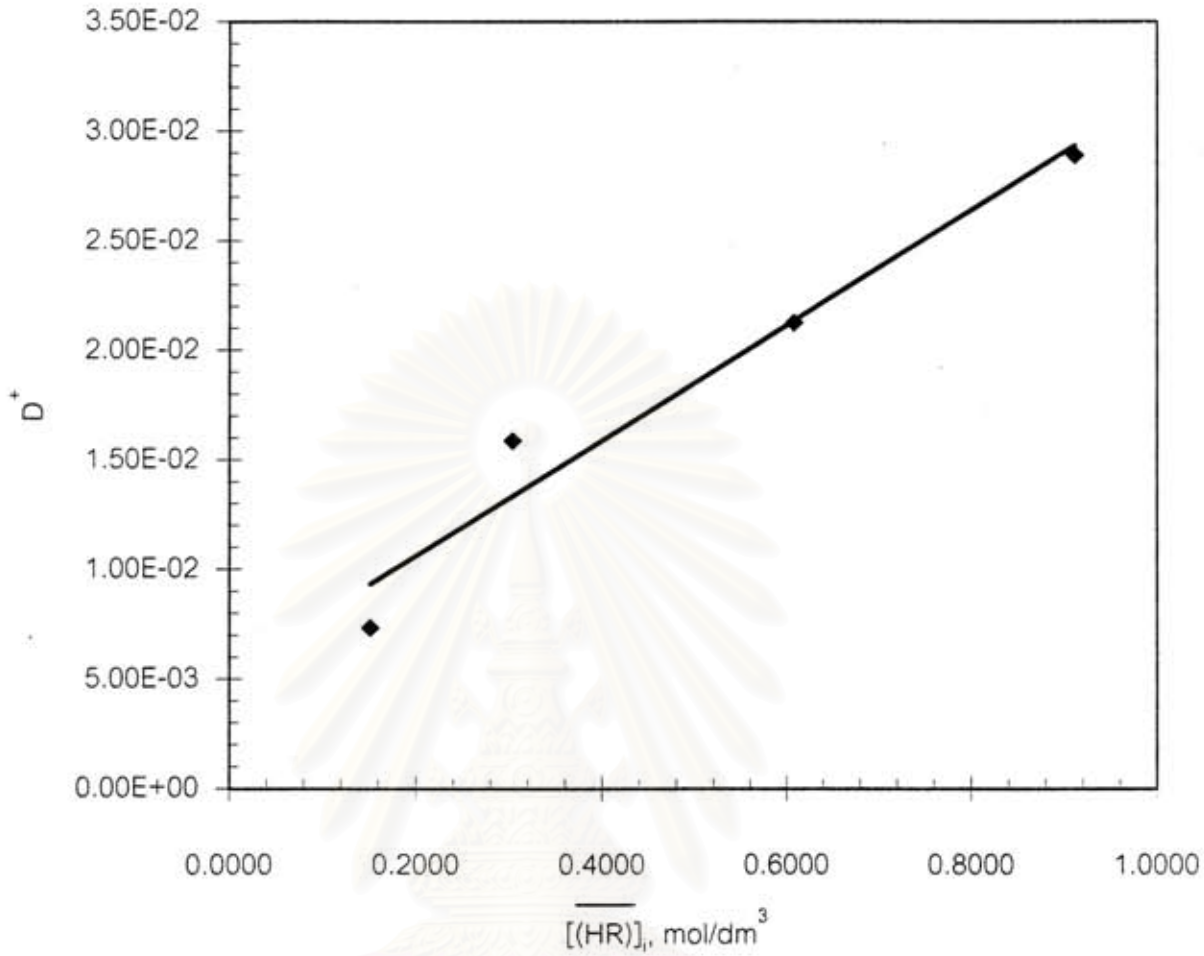


Figure 4.6 D^+ vs $\overline{[(HR)]_l}$ of L-lysine in Mother Liquor

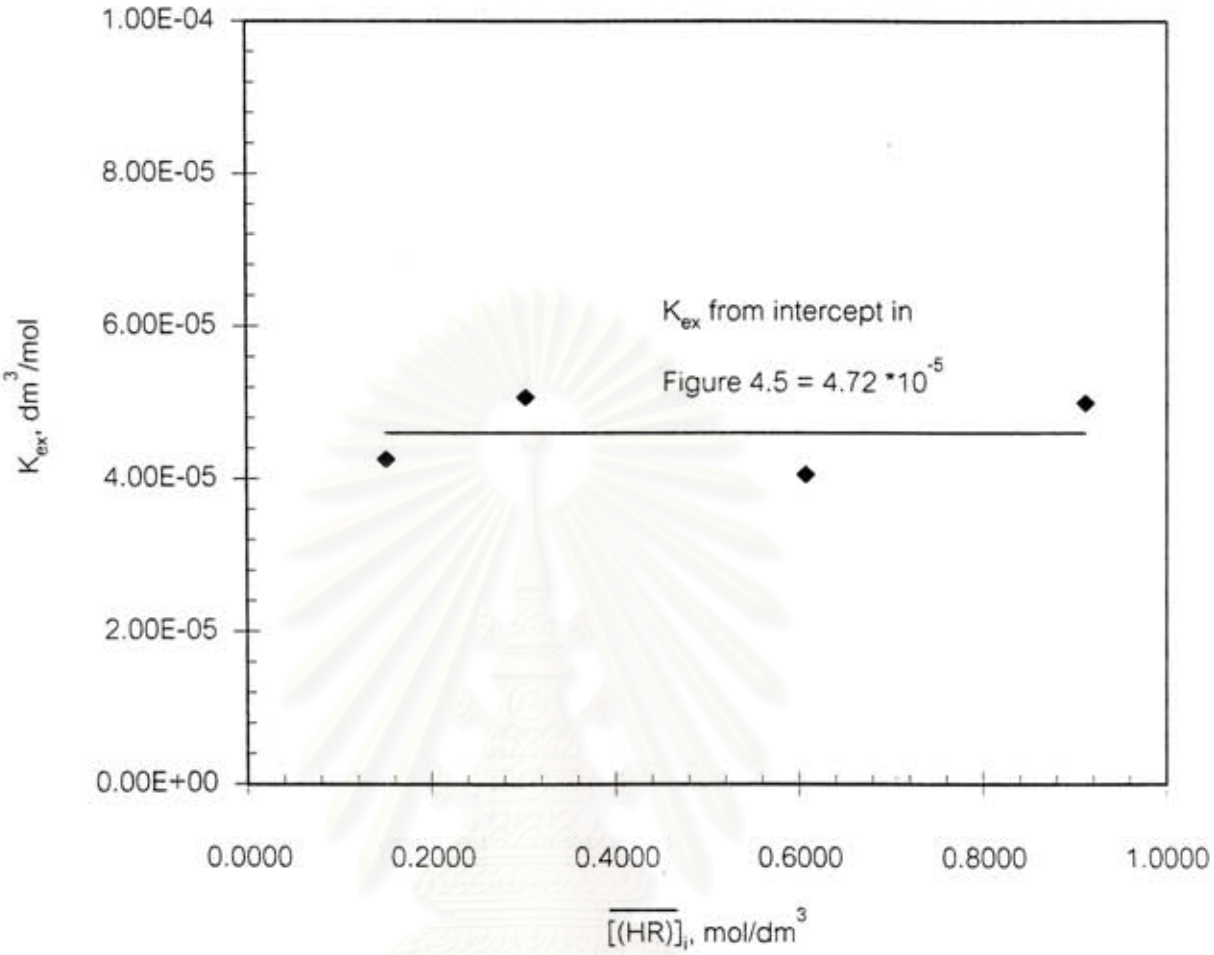


Figure 4.7 K_{ex} of L-lysine in Mother Liquor vs $\overline{[(HR)]_i}$

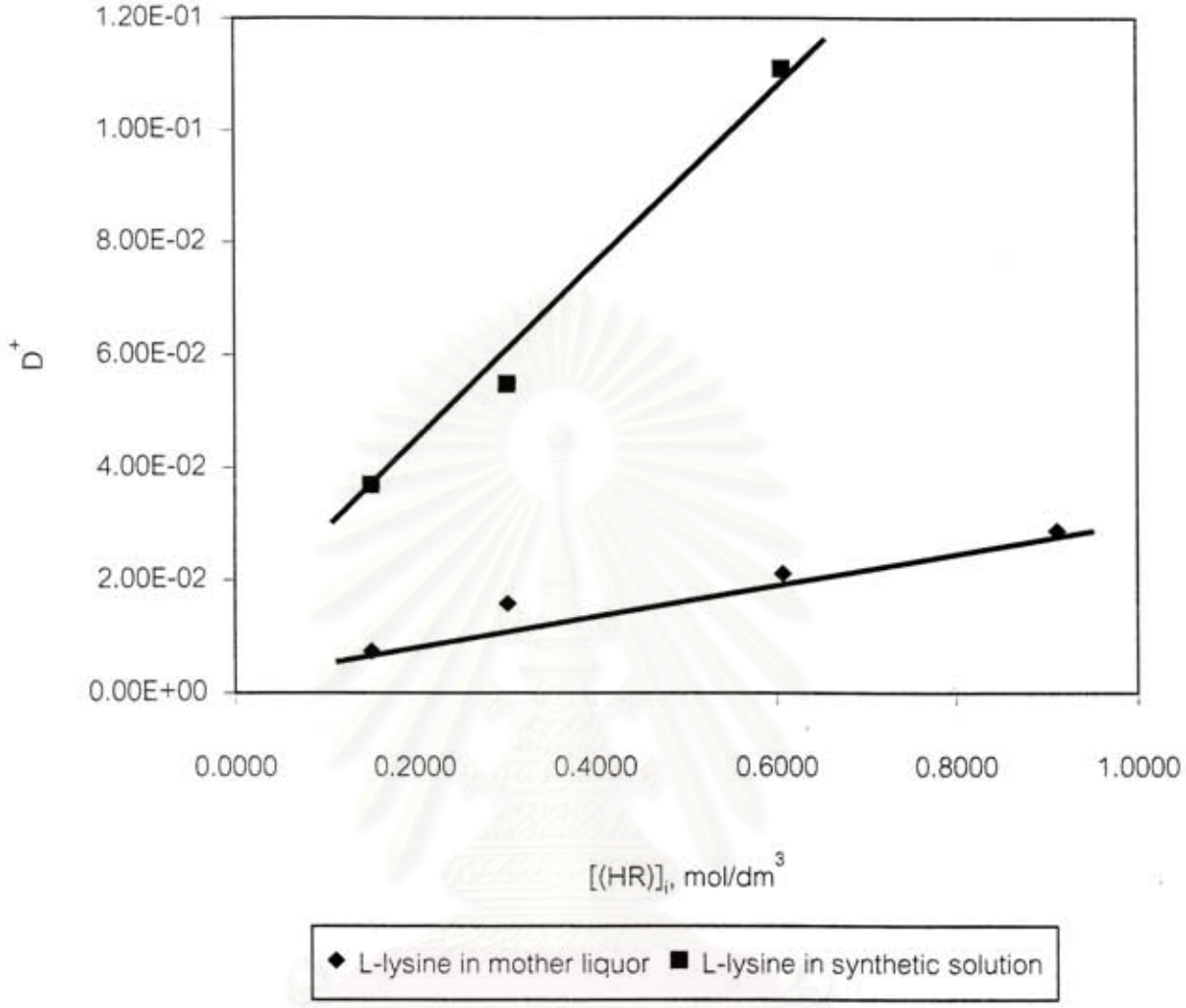


Figure 4.8 Comparison of D^+ from synthetic L-lysine solution and mother liquor at various initial carrier concentration

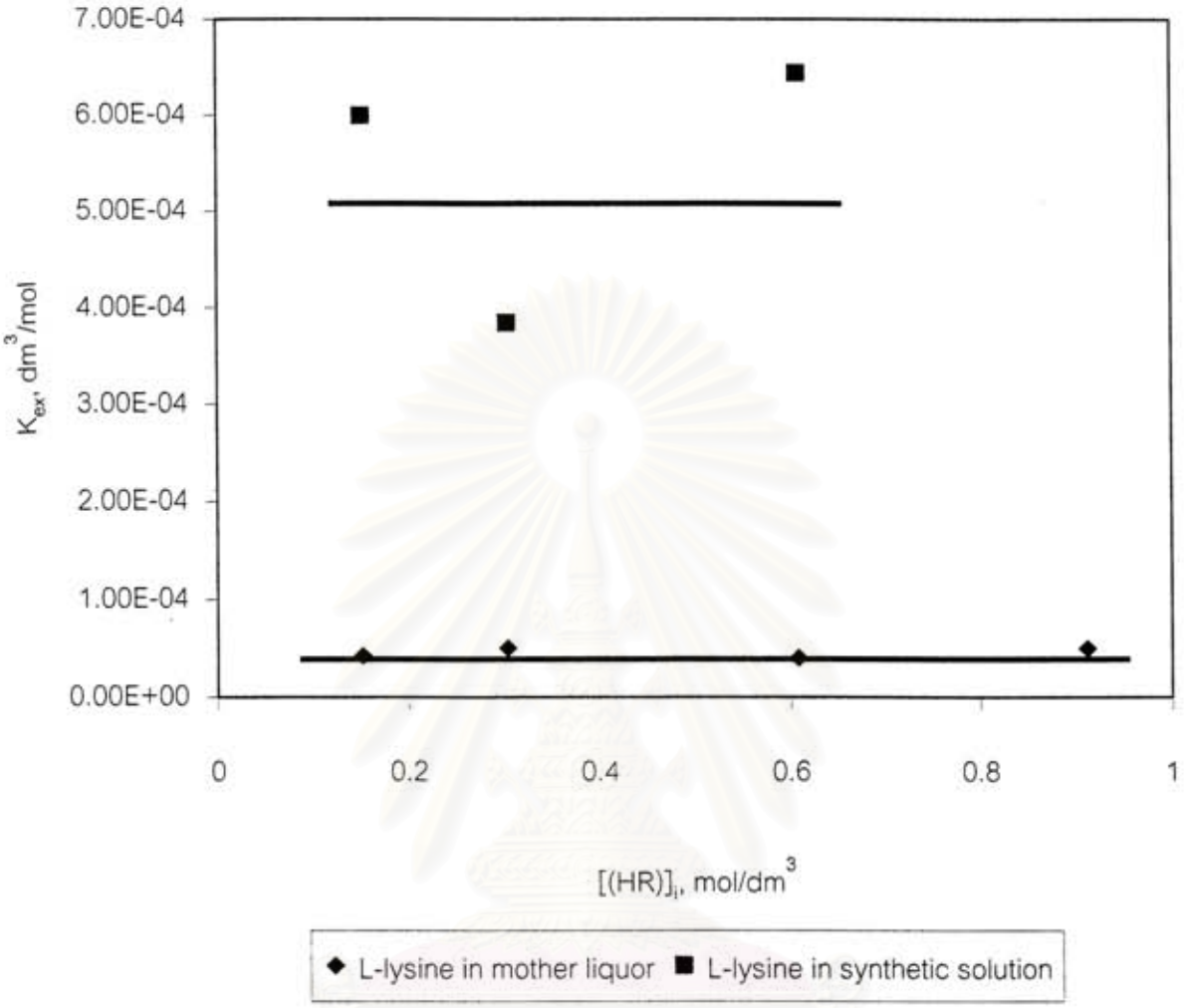


Figure 4.9 Comparison of K_{ex} from synthetic L-lysine solution and mother liquor at various initial carrier concentration

CHAPTER 5

EMULSION LIQUID MEMBRANE

This chapter presents the results of the batch extraction of L-lysine with Facilitated Extraction. The internal phase was hydrochloric acid solution. The emulsifying agent, Span 80; carrier, D2EHPA; and n-Dodecane were the components in the organic membrane phase. The external phase in these experiments was Mother liquor.

5.1 Experimental Materials

The reagent used in these experiments was previously described in the chapter 4. The emulsion liquid membrane process consisted of three parts as follows:

5.1.1 External phase

External phase in this experiment was mother liquor which was given by Ajinomoto Co., (Thailand) Ltd. The specification of mother liquor was reported as follow; L-lysine content: 350-400 g/l, pH: 6.0-6.5. The pH of the external phase was adjusted with concentrated sulphuric acid.

5.1.2 Membrane Phase

a. Surfactant : Sorbitan monooleate (Span 80)
b. Carrier : Di (2-ethylhexyl) phosphoric acid (D2EHPA)
c. Solvent : n-Dodecane

5.1.3 Internal Phase

The internal phase solution was HCl, which ionized to H^+ and acted as driving force for L-lysine transfer.

These experiments used L-lysine (pure, Sigma Chemical Co.) as standard tester for determination of L-lysine concentration in mother liquor.

5.2 Experimental Methods

First of all, the w-o type emulsion was prepared by homogenizing 30 ml of internal phase and 30 ml of membrane phase with a high-speed homogenizer at 8000 rpm. The w-o emulsion (50 ml) thus prepared was poured and dispersed to form w-o-w multiphase emulsion under stirring at 420 rpm in a standard baffle stirred contactor with two impellers containing mother liquor as the external phase (100 ml).

The extraction time for each example, which were taken throughout the experiment via a sampling port at the bottom of the contactor, was started from the time that the emulsion was poured. After extraction, all solution was removed from the contactor. Then, the emulsion phase was quickly separated from the external phase sample. The volume of each phase was measured and L-lysine concentrations in the external phase were measured by Ninhydrin method using Spectrophotometer at 475 nm. The pH of the external phase solutions was also measured by using pH meter. The experiments were carried out under the conditions shown in Table 5.1.

Table 5.1 Experimental Conditions of L-lysine Extraction on ELM Process at Room Temperature (about 27 $^{\circ}$ C)

Parameters	Conditions
Initial pH in external phase	3, 4, 5, 6, and 8
Internal HCl concentration	1, 2, 4, and 6 (N)
Surfactant concentration (Span 80)	0.5, 1, 2, and 3% (v/v)
Carrier concentration (D2EHPA)	5, 10, 20, and 30% (v/v)
W-O Phase : external phase volume ratio	1:0.5, 1:1, 1:2 (v/v)
Mother liquor characteristic	Filtrated and no-filtrated mother liquor
Agitation Speed	300, 360, 420, and 480 rpm
Source of L-lysine	Synthetic solution and mother liquor

5.3 Calculation of % Swell in the Internal Phase

The calculation of % swelling in the internal phase, which can be done by measuring the internal droplets size by particle size analyzer (COULTER LS SERIES), were measured only 0 and 1 minute. The percentage swelling can be calculated as the following:

The optimum conditions for L-lysine extraction from mother liquor were:

Experimental Conditions:

External phase : pH of mother liquor was adjusted to 5.0

Membrane phase : 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)

Internal phase : 2N HCl

Membrane preparation: at 8000 rpm of homogenizing speed for 10 minutes

W-O phase : external phase volume ratio : 1:2

Agitation speed : 360 rpm

Temperature : room temperature

Data of internal droplet size:

Time (min)	Internal droplet size (μm)
0	1.32
1	1.45

At 0 minute, internal droplet volume = $4/3\ (\pi r^3)$

= $4/3\ [\pi * (0.66 * 10^{-6})^3]$

= $1.21 * 10^{-18}\ m^3$

At 1 minute, internal droplet volume = $4/3\ [\pi * (0.73 * 10^{-6})^3]$

= $1.60 * 10^{-18}\ m^3$

%swelling in 1 minute = $[(1.60 - 1.21) * 10^{-18}] * 100 / (1.21 * 10^{-18})$

= 32.23%

5.4 Calculation of L-lysine Concentration in the Internal Phase

In emulsion liquid membrane extraction, the concentrations of L-lysine in the external phase were measured and the concentrations of L-lysine in the internal phase were calculated by mass balance based on the assumption that there was no accumulation of L-lysine in the membrane phase. The following is an example of how the concentration is calculated.

Experimental Conditions:

External phase	:	pH of mother liquor was adjusted to 5.0
Membrane phase	:	1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	:	2N HCl
Membrane preparation:		at 8000 rpm of homogenizing speed for 10 minutes
W-O phase : external phase volume ratio :		1:2
Agitation speed	:	360 rpm
Temperature	:	room temperature

The initial concentration of L-lysine in the external phase was 406.09 g/l.

The concentration of L-lysine in external phase after 1 minute extraction was 324.72 g/l.

The amount of L-lysine that penetrated into the internal phase was 406.09 - 324.72 = 81.37 g/l.

The volume of external phase was 100 ml.

Therefore, amount of L-lysine in external phase 100 ml was $\frac{81.37*100}{1000} = 8.14$ g.

By assumption that no accumulation of L-lysine in membrane phase, 8.14 g of L-lysine must permeate into internal phase.

At initial, the volume of internal phase was 25 ml.

At 1 minute, the volume of internal phase was increased to 33 ml by swelling 32.23%

Therefore, the internal phase L-lysine concentration was $\frac{8.14 * 1000}{33} = 246.67$ g/l.

5.5 Results and Discussion

5.5.1 The Effect of Initial pH of The External Phase

From Figure 3.9, the ionic structure of L-lysine changes significantly with changes in pH. In these experiments D2EHPA, which is a cationic carrier, is used so L-lysine must exist in cationic form. In order to forward L-lysine into the internal phase, a large difference of H^+ between the internal and the external phase must be established. The residual concentration ratio-time course and relationship between initial pH of external phase and L-lysine extraction are shown in Figure 5.1 and 5.2. The data are from Table B.1 and B.2 in Appendix B. The experimental conditions operated at room temperature and 420 rpm. agitation speed were as follow: mother liquor as external phase at various initial pH within the range 3, 4, 5, 6 and 8; 1% (v/v) of span 80, 10% (v/v) of D2EHPA and n-dodecane as membrane phase. The internal phase was 2N HCl solution.

Figure 5.2 shows %initial extraction at various initial pH of external phase (at first 1 minute). It was found that as pH was increased up to 5, %initial extraction of L-lysine increased. %Initial extraction of L-lysine started to decrease at pH higher than 5, because at higher pH in external phase, less Lys^+ was obtained due to incapability in dissociation to cationic form. Figure 5.3 showed the change of pH in external phase during L-lysine extraction by emulsion liquid membrane that when pH decreased to about 2 L-lysine can not get better because L-lysine cannot dissociate to cationic form. The data are from Table B.3 in Appendix B.

The maximum %initial extraction at pH 5.0 was 17.62. From the result can be conclude that at the initial pH of external phase equal to 5.0 is the optimum condition for L-lysine from mother liquor by ELM.

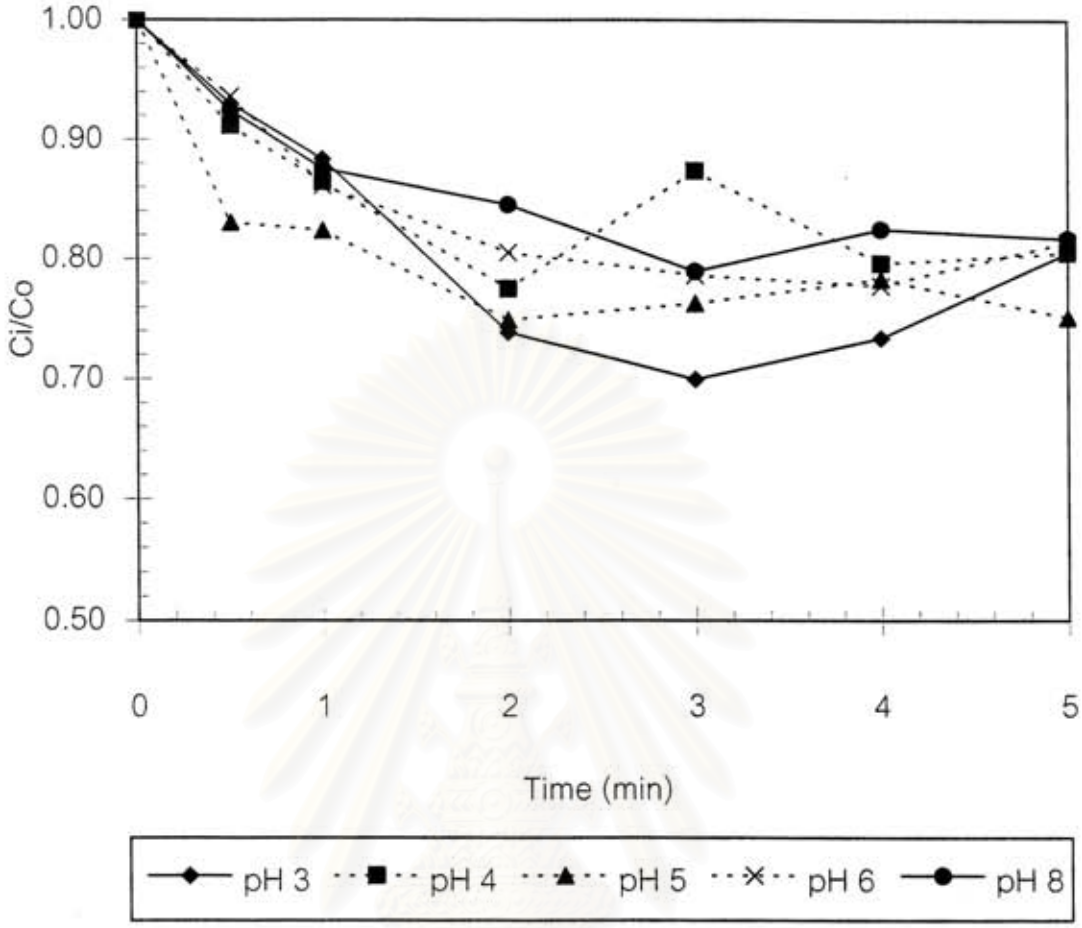


Figure 5.1 Effect of pH on ELM extraction of mother liquor at various initial pH

Experimental Conditions

External phase	: Mother liquor at various initial pH
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

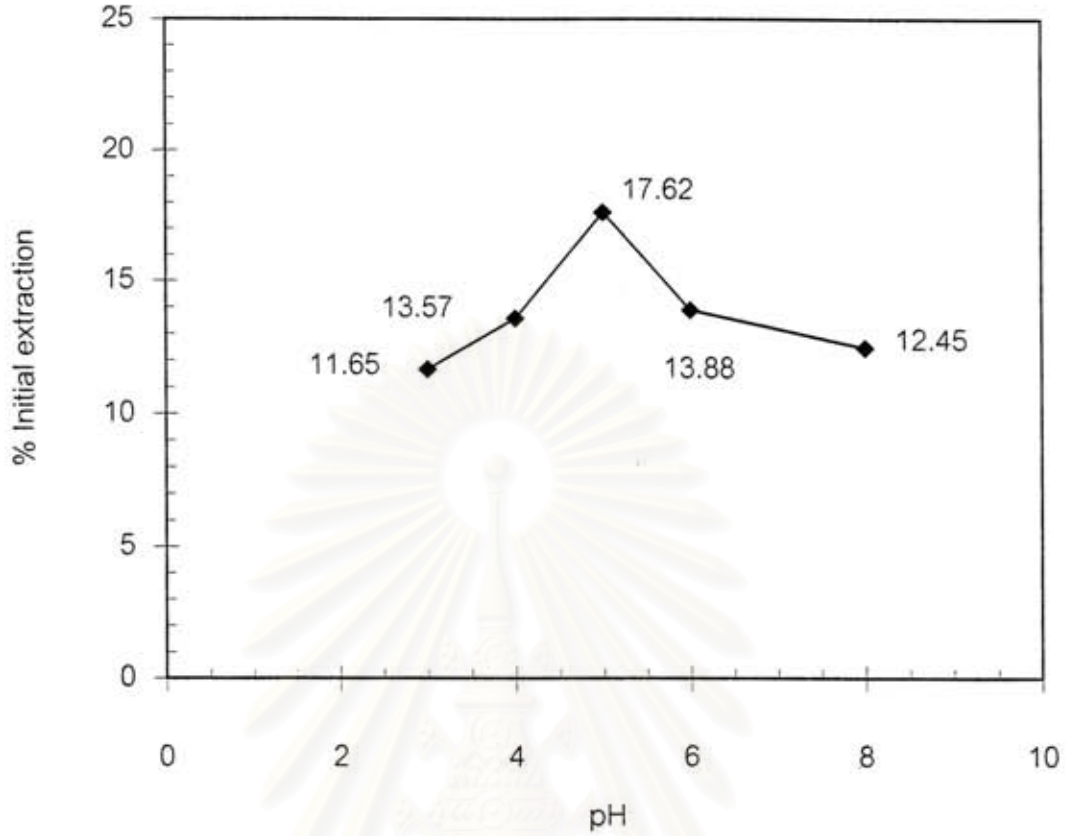


Figure 5.2 % Initial extraction on ELM extraction of mother liquor at various initial pH (at first 1 minute)

Experimental Conditions

External phase	: Mother liquor at various nitial pH
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

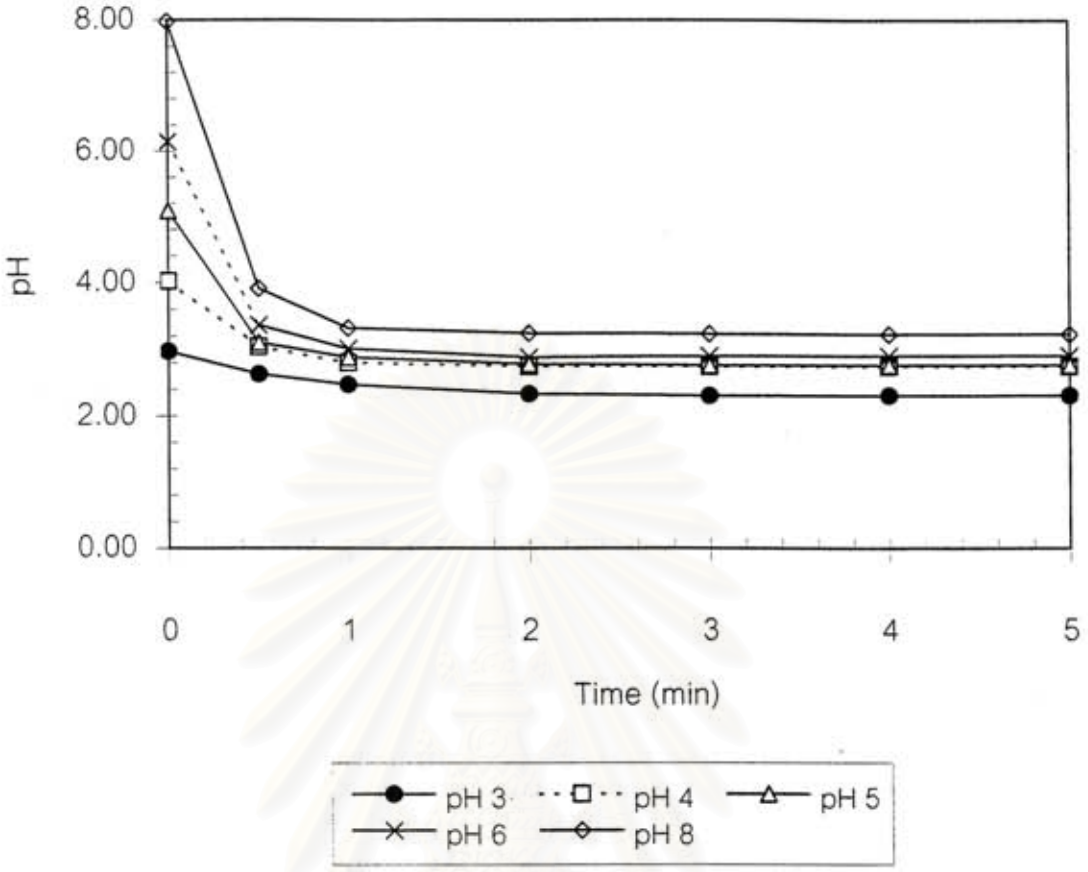


Figure 5.3 Change of pH in external phase during L-lysine extraction on emulsion liquid membrane at various initial pH

Experimental Conditions

External phase	: Mother liquor at various initial pH
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

5.5.2 The Effect of Initial Hydrochloric Acid Concentration in the Internal Phase

The relationship between initial hydrochloric concentration and L-lysine extraction is shown in Figure 5.4. The data are from Table B.4 and B.5 in Appendix B. The experimental conditions operated at room temperature and 420 rpm agitation speed were as follow: mother liquor adjusted pH to 5.0 as external phase; 1% (v/v) of span 80, 10% (v/v) of D2EHPA and n-dodecane as membrane phase. The internal phase was varied within the range 1, 2, 4, and 6N HCl solution.

As mentioned above, the difference in hydrogen ion concentration between the external phase and the internal phase is the driving force in this ELM process. The experimental results showed in Figure 5.4 that HCl concentration was increased from 1 to 2N, %initial extraction (at first 1 minute) increased. When it was further increased from 2 to 6N, %initial extraction (at first 1 minute) decreased. Because the swelling increase linearly with increase in the initial concentration of hydrochloric acid in the internal phase as can be seen in Figure 5.6. Moreover, the water transported to the internal phase appears to increase the breakage by making the emulsion increasingly unstable.

The maximum %initial extraction used 2N HCl as internal phase was 17.62. From the result can be conclude that at initial hydrochloric acid concentration equal to 2N is the optimum condition for L-lysine from mother liquor by ELM.

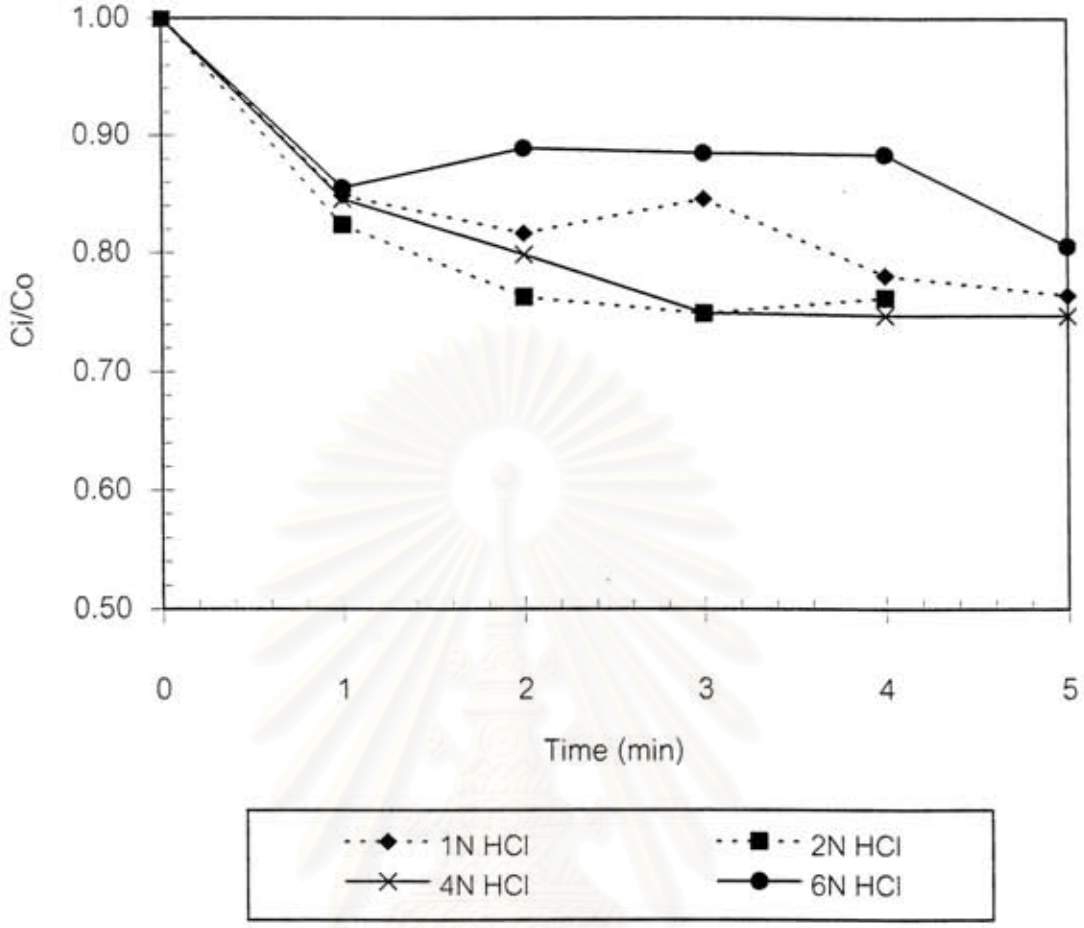


Figure 5.4 Effect of HCl concentration on ELM extraction of mother liquor at various HCl Concentration

<u>Experimental Conditions</u>

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: HCl solution at various concentrations
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

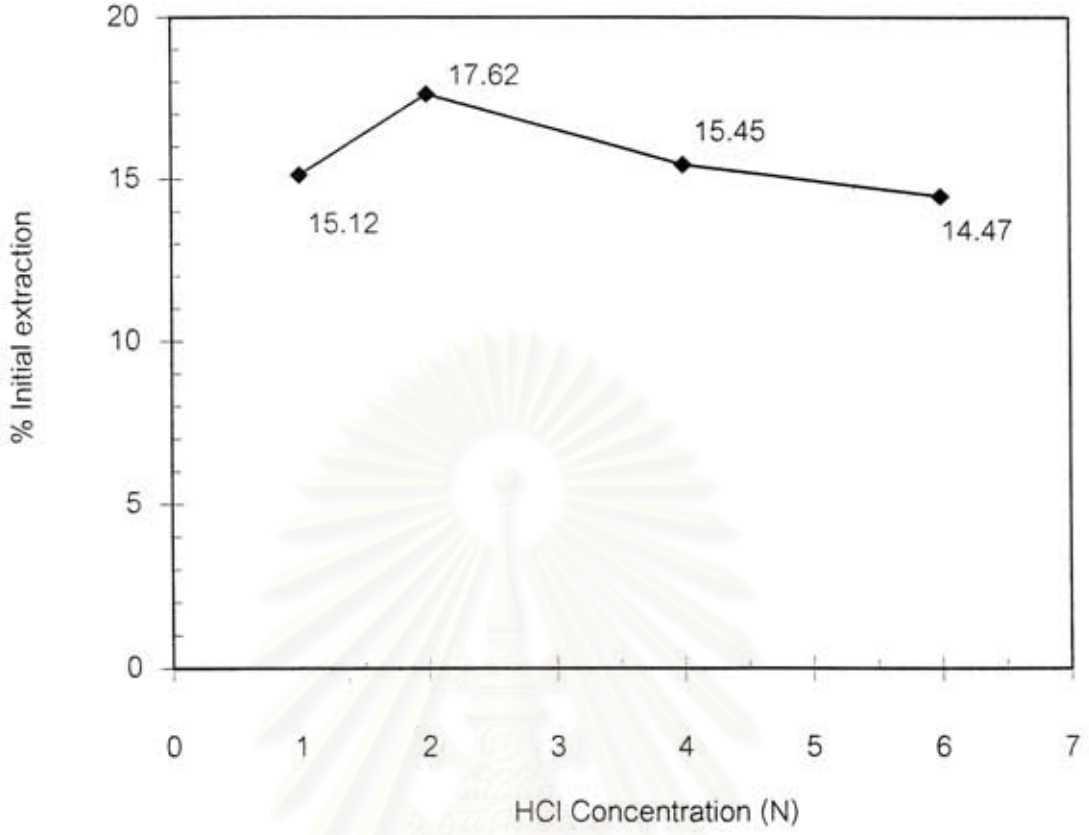


Figure 5.5 % Initial extraction on ELM extraction of mother liquor at various HCl concentration (at first 1 minute)

Experimental Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: HCl solution at various concentrations
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

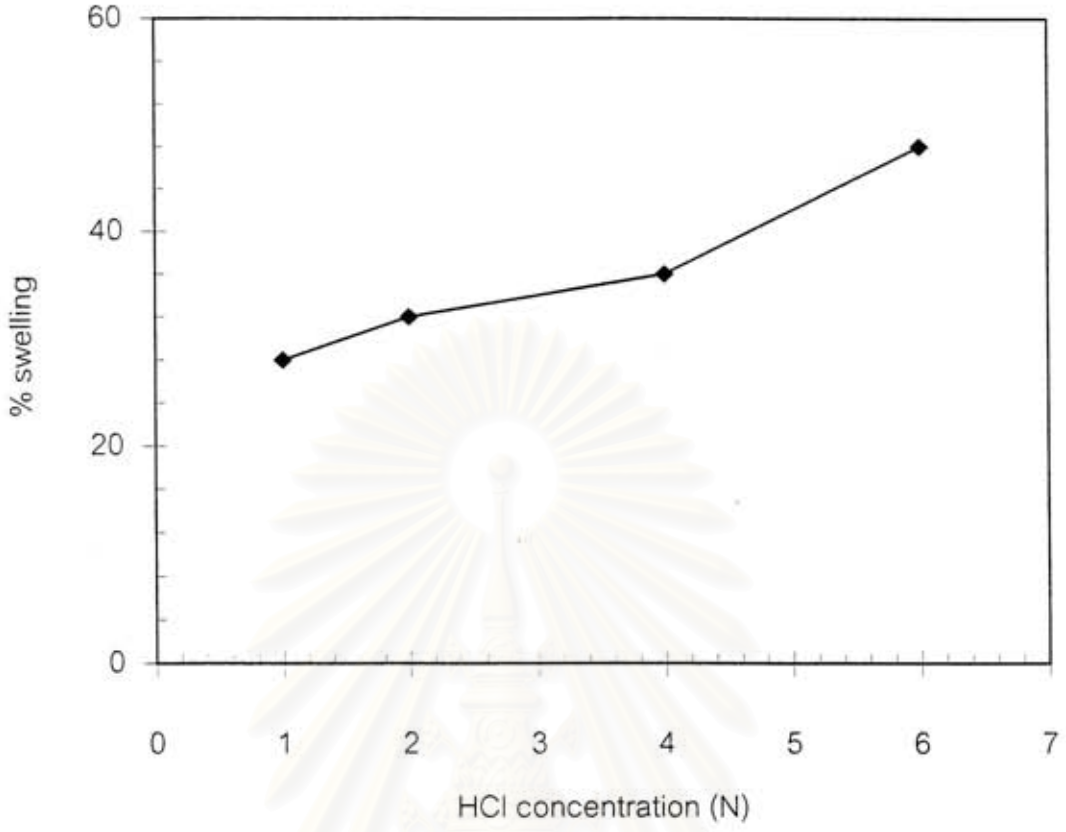


Figure 5.6 % Swelling on ELM extraction of mother lLiquor at various HCl concentration (after extraction)

Experimental Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: HCl solution at various concentrations
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

5.5.3 The Effect of Surfactant Concentration

The relationship between surfactant (Span 80) concentration and L-lysine extraction is shown in Figure 5.7. The data are from Table B.7 and B.8 in Appendix B. The experimental conditions operated at room temperature and 420 rpm agitation speed were as follow: mother liquor adjusted pH to 5.0 as external phase; the span 80 concentration within the range 0.5, 1, 2, and 3% (v/v), 10% (v/v) of D2EHPA and n-dodecane as membrane phase. The internal phase was 2N HCl solution. Figure 5.8 show %initial extraction at various surfactant concentration (at first 1 minute). It was found that as surfactant concentration was increased from 0.5 to 1% (v/v) the L-lysine extraction also increased. However, when it was further increased from 1 to 3 %(v/v), L-lysine extraction could not get better. This behavior can explain that as the span 80 concentration was increased from 1 to 3% (v/v), the extent of swelling depended strongly on membrane viscosity by increasing concentration of span 80 and the swelling increase with the quantity of hydrophillic in the surfactant. On the other hand, when the span 80 was extremely low, good recovery of L-lysine by ELMs did not occur due to the low stability of the emulsion.

The maximum %initial extraction used 1% (v/v) span 80 was 17.62. From the result can be conclude that at surfactant (span 80) equal to 1% (v/v) is the optimum condition for L-lysine from mother liquor by ELM.

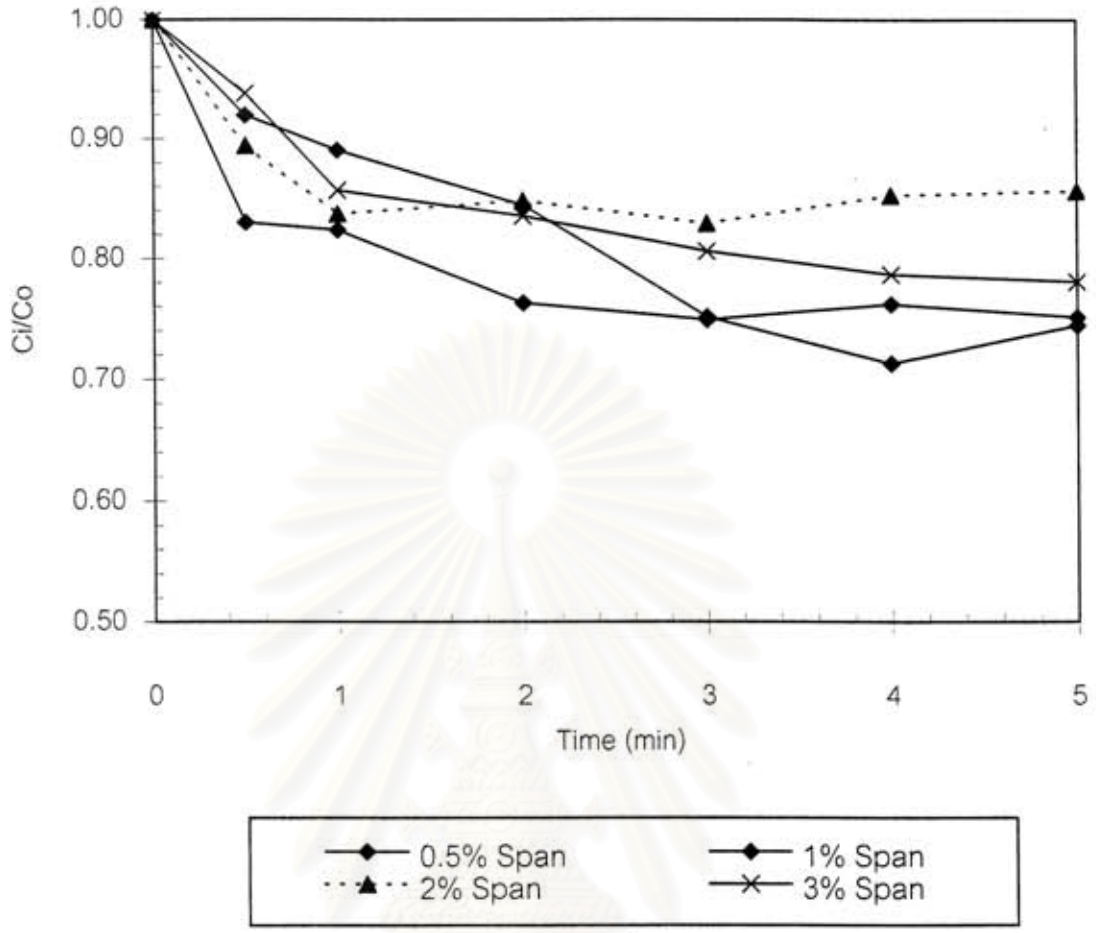


Figure 5.7 Effect of surfactant concentration on ELM extraction of mother lLiquor at various surfactant concentration

Experimental Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: Span 80 at various concentration and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

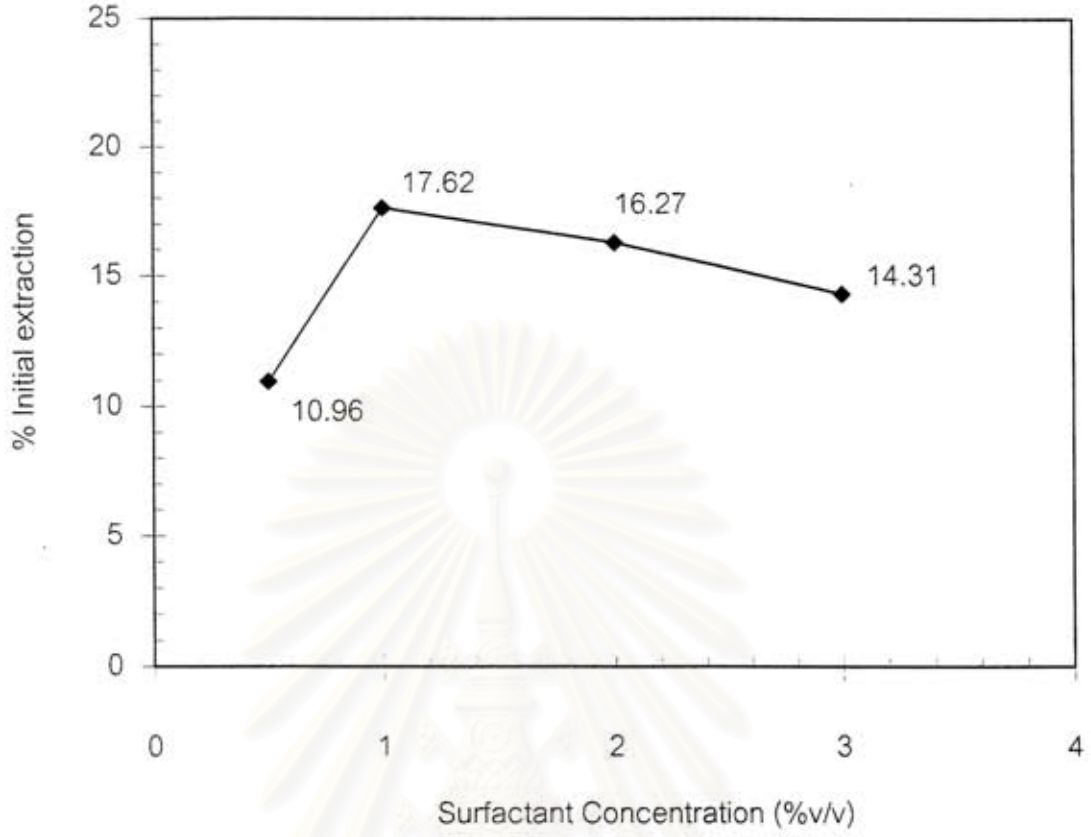


Figure 5.8 % Initial extraction on ELM extraction of mother lLiquor at various surfactant concentration (at first 1 minute)

Experimental Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: Span 80 at various concentration and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

5.5.4 The Effect of Carrier Concentration

The relationship between carrier (D2EHPA) concentration and L-lysine extraction is shown in Figure 5.9. The data are from Table B.10 and B.11 in Appendix B. The experimental conditions operated at room temperature and 420 rpm agitation speed were as follow: mother liquor adjusted pH to 5.0 as external phase; 1% (v/v) of span 80, the D2EHPA concentration within the range 5, 10, 20, and 30% (v/v) of D2EHPA and n-dodecane as membrane phase. The internal phase was 2N HCl solution.

Figure 5.10 show %initial extraction at various carrier concentration (at first 1 minute). It was found that, from 5 % to 10% of the D2EHPA concentration was increased, the L-lysine extraction increased rapidly while slowly increasing extractions were observed when the extraction was performed from 10% to 30% of D2EHPA. This implied that solute-carrier complex existed around peripheral emulsion globule, therefore non-complex carrier can not easily react with L-lysine at the external phase-membrane interface. The change of the carrier concentration does not change the final equilibrium condition of the system, but does how fast equilibrium is reached.

The maximum %initial extraction used 10% (v/v) D2EHPA was 17.62. From the result can be conclude that at carrier (D2EHPA) equal to 10% (v/v) is the optimum condition for L-lysine from mother liquor by ELM.

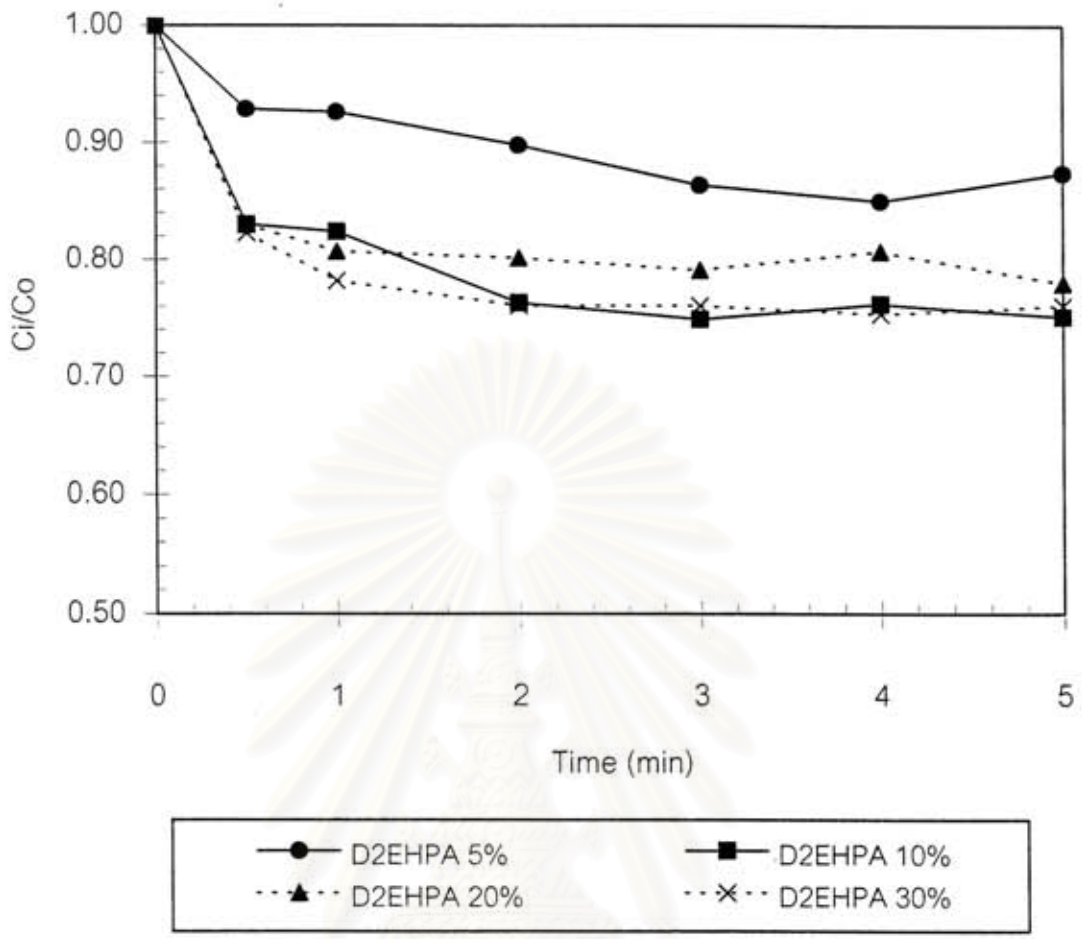


Figure 5.9 Effect of carrier concentration on ELM extraction of mother liquor at various carrier concentration

Experimental Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and D2EHPA at various concentration dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

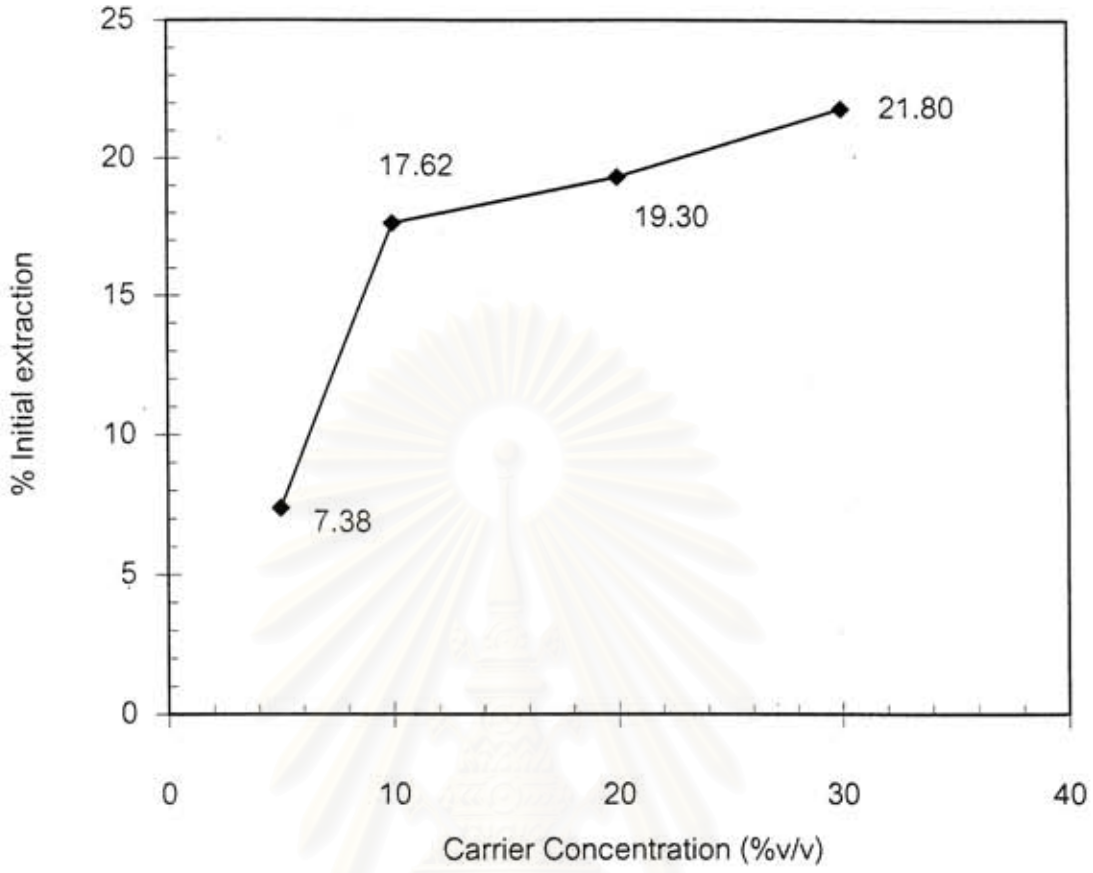


Figure 5.10 % Initial extraction on ELM extraction of mother liquor at various carrier concentration (at first 1 minute)

Experimental Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and D2EHPA at various concentration dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

5.5.5 The Effect of W-O Phase and External Phase Volume Ratio

These experiments used to investigate whether more emulsion volume could extract more L-lysine. The relationship between w-o phase and external phase volume ratio and L-lysine extraction is shown in Figure 5.11. The data are from Table B.13 and B.14 in Appendix B. The experimental conditions operated at room temperature and 420 rpm agitation speed were as follow: mother liquor adjusted pH to 5.0 as external phase; 1% (v/v) of span 80, 10% (v/v) of D2EHPA concentration and n-dodecane as membrane phase. The internal phase was 2N HCl solution. W-O phase and external phase volume ratio was varied within the range 1 : 0.5, 1 : 1, and 1 : 2. From the observation there was phase inversion for volume ratio 1:0.5 as shown in Figure 5.12B which create the adhesion between external phase emulsion and internal phase emulsion (Figure 5.12C) and finally (Figure 5.12D and 5.12E) coalesce into one aqueous phase. This phenomena was prove by measuring the external phase volume as shown in Figure 5.13 and we found that, at volume ratio of 1 : 0.5, external phase volume increased rapidly.

From the result can be conclude that at w-o phase and external phase volume ratio equal to 1 : 2 is the optimum condition for L-lysine from mother liquor by ELM.

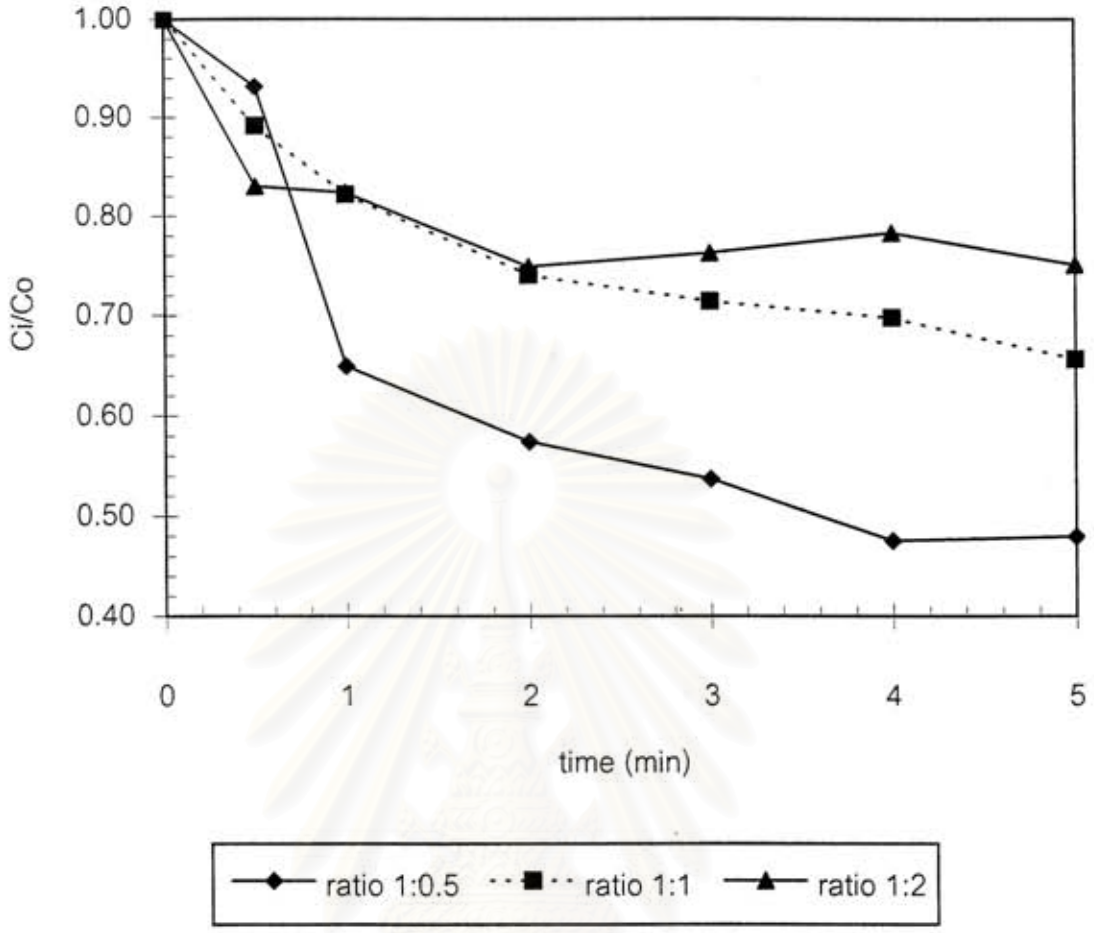


Figure 5.11 Effect of W-O phase and external phase volume ratio on ELM extraction of mother liquor at various volume ratio

Experimental Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: at various Volume ratio
Agitation speed	: 420 rpm
Temperature	: room temperature

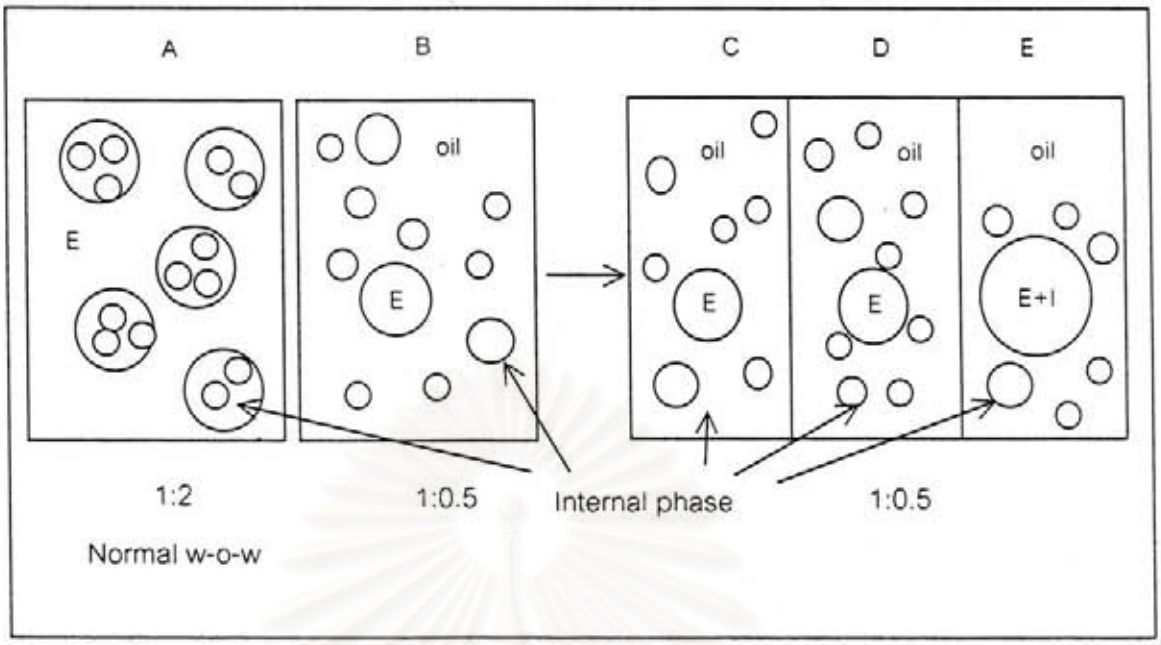


Figure 5.12 Schematic of phase inversion and coalesce of aqueous emulsion at volume ratio1:0.5

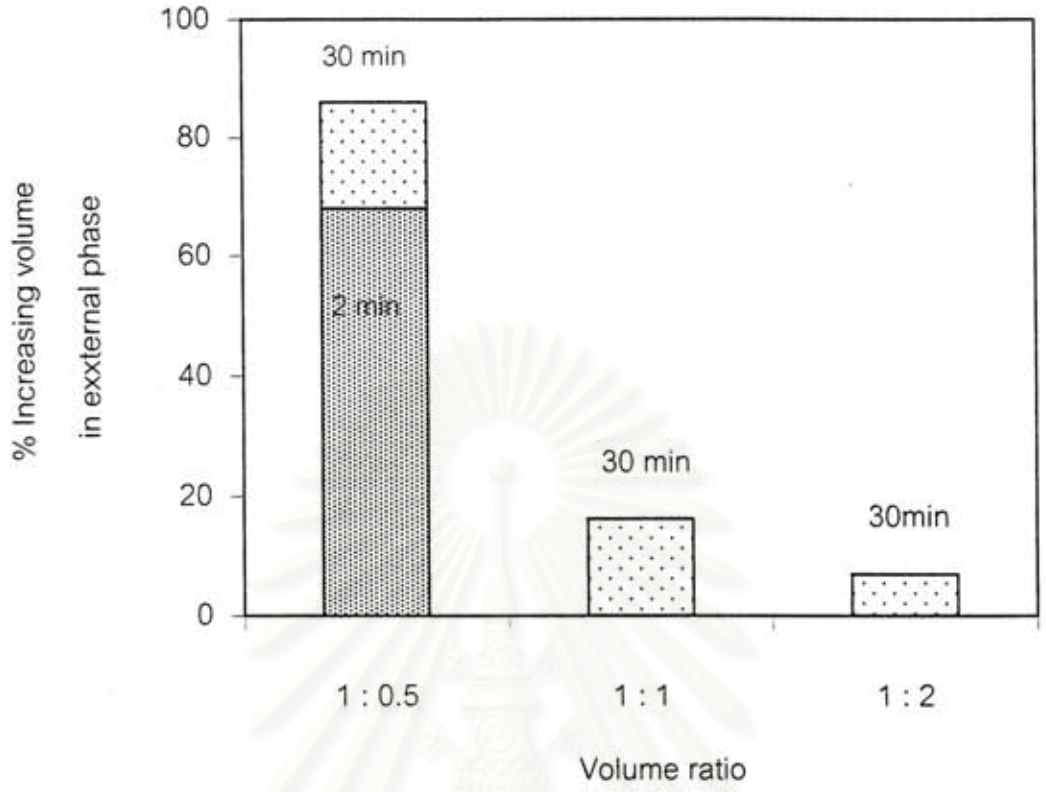


Figure 5.13 % Increasing volume in external phase measured after 2 and 30 minutes at various W-O phase and external phase volume ratio

Experimental Conditions

External phase	: Mother liquor
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: at various Volume ratio
Agitation speed	: 420 rpm
Temperature	: room temperature

5.5.6 The Effect of Mother Liquor Characteristic

The relationship between mother liquor characteristic and L-lysine extraction is shown in Figure 5.14. The data are from Table B.16 and B.17 in Appendix B. The experimental conditions operated at room temperature and 420 rpm agitation speed were as follow: mother liquor at various characteristic adjusted pH to 5.0 as external phase; 1% (v/v) of span 80, 10% (v/v) of D2EHPA concentration and n-dodecane as membrane phase. The internal phase was 2N HCl solution.

Figure 5.15 show %initial extraction at various characteristic of mother liquor (at first 1 minute). Since the content of L-lysine in mother liquor is very large, we used these experiments to prove whether in the presence of L-lysine crystals had effected on L-lysine extraction or not. It was found that, % initial extractions are 19.46 and 17.62 of filtrated and no-filtrated mother liquor, respectively. The results showed that L-lysine crystals had little effected on % initial extractions L-lysine extraction.

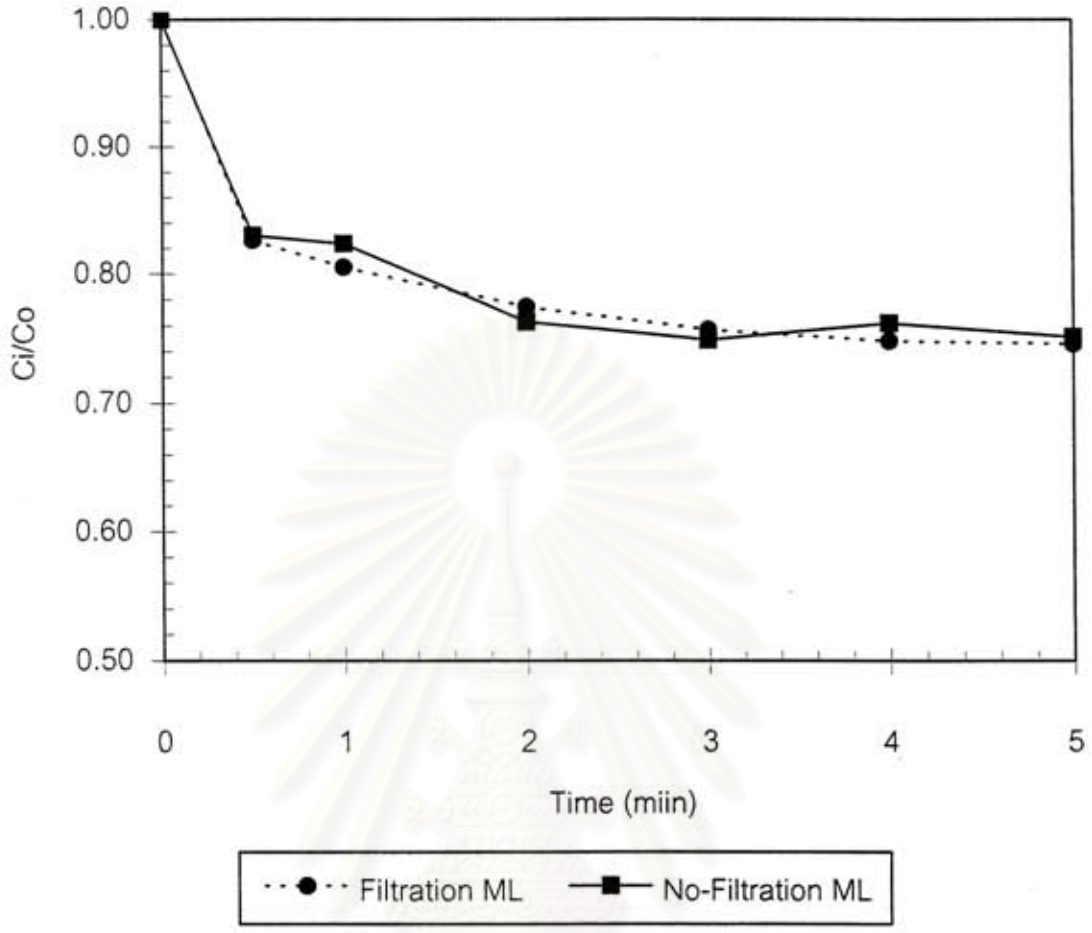


Figure 5.14 Effect of ML characteristic (Filtration or no-filtration) on ELM extraction of mother liquor

Experimental Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

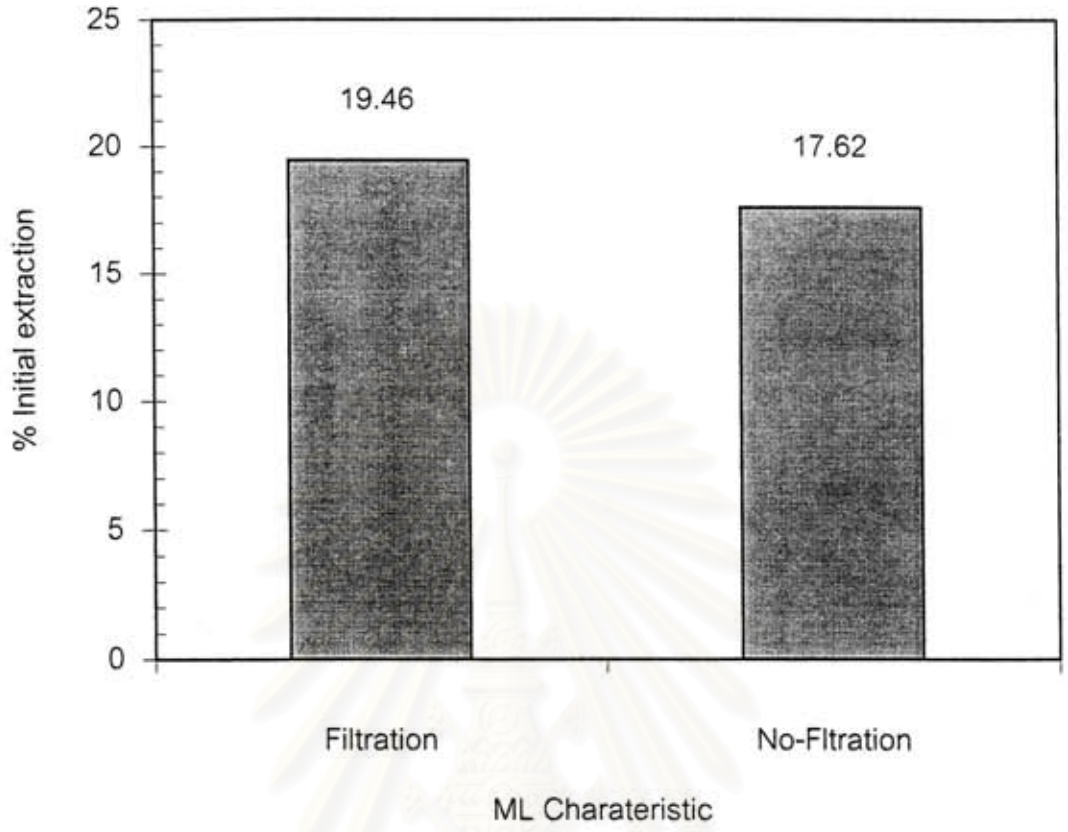


Figure 5.15 % Initial extraction on ELM extraction of mother liquor at various ML characteristic (at first 1 minute)

Experimental Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 420 rpm
Temperature	: room temperature

5.5.7 The Effect of Agitation Speed

The relationship between agitation speed and L-lysine extraction is shown in Figure 5.16. The data are from Table B.19 and B.20 in Appendix B. The experimental conditions operated at room temperature were as follow: mother liquor adjusted pH to 5.0 as external phase; 1% (v/v) of span 80, 10% (v/v) of D2EHPA concentration and n-dodecane as membrane phase. The internal phase was 2N HCl solution. Agitation speed used in these experiments was varied within the range 300, 360, 420, and 480 rpm.

Figure 5.17 show %initial extraction at various agitation speed (at first 1 minute). It was found that, as the agitation speed increased the mass transfer coefficient of the external phase film and the surface area of the emulsion globules increased resulting to increase %initial extraction. Although, we can observe that at higher speed, shear force will induce the breakage of emulsion.

The maximum %initial extraction used 360 rpm was 20.04. From the result can be conclude that at agitation speed equal to 360 rpm is the optimum condition for L-lysine from mother liquor by ELM.

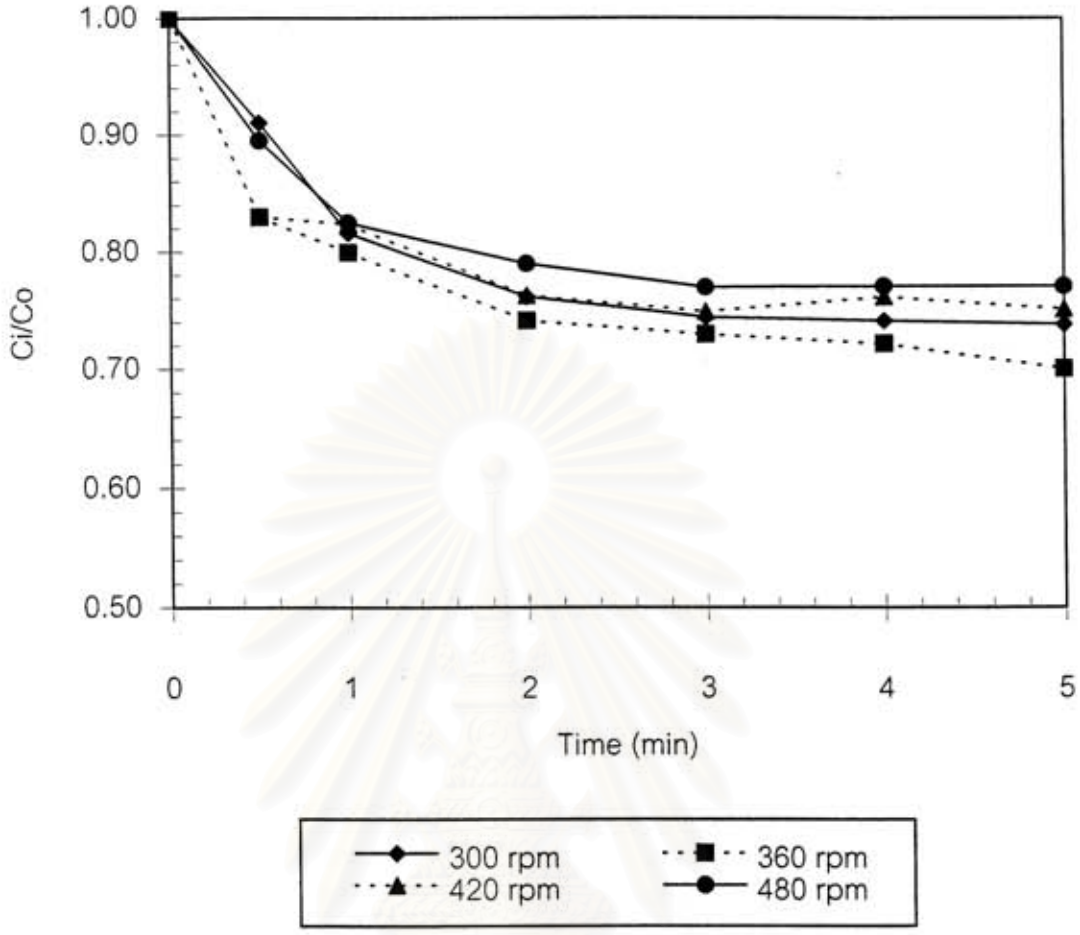


Figure 5.16 Effect of agitiation speed on ELM extraction of mother liquor at various agitation speed

<u>Experimental Conditions</u>

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: agitated at various speed
Temperature	: room temperature

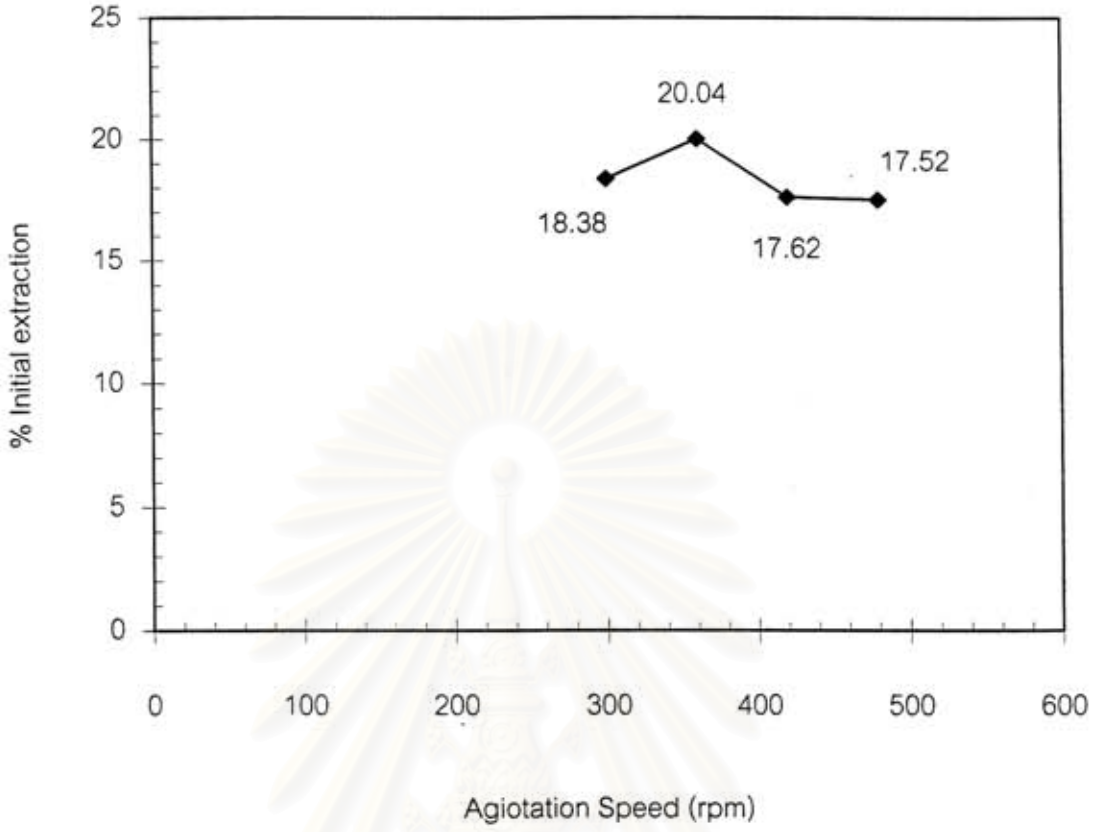


Figure 5.17 % Initial extraction on ELM extraction of mother liquor at various agitation speed (at first 1 min)

Experimental Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: agitated at various speed
Temperature	: room temperature

5.5.8 The Effect of Source of L-lysine

The relationship of source of L-lysine (L-lysine from synthetic solution with from mother liquor) at the same concentration and L-lysine extraction is shown in Figure 5.18. The data are from Table B.22 and B.23 in Appendix B. The experimental conditions operated at room temperature and 360 rpm agitation speed were as follow: synthetic L-lysine and mother liquor at adjusted pH to 5.0 as external phase; 1% (v/v) of span 80, 10% (v/v) of D2EHPA concentration and n-dodecane as membrane phase. The internal phase was 2N HCl solution. This experiment, we want to know whether the impurities in mother liquor are capable to obstruct much or less L-lysine permeation.

Figure 5.19 shows the comparison of %initial extraction of L-lysine from synthetic solution with from mother liquor (at first 1 minute). It was found that, % initial extraction of synthetic solution is slightly higher than mother liquor.

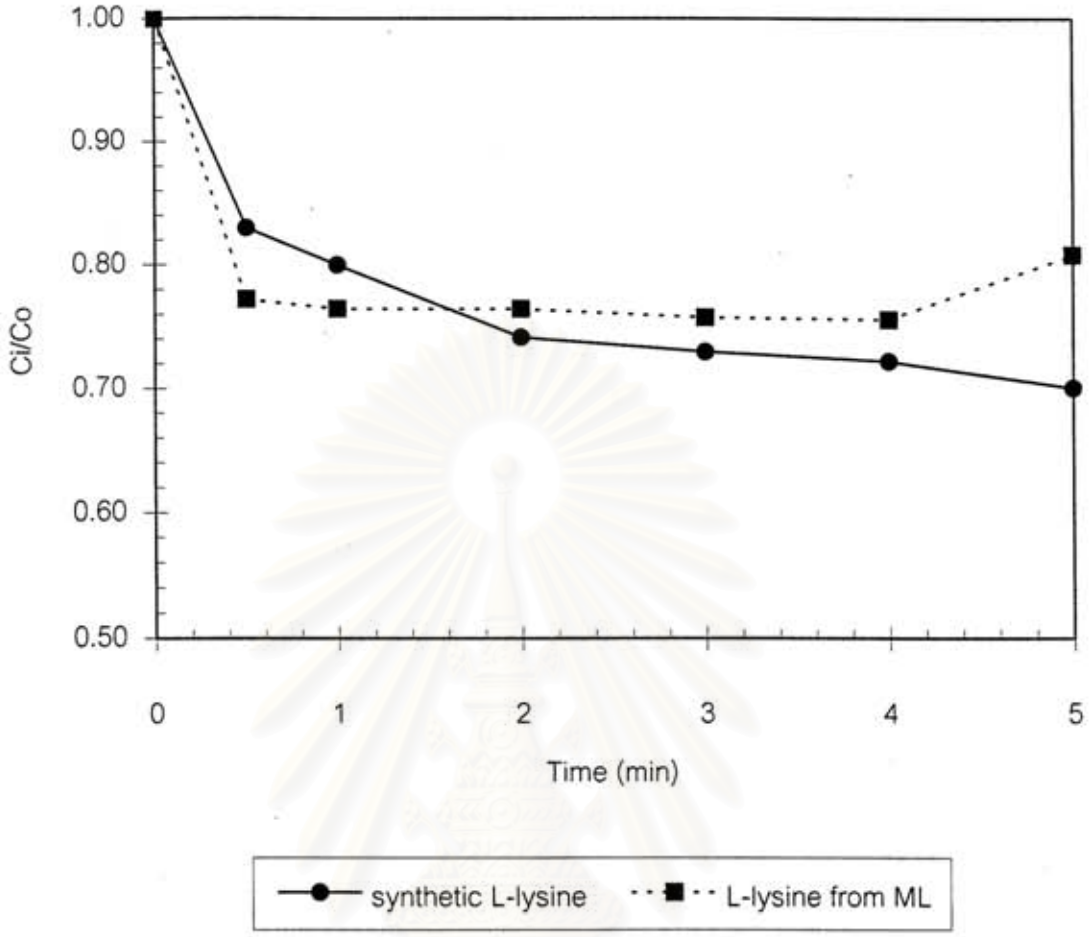


Figure 5.18 Effect of source of L-lysine on ELM extraction of L-lysine at various source of L-lysine

Experimental Conditions

External phase	:	Conc L-lysine at various source adjusted to pH 5.0 with H_2SO_4
Membrane phase	:	1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	:	2N HCl
Membrane preparation	:	at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	:	1 : 2
Agitation speed	:	360 rpm
Temperature	:	room temperature

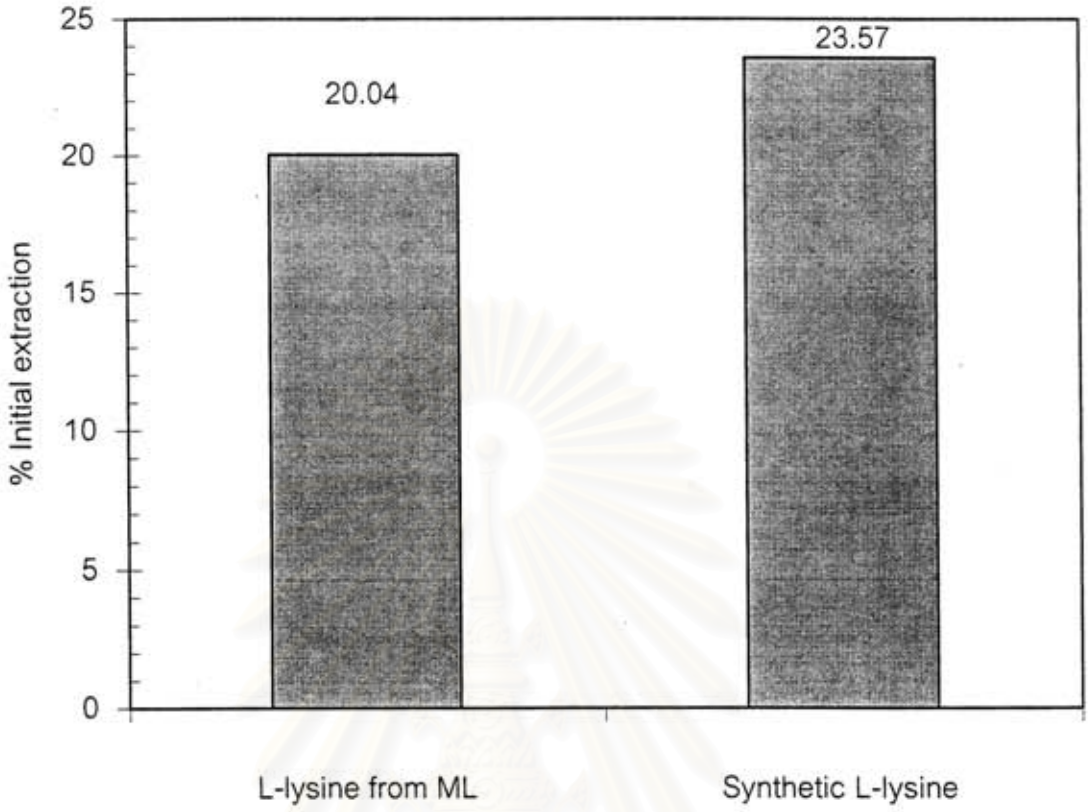


Figure 5.19 % Initial extraction on ELM extraction of L-lysine at various source of L-lysine (at first 1 minute)

Experimental Conditions

External phase	: Conc L-lysine at various source adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 360 rpm
Temperature	: room temperature

5.6 Possibility of Multicycle Extraction to Enhance L-lysine Recovery

As the results of these experiments, the optimum for L-lysine extraction from mother liquor by emulsion liquid membrane process as follows: initial pH in external phase was 5, membrane phase consisted of 1% span 80 and 10% D2EHPA dissolved in n-dodecane, HCl concentration in internal phase is 2N, w-o phase : external phase volume ratio was 1 : 2, and agitation speed was 360 rpm. Because we used mother liquor with high L-lysine concentration as external phase, K_{ex} of L-lysine in mother liquor was small (as mentioned in chapter 4). Therefore, %initial extraction of L-lysine by these conditions at 1 minute was low, 20.04.

From the optimum condition operation, the experimental results such as fraction of recovery after 5 minutes and pH were reported in Figure 5.20. After 5 minutes of extraction in the first cycle, the aqueous external phase, which has pH about 2, was separated from the emulsion. The pH of aqueous solution was adjusted again with 1N NaOH to pH 5.0 . Then the second extraction cycle was carried out by ELM. As can be seen in Figure 5.21, The pH in external phase was not decreased, that means there was no counter ion exchange between H^+ in internal phase and Lys^+ in external phase. This behavior can be explained, that the stability of w-o emulsion may be destroyed by NaOH. (Hirato et al., 1990)

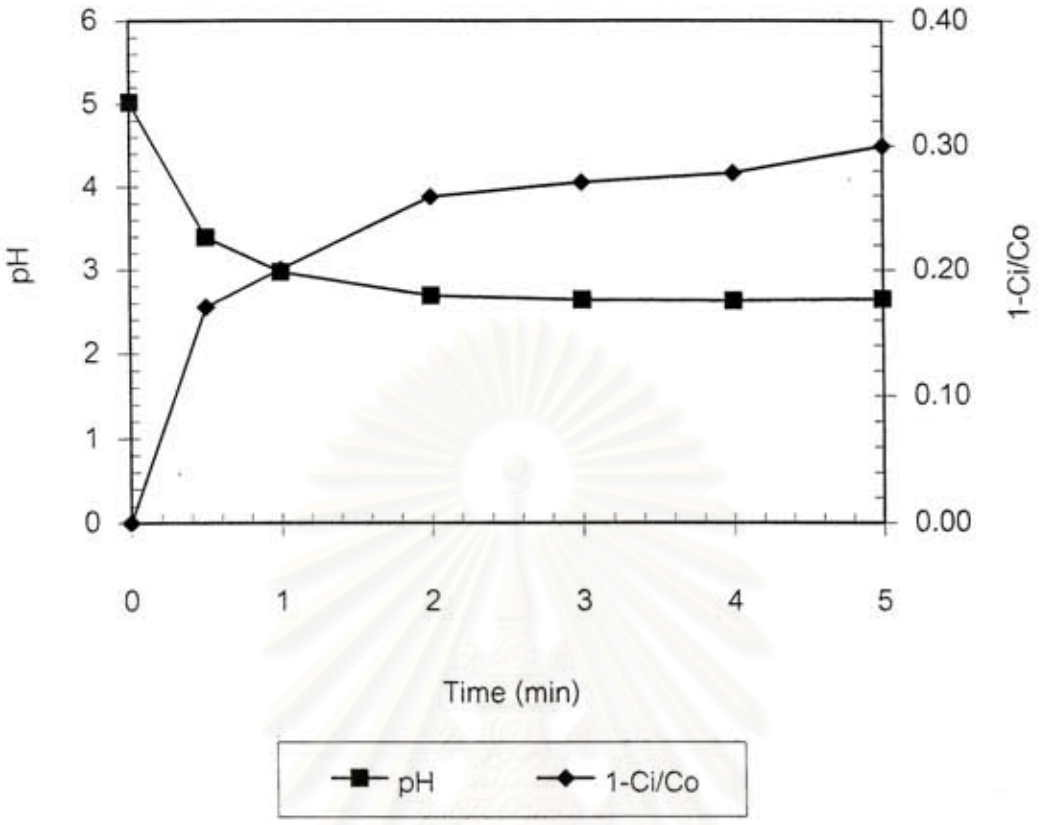


Figure 5.20 Time course of 1-Ci/Co and pH of the optimum conditions for L-lysine extraction by Emulsion Liquid Membrane

Optimum Conditions

External phase	: Mother liquor adjusted to pH 5.0 with H_2SO_4
Membrane phase	: 1% Span 80 and 10% D2EHPA dissolved in n-Dodecane (v/v)
Internal phase	: 2N HCl
Membrane preparation	: at 8000 rpm of homogenizing speed for 10 minutes
W-O Phase : external phase ratio	: 1 : 2
Agitation speed	: 360 rpm
Temperature	: room temperature

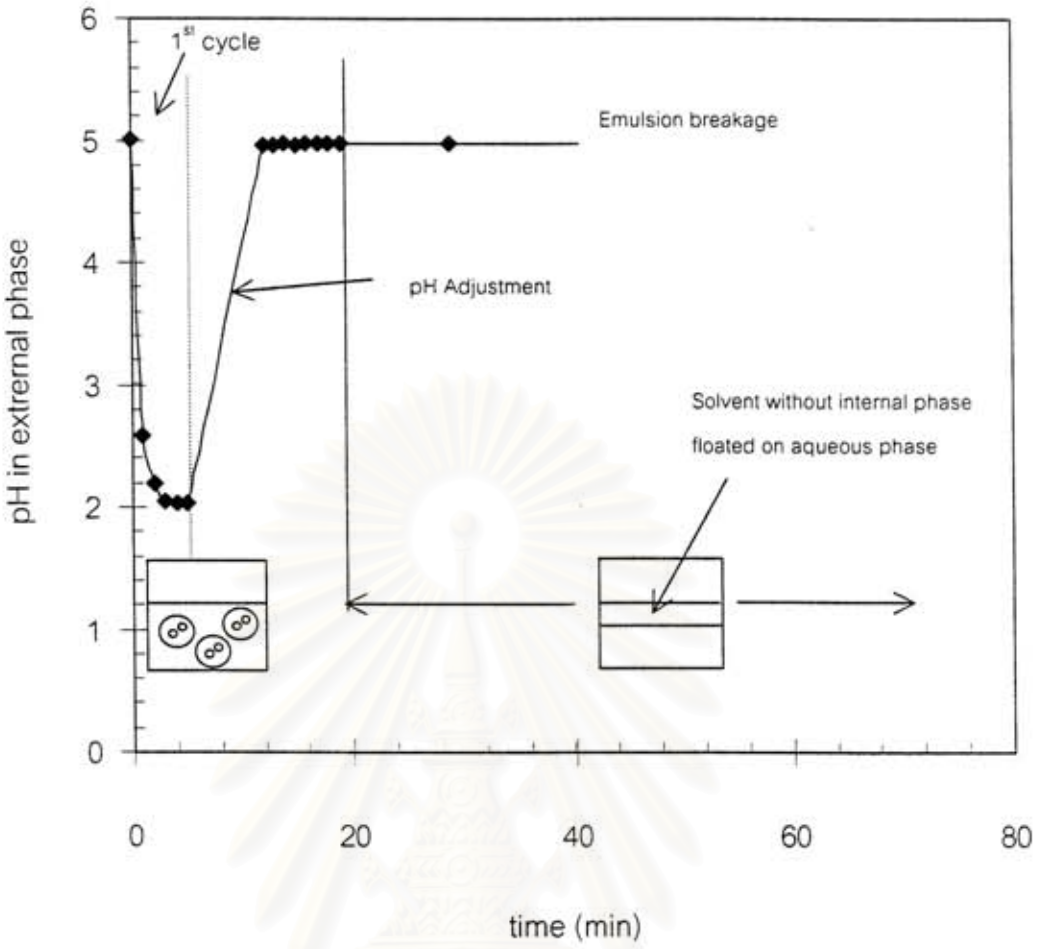


Figure 5.21 pH in External phase after adjusted pH to 5.0 with 1N NaOH

CHAPTER 6

TRANSPORT MECHANISM

6.1 Mass Transfer Model

This chapter describes the theory about batch extraction with emulsion liquid membranes. The theory of batch extraction may be classified into categories: (1) diffusion-type mass transfer models for Type 1 Facilitation and (2) carrier facilitated transport models for Type 2 facilitatation (Larbach and Marr 1987).

Transport mechanism in ELM systems have been proposed in the literature to explain and predict the rate of L-lysine transfer and the effect of operating parameters on this rate. The following assumptions of ELM models are:

1. Mass transfer resistance is negligible because the phases on either side of the membrane are well mixed.
2. The membrane phase is stagnant.
3. The system is at steady state.
4. The diffusion coefficient in the membrane phase is constant
5. Chemical equilibrium exists at both interfaces (interface between external phase and membrane phase and interface between membrane phase and internal phase).

In this experiment, we studied batch extraction of L-lysine in mother liquor with ELM by carrier facilitated transport for Type Counter Transport. Therefore, the carrier facilitated transport will be briefly described.

6.2 Literature Review on Transport Mechanism Models

In this type, a "carrier" compound incorporate in the membrane phase carries the solute across the membrane phase. Reactions involving the carrier and the solute take place both at the external interface between the external and the membrane phases and internal interface between the membrane and internal phases. The reactions at the external and internal interfaces are ion exchange between ion of solute and protons, and a high

extraction rate is achieved via driving force of continuous transport of protons from the internal phase to the external phase. A concentrated acid in the internal phase allows the ion of solute to be concentrated effectively in this phase, resulting in a high extraction capacity. The driving force of proton transport "pumps" the transport of the ion of solute against its own concentration gradient between the internal and external phases. Literature review on proposed model for ELM as follow:

Matulevicius and Li (1975) proposed hollow sphere model and assumed the emulsion globules are perfectly mixed. This implied that the internal phase droplets are freely mobile, and the internal phase concentration is everywhere equal to its average value. Solute mass transfer is thus envisaged to take place across the film of membrane phase of constant thickness to a well-mixed internal pool of internal phase. However, there is evidence that the emulsion globules are not well mixed in the time scales encountered and that the effect diffusion distance changes with time. This concept is expressed in Figure 6.1.

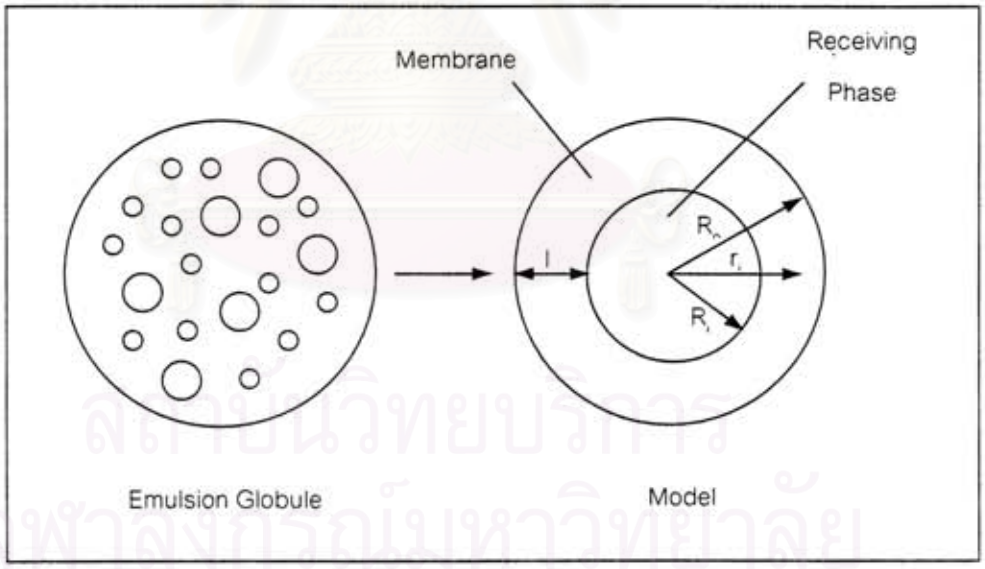


Figure 6.1 Simplified model of an emulsion globule

Martin and Davies (1977) assumed the water-in-oil (w-o) emulsion drop to be a hollow sphere in their models, where all the internal water droplets within the drop have

coalesced into single droplet, and the mass transfer process consists of diffusion across a hollow spherical oil membrane. They thus oversimplified the composite structure of the emulsion drop.

Ho et al. (1982) has developed the advancing front model for a spherical geometry, as shown in Figure 6.2. It is assumed that all emulsion globules in the system are uniform in size, and that mass transfer without the globules is assumed to be negligible because the external phase is well stirred. The emulsion itself can be treated as a continuum and the encapsulated internal reagent is considered to be a uniformly distributed and immobile species within the continuum. Interfacial chemical reactions are considered to be as equilibrium. Hence the solute is unable to permeate into the globule beyond those droplets that are completely depleted of reagent. Thus there must exist a sharp boundary, or reaction front, at which the reaction takes place, and which contains no reagent. As the reagent is consumed by the reaction, this reaction front advances into the globule. External phase mass transfer resistance is assumed to be negligible, owing to the sufficient agitation of this phase. The advancing front model of Ho depend on two dimensionless parameter, ε and E. Physically, E is three time the original mole ratio of internal reagent to bulk solute. For long time, If E/3 is greater than 1, there is sufficient reagent to completely remove the solute and no equilibrium is established. The second dimensionless group, ε, measures the globule capacity for unreacted solute relative to the reaction capacity provided by the reagent. The value of ε is generally much less than 1. A notable feature of the advancing front theory is its algebraic solution permitting easy calculation. One limitation of this approach is the assumption of reaction irreversibility, which, when combined with instantaneous kinetically zero in the reacted region. This situation is asymptotically achieved only for a large equilibrium constant and large solute concentration.

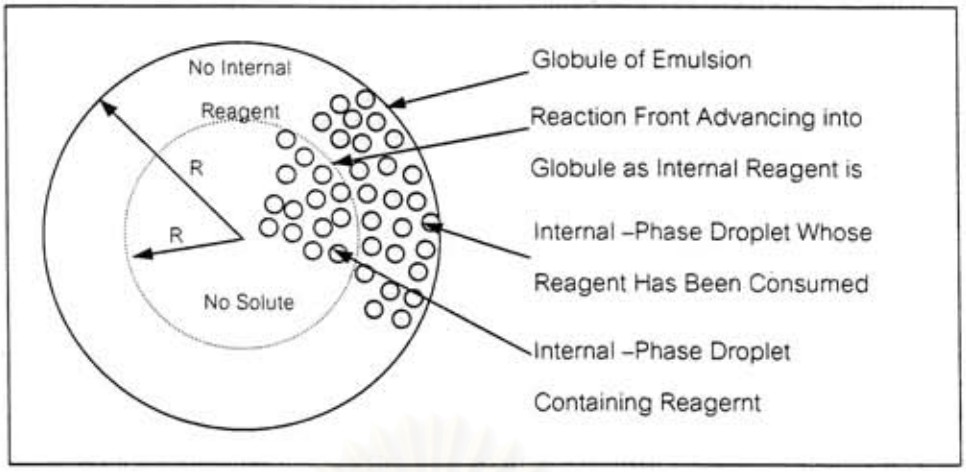


Figure 6.2 Schematic Diagram of the Advancing-Front Model

Gu et al. (1983) developed a model of diffusion-controlled mass transfer in liquid surfactant membrane for fast chemical reaction. This model takes into account the diffusion both across the outer surfactant layer and through the inner core of the emulsion globules. Their results indicate that the thin layer of surfactant existing at the interface between emulsion globules and continuous aqueous phase offers the predominant barrier to mass transfer in a liquid surfactant membrane system.

Teramoto et al. (1983) proposed models that take into account the composite nature of the emulsion drop and the resistance of the interfacial reaction. However, they fixed such parameters as the effective diffusivity in the emulsion phase and the mass transfer coefficient in the peripheral thin oil layer, required by the models, so that the model predictions might fit the experimental data.

Chan and Lee (1984) reviewed the various models. The simplest representation characterized the emulsion globule (Membrane phase) as a spherical shell of constant thickness surrounding a single phase droplet. This representation is equivalent to assuming that the membrane and internal phase are welled mixed. In practice, this is usually a poor assumption. The spherical-shell approach is mathematically simple but fails to provide accurate results for many systems of interest. Properties such as diffusion coefficients and permeabilities estimated with the spherical-shell approach will vary with extraction. When reaction occurs in the internal phase, one use of this approach is to assume that the solute diffuses through the globule to a reaction front where it is removed instantaneously and

irreversibly by reaction with an internal reagent. A reaction front is formed and proceeds toward the center as the reaction proceeds.

Lee and Ihm (1985) simulated the permeation of chromium ion by the advancing front model. This assume that the internal droplets are homogeneously dispersed and immobilized in the emulsion drop, and that between the outer region saturated with chromium and the inner saturated region there exists a reaction front which advances towards the center of the emulsion drop. The model can be therefore applied only to the case of a reaction between metal-carrier complex and internal reagent that is irreversible and fast.

Ho et al. (1987), Chan and Lee (1987) proposed advancing front model which conceptually the same as the " shrinking-core" model encountered in fluid particle systems (Levenspiel, 1972). The internal phase droplets are assumed to be stationary in the globule (because of the effect of surfactant and membrane phase viscosity): as the solute-reagent reaction proceeds the droplets at the interface become saturated and so the solute has to diffuse further into the emulsion droplet to reach unreacted solute.

Kopp et al. (1987) has assumed that the encapsulated droplets are symmetrically distributed and fixed inside the emulsion globules. They proposed a model to describe the mass transfer process in the emulsion globule for copper extraction in term of a moving boundary at which a reaction between copper complex and the internal reagent occurs. This boundary moves toward the globule center as the internal reagent as consumed.

Chaudhuri at al. (1992) developed model here assumes two transfer mechanism operates in the membrane phase (as seen in Figure 6.4): facilitated solute transport, and convective solute transport as a result of water transport. Transport of the solute from the bulk external phase to the globule is characterized by a mass transfer coefficient, and a shrinking core diffusion model describes the solute transport within the globule. In their development of the kinetic model they have made the following assumptions:

1. The internal phase droplets behave as homogeneously dispersed solute sinks of finite capacity.

2. The internal phase surface area is very large and it is assumed that the stripping reaction occurs at the interface and is very fast so that it does not control the overall transfer mechanism.
3. The internal phase droplets are immobile and so there is no circulation of droplets within the globules.
4. A reaction front is assumed to exist within the emulsion globule, which separates an unreacted reagent core from droplets containing the reaction products.
5. The effect of coalescence and/or breaking of the droplets or globules are ignored, despite swelling.
6. The solute is not very soluble in the membrane phase so that the extraction by unfacilitated transport is negligible in comparison to facilitated and convective transport.

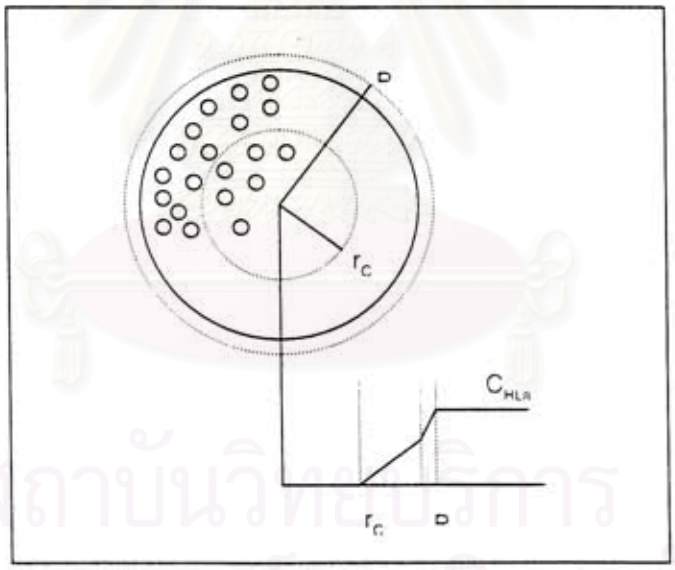


Figure 6.3 Shrinking-Core Model and concentration profile of solute transport in an emulsion globule assuming a Two Film Model.

6.3 Transport Mechanism of L-lysine in Mother Liquor

In this study, model is presented for facilitated extraction of L-lysine by emulsion liquid membrane system, using the two-film theory. There are two mass transfer resistances for ELM extraction. One is the resistance to the transfer of L-lysine from the bulk of the external phase to the emulsion globule interface (External resistance), the second is the resistance to L-lysine diffusion through the globule to the reaction front (Membrane phase resistance). In this system the factor controlling the L-lysine yield and selectivity is the distribution (Partition) coefficient of the Lys^{+}. The extraction rate is controlled by the external phase mass transfer coefficient.

Although, Advancing front Model is common used model to describe ELM system, it must exist require many assumptions and unknown parameters to proposed model. Mechanism of mass transfer of amino acid in ELM seems to be very complicated especially on the surface of the membrane. The size of small droplets in globule varies on the agitation condition so, it is impossible to get real diameter every time. Moreover, swelling and breakage of w-o emulsion may be occurred during extraction. Therefore, the most simplest model for these experiment is the Uniform Flat Sheet Model. For these experiment, because of ratio of membrane and internal phase equal to 1 : 1, the membrane phase thickness is assumed to be very small compared to the size of the globule and the radius curvature can be neglected so we can assume planar geometry. Thus this model is similar to the supported liquid membrane as seen in Figure 6.5.

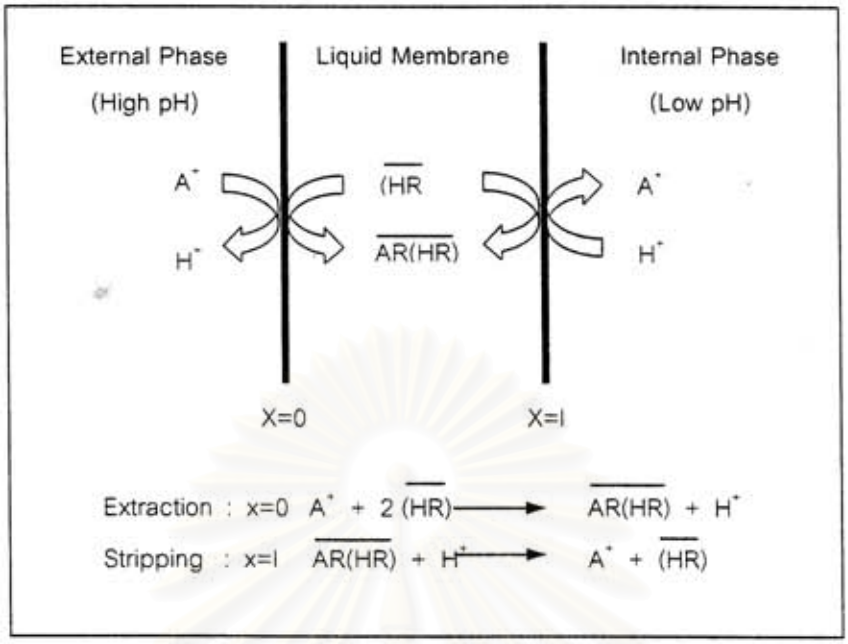


Figure 6.4 Uniform Flat Sheet Model for Amino Acid Permeation (Noppaporn, 1994)

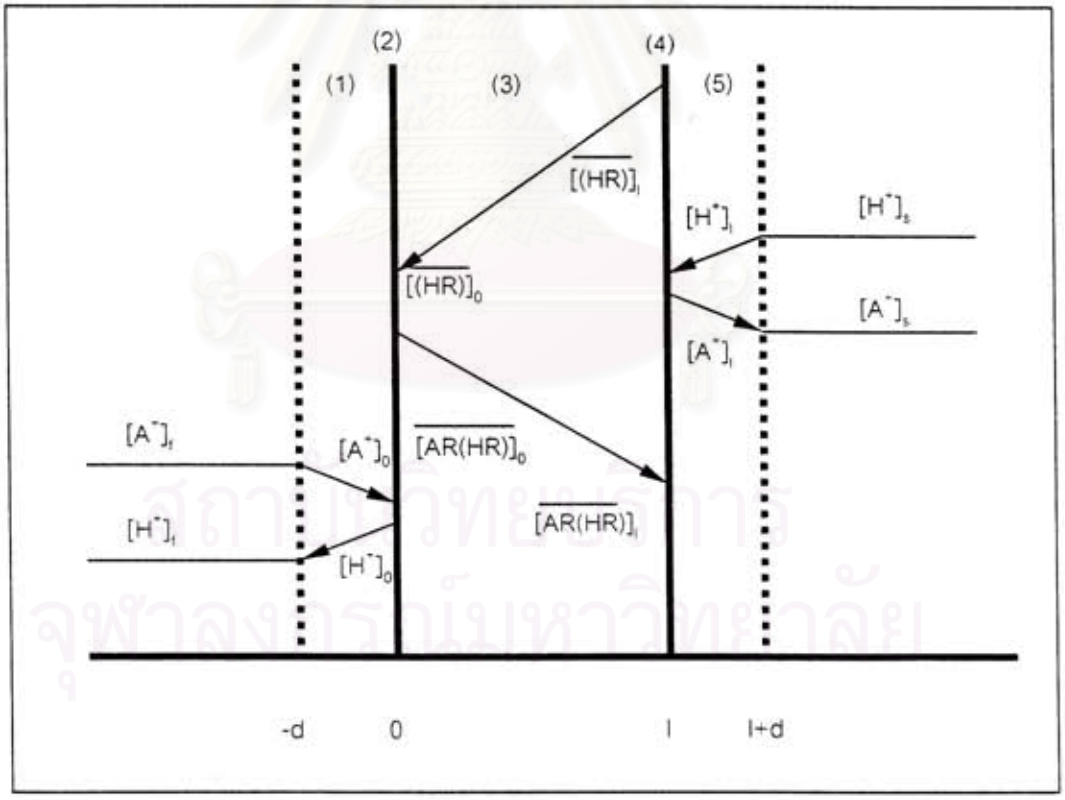


Figure 6.5 Schematic Concentration Profile of L-lysine Permeation

From equilibrium extraction of L-lysine from mother liquor in Chapter 4, Eqs (6.1) can be obtained:

$$A^- + 2\,\overline{(HR)} \longleftrightarrow \overline{AR(HR)} + H^- \qquad (6.1)$$

The flux of L-lysine from the bulk of external phase to the interface with the membrane phase is given by

$$J_{A,f} = \frac{(D_{A,f})}{\delta}(\overline{[A^+]}_f - [A^+]_0)$$

$$J_{A,f} = k_{A,f}(\overline{[A^+]}_f - \overline{[A^+]}_0) \qquad (6.2)$$

Where $k_{A,f}$ is the external phase mass transfer coefficient, $[A^-]_f$ is L-lysine concentration in the bulk of the external phase, and $[A^-]_0$ is the concentration on the external phase side of the external and membrane phase interface. It is assumed that the organic and aqueous are immissible and that the D2EHPA is insoluble in the aqueous phase. It is suggested that L-lysine react with D2EHPA at the interface between external phase and membrane phase as follow:

$$R_1 = k_1([A^+]_0\overline{[(HR)]}_0^2) - k_{-1}(\overline{[A^+]}_0[H^+]_0) \qquad (6.3)$$

We consider diffusion of L-lysine-D2EHPA complex through the membrane phase and the flux of the complex in the membrane phase is given by:

$$J_C = \frac{D_C}{\tau l}(\overline{[A^+]}_0 - \overline{[A^+]}_l) \qquad (6.4)$$

Where D_c is diffusivity of L-lysine-D2EHPA complex, AR(HR), τ is membrane constant, l is thickness of the membrane, and $[A^-]_l$ is the concentration on the internal phase side of the membrane – internal phase interface. This L-lysine-D2EHPA complex then diffuses through the membrane toward the interface X=l, where amino acid ion is stripped

back to the stripping solution. The reaction of L-lysine-D2EHPA complex and H^+ in stripping phase tack place as Eqs (6.5).

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

Where k_1, k_{-1} are interfacial reaction constant, $\overline{(HR)}$ is monomeric form of D2EHPA in the membrane phase and $[H^+]$ is hydrogen ion concentration. Then L-lysine permeated in the internal phase as follows:

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

$$J_{A,f} = k_{A,S}([A^+]_l - [A^+]_S) \qquad (6.6)$$

Where $k_{A,s}$ is the internal phase mass transfer coefficient, $[A^+]_s$ is L-lysine concentration in the internal phase, δ is thickness of the aqueous film.

When quasi-steady state the is reached,

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

Combining above equation (6.2) to (6.6), the following equation, permeation flux of L-lysine can be derived.

$$J_c = \frac{D_c}{\tau l}\left\{\frac{[A^+]_0}{k_{-1}[H^+]}\left(k_1\overline{[(HR)]_0^2} + k_{A,f}\right) - \frac{k_{A,f}[A^+]_f}{k_{-1}[H^+]_0} - \frac{[A^+]_l}{k_{-1}[H^+]_l}\left(k_{A,S} + k_1\overline{[(HR)]_l^2}\right) + \frac{k_{A,f}[A^+]_S}{k_{-1}[H^+]_l}\right\}$$

Addition assumption for this equation as follows:

a) All species have an equal diffusivity in the membrane, therefore, $k_{A,f}$ equal to $k_{A,s}$.

b) D2EHPA and the L-lysine-D2EHPA complex are soluble only in the liquid membrane.

c) There are no external and internal resistance, therefore, $[A^-]_0$ equal to $[A^-]_f$ and $[A^-]_i$ equal to $[A^-]_s$.

d) At initial state, $[A^-]_s$ assume to be zero.

e) Equiliqrium constant $(K_{ex}) = \frac{k_1}{k_{-1}}$

Therefore, this equation can be obtained:

$$J = \frac{K_{ex} D_c}{\tau l} \left(\frac{[A^+]_f [\overline{(HR)}]_i^2}{[H^+]_0} \right) \qquad (6.7)$$

Therefore, from Eqs (6.7), the permeation flux multiplied by total area of single internal spherical droplet will be equal to permeation rate.

6.4 Example of Permeation Rate Calculation

According to Eqs (6.7), the permeation rate at the initial state can be calculated as follows:

6.4.1 Calculation of Membrane Thickness

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

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

a) Diameter of Inner Sphere (D_i)

Volume of inner sphere = $0.025 \ dm^3$

$1/6 (\pi D_i^3)$ = $0.025 * 10^{-3} \ m^3$

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

D_i = $0.04 \ m$

b) Diameter of Outer Sphere (D_o)

Volume of outer sphere = 0.05 dm^3

1/6 (πD_i^3) = $0.05 * 10^{-3}$ m^3

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

D_i = 0.0457 m

$$\text{Membrane thickness (l)} = \frac{D_0 - D_i}{2} = \frac{0.0457 - 0.0363}{2} \text{ m}$$

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

6.4.2 Calculation of Permeation Rate from the Model Equation

$$J = \frac{K_{ex} D_c}{\tau l} \left(\frac{[A^+]_f [\overline{(HR)}]_o^2}{[H^+]_0} \right)$$

K_{ex} = $4.7 * 10^{-3}$ m^3/mol (from this study)

$[\overline{(HR)}]$ = 0.30 mol/dm^3 = 303.97 mol/m^3

$[A^*]_f$ at pH 5.02 = 2,301.95 mol/m^3

$[H^*]$ = $9.55 * 10^{-3}$ mol/m^3

l = $4.7 * 10^{-3}$ m

D_c = $7.56 * 10^{-10}$ m^2/s (see Appendix D)

Assumed τ = 1

Therefore,

$$J = \frac{(4.7 \times 10^{-8})(17.65 \times^{-10})}{(1)(4.7 \times 10^{-3})} \left[\frac{(2301.95)(303.97)^2}{(9.55 * 10^{-3})} \right]$$

$$= 1.68 * 10^{-4} \quad mol/(m^2.s)$$

Volume of single internal spherical droplet was 25 ml.

Surface of single internal spherical droplet was $2.50 * 10^{-5}$ m^2.

Therefore,

$$\text{Permeation rate from model} = (1.68 * 10^{-4})(2.50 * 10^{-5}) = 4.22 * 10^{-9} \text{ mol/s}$$

Table 6.1 Calculated and Experimental Value of Initial Permeation Rate of Mother Liquor

$[D2EHPA]_i$ (mol/m^3)	Experimental Results J ($mol/m^2.s$)	Model Equation J ($mol/(m^2.s)$)
0.15	5.06E-06	4.02E-05
0.30	1.15E-05	1.68E-04
0.61	1.20E-05	6.42E-04
0.92	1.25E-05	1.45E-03

It can be seen from Figure 6.6 that carrier concentration has strongly effect on permeation rate of L-lysine from mother liquor because its power is 2. The permeation rate for 5 minutes of L-lysine in mother liquor that given from experiments were also illustrated in Figure 6.7. The results showed the same trend as 1 minute of extraction (Figure 5.10) except at 30% carrier, the permeation rate decreased rapidly due to obstruction of solute-carrier complexes around the peripheral globules.

The comparison of L-lysine permeation rate from experimental results and from the prediction model as illustrated in Figure 6.8 showed large deviation between model and experimental results. The cause of this deviation might become from membrane configuration difference between spherical emulsion (High transfer area) and single internal spherical droplet geometry.

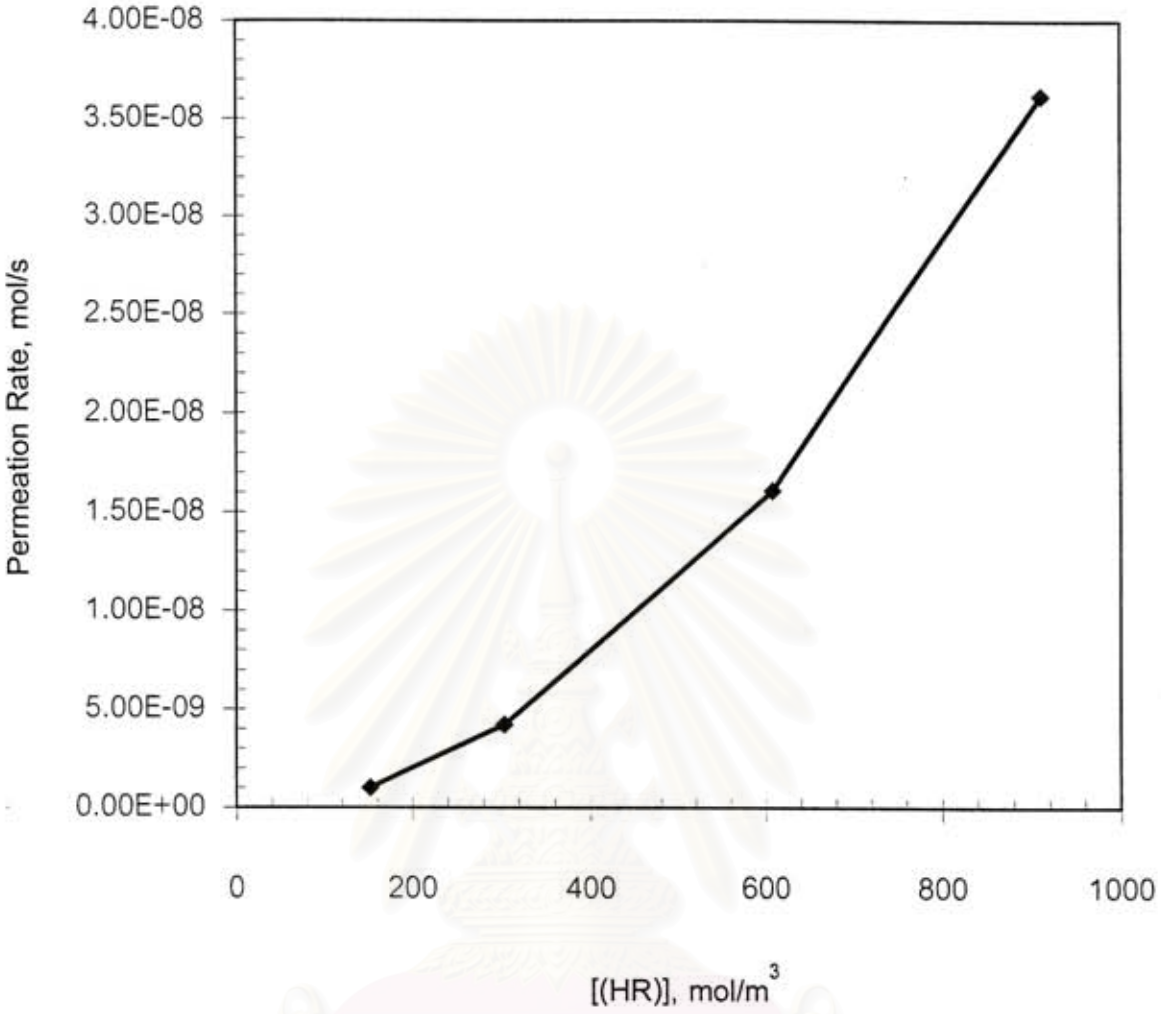


Figure 6.6 Permeation rate calculated from model at variuos carrier Concentration

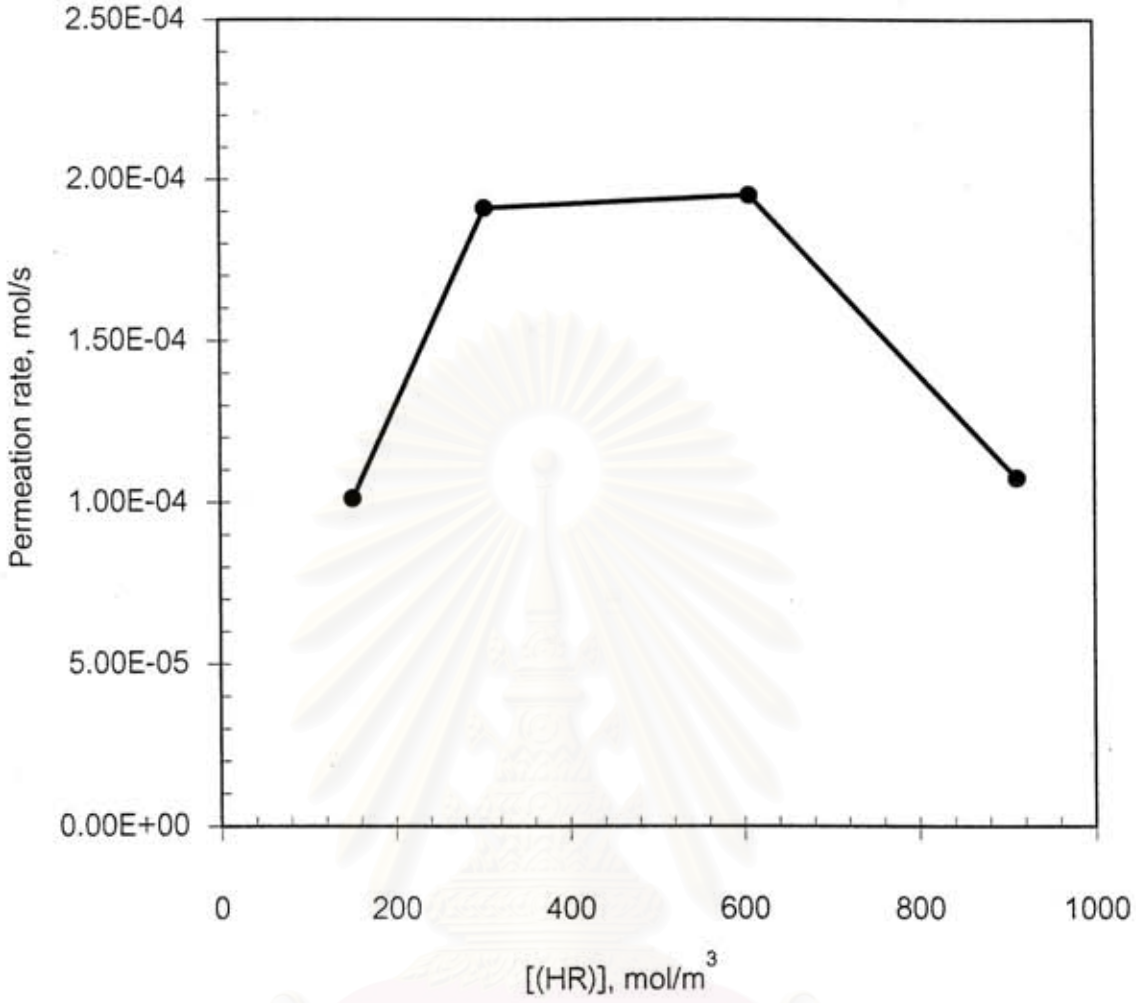


Figure 6.7 Permeation rate from experimental results at various carrier concentration (for 5 minutes)

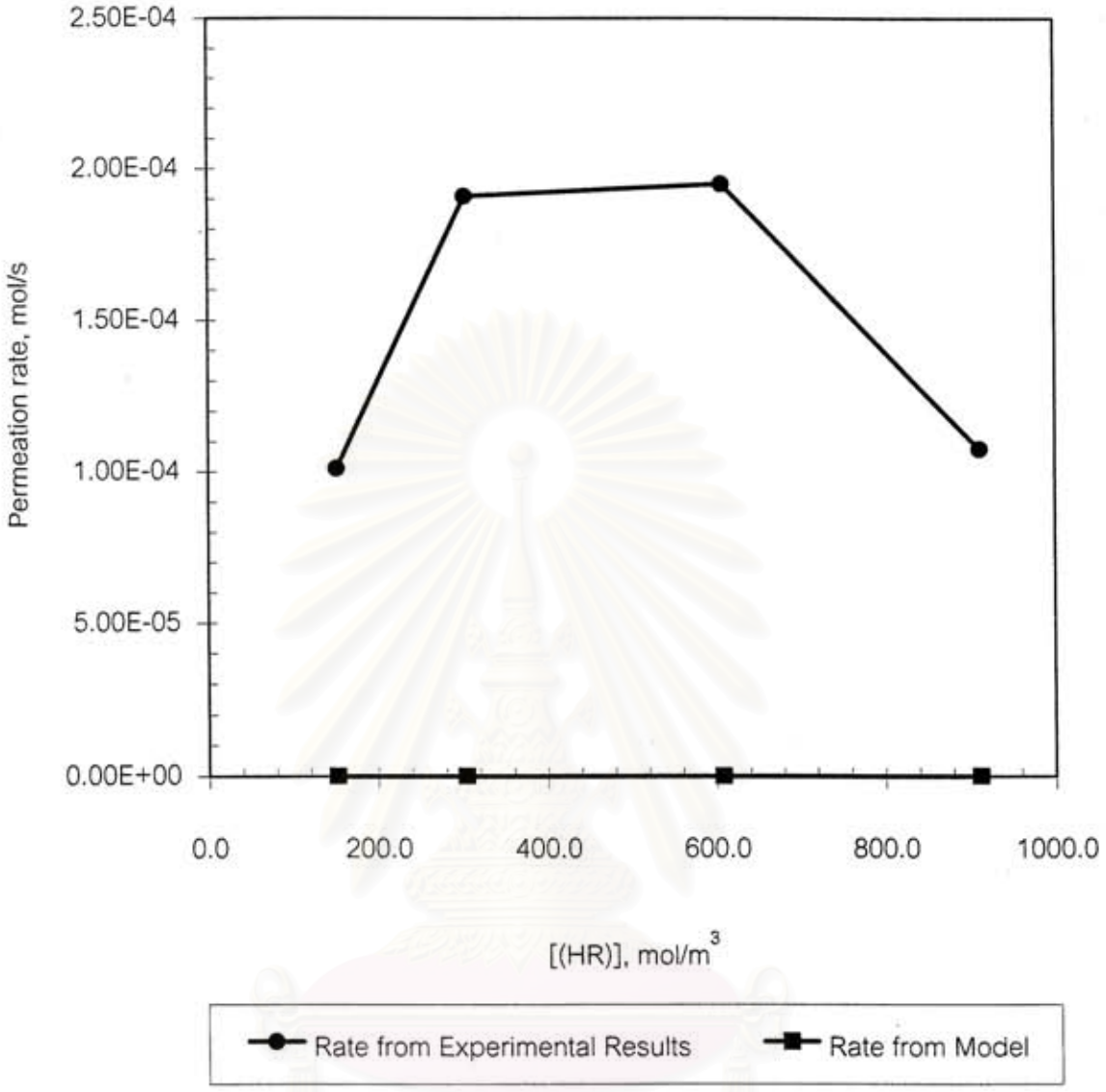


Figure 6.8 Comparison permeation rate from model with from experimental results at various carrier concentration

CHAPTER 7

CONCLUSIONS AND FURTHER STUDY

7.1 Conclusions

The conclusions of the experimental results are following:

1. From the extraction equilibrium experiment of L-lysine in synthetic solution and mother liquor, It was found that the distribution coefficient of synthetic solution higher than of mother liquor due to the presence of impurities in mother liquor and both values vary with the carrier concentration.

2. From the extraction equilibrium study, It was found that the average K_{ex} from the intercept for L-lysine in synthetic solution is 5.26 $x10^{-4}$ dm^3/mol and for L-lysine in mother liquor is 4.72 $x10^{-5}$ dm^3/mol. Both K_{ex} are not varied with carrier concentration.

3. It was found that the 1 mole of Lys^+ (in synthetic solution) reacted with 1.2 mole of monomeric form of D2EHPA and 1 mole of Lys^+ (in mother liquor) reacted with 2 moles of monomeric form of D2EHPA to form complex in the membrane phase.

4. From the experimental results of L-lysine extraction from mother liquor on the emulsion liquid membrane, it was found that the suitable conditions were shown in Table 7.1

Table 7.1 Suitable Conditions for L-lysine Extraction from Mother Liquor on the Emulsion Liquid Membrane Process

Parameters	Suitable Conditions
Initial pH in external phase	pH 5.0
Internal phase concentration (HCl)	2.0 N
Surfactant (Span 80) concentration	1% (v/v)
Carrier (D2EHPA) concentration	10% (v/v)
Agitation speed	360 rpm
W-O phase and external phase volume ratio	1 : 2

At this suitable condition which was operated in single batch extraction within 1 minute, the percentage recovery of L-lysine from mother liquor was about 20%.

5. Re-extraction by adjusting pH to 5.0 was not achieved.

6. By using simple Uniform Flat Sheet Model to predict the influence of carrier concentrations on the permeation rates, high deviations of permeation rates from the experimental data were observed due to the different internal phase geometry.

7.2 Further Study

1. From the batch of emulsion liquid membrane study, the primary conditions could be used for study the continuous extraction of L-lysine from fermentation broth.

2. To give accuracy results, w-o emulsion must be broken to measure L-lysine concentration in internal phase.

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APPENDICES

APPENDIX A

EXTRACTION EQUILIBRIUM CALCULATION

Table A.1 Extraction coefficient calculation data on carrier variable for Synthetic L-Lysine

Initial			Equilibrium							
[D2EHPA] %(v/v)	$[A^*]$ (mol/dm^3)	[(HR)] (mol/dm^3)	pH	$[H^*]$ (mol/dm^3)	$[A^*]$ (mol/dm^3)	$[AR(HR)_{m-1}]$ (mol/dm^3)	[(HR)] (mol/dm^3)	D^*	$D^*[H^*]$	K_{e_1}
5	2.53	0.15	3.46	3.47E-04	2.44	0.09	0.04	3.70E-02	1.28E-05	5.99E-04
10	2.53	0.30	3.18	6.61E-04	2.39	0.13	0.15	5.48E-02	3.62E-05	3.85E-04
20	2.53	0.61	2.87	1.35E-03	2.27	0.25	0.31	1.11E-01	1.50E-04	6.44E-04

Table A.2 Extraction coefficient calculation data on carrier variable for Mother liquor

Initial			Equilibrium							
[D2EHPA] %(v/v)	$[A^*]$ (mol/dm^3)	[(HR)] (mol/dm^3)	pH	$[H^*]$ (mol/dm^3)	$[A^*]$ (mol/dm^3)	$[AR(HR)_{m-1}]$ (mol/dm^3)	[(HR)] (mol/dm^3)	D^*	$D^*[H^*]$	K_{e_1}
5	2.86	0.15	4.15	7.08E-05	2.83	0.02	0.11	7.33E-03	5.19E-07	4.25E-05
10	2.86	0.30	3.83	1.48E-04	2.81	0.04	0.22	1.58E-02	2.34E-06	5.07E-05
20	2.86	0.61	3.34	4.57E-04	2.79	0.06	0.49	2.12E-02	9.71E-06	4.05E-05
30	2.86	0.91	3.01	9.77E-04	2.77	0.08	0.75	2.89E-02	2.82E-05	5.00E-05

APPENDIX B

EXTRACTION EXPERIMENTAL DATA

Part I External Phase pH Variable

Experimental Conditions

W-O emulsion : external phase = 1 : 2

External phase : mother liquor at various pH (adjusted by H_2SO_4)

Membrane phase : 1% span, 10% D2EHPA dissolved in n- dodecane

Internal phase : 2N HCl

Membrane preparation: at homogenizing speed 8000 rpm for 10 minutes

Agitation speed : 420 rpm

Table B.1 Experimental data for extraction L-lysine from mother liquor by ELM at various external phase pH

Time (min)	Ci (g/l)				
	pH 3.0	pH 4.0	pH 5.0	pH 6.0	pH 8.0
0	334.51	334.35	336.52	332.77	332.32
0.5	311.10	304.82	279.37	311.51	307.11
1	311.78	289.00	277.22	286.59	290.94
2	260.70	259.11	256.73	267.89	280.78
3	246.83	286.18	252.06	261.66	262.35
4	259.01	260.87	256.37	258.73	274.01
5	284.04	263.68	252.78	270.82	271.37

Table B.2 Calculation Ci/Co for extraction L-lysine from mother liquor by ELM at various external phase pH

Time (min)	Ci /Co				
	pH 3.0	pH 4.0	pH 5.0	pH 6.0	pH 8.0
0	1.00	1.00	1.00	1.00	1.00
0.5	0.93	0.91	0.83	0.94	0.92
1	0.88	0.86	0.82	0.86	0.88
2	0.74	0.78	0.76	0.81	0.84
3	0.70	0.87	0.75	0.79	0.79
4	0.73	0.80	0.76	0.78	0.82
5	0.80	0.80	0.75	0.81	0.82

Table B.3 Experimental data of pH change for extraction L-lysine from mother liquor by ELM at various external phase pH

Time (min)	pH				
	pH 3.0	pH 4.0	pH 5.0	pH 6.0	pH 8.0
0	2.97	4.02	5.02	6.15	7.98
0.5	2.63	3.04	3.14	3.36	3.91
1	2.47	2.80	2.88	3.01	3.32
2	2.33	2.74	2.80	2.88	3.24
3	2.30	2.74	2.80	2.90	3.23
4	2.30	2.74	2.81	2.90	3.22
5	2.30	2.74	2.81	2.90	3.22

Part II HCl Concentration in Internal Phase Variable

Experimental Conditions

W-O emulsion : external phase = 1 : 2

External phase : mother liquor adjusted pH to 5.0 by H_2SO_4)

Membrane phase : 1% span, 10% D2EHPA dissolved in n- dodecane

Internal phase : HCl at various concentrations

Membrane preparation: at homogenizing speed 8000 rpm for 10 minutes

Agitation speed : 420 rpm

Table B.4 Experimental data for extraction L-lysine from mother liquor by ELM at various HCl concentrations in internal phase

Time	Ci (g/l)			
(min)	1N HCl	2N HCl	4N HCl	6N HCl
0	337.33	336.52	332.32	283.37
1	286.31	277.22	280.98	242.37
2	275.40	252.06	265.38	251.86
3	285.28	256.73	249.03	250.72
4	263.39	263.56	248.27	250.34
5	257.81	252.78	248.27	228.32

Table B.5 Calculation Ci/Co for extraction L-lysine from mother liquor by ELM at various HCl concentrations in internal phase.

Time	Ci/Co			
(min)	1N HCl	2N HCl	4N HCl	6N HCl
0	1.00	1.00	1.00	1.00
1	0.85	0.82	0.85	0.85
2	0.82	0.76	0.20	0.11
3	0.85	0.75	0.25	0.12
4	0.78	0.76	0.25	0.12
5	0.76	0.75	0.25	0.19

Table B.6 Experimental data of pH change for extraction L-lysine from mother liquor by ELM at various HCl concentrations in internal phase

Time	pH			
(min)	1N HCl	2N HCl	4N HCl	6N HCl
0	5.02	5.02	5.02	5.02
1	2.88	3.14	2.88	2.26
2	2.80	2.88	2.80	2.04
3	2.81	2.80	2.81	1.68
4	2.81	2.81	2.81	1.56
5	2.81	2.81	2.81	1.56

Part III Surfactant (span 80) Concentration Variable

Experimental Conditions

W-O emulsion : external phase = 1 : 2

External phase : mother liquor adjusted pH to 5.0 by H_2SO_4)

Membrane phase : Span 80 at various concentrations, 10% D2EHPA dissolved in n- Dodecane

Internal phase : 2N HCl

Membrane preparation: at homogenizing speed 8000 rpm for 10 minutes

Agitation speed : 420 rpm

Table B.7 Experimental data for extraction L-lysine from mother liquor by ELM at various surfactant (Span 80) concentrations

Time	Ci (g/l)			
(min)	0.5%	1.0%	2.0%	3.0%
0	354.13	336.52	320.35	354.13
0.5	325.74	279.37	286.56	332.21
1	315.32	277.22	268.23	303.46
2	299.14	256.73	271.83	295.91
3	266.08	252.06	265.72	285.48
4	252.42	256.37	273.26	278.66
5	263.56	252.78	274.34	276.50

Table B.8 Calculation Ci/Co for extraction L-lysine from mother liquor by ELM at various surfactant (Span 80) concentrations

Time (min)	Ci/Co			
	0.5%	1.0%	2.0%	3.0%
0	1.00	1.00	1.00	1.00
0.5	0.92	0.83	0.89	0.94
1	0.89	0.82	0.84	0.86
2	0.84	0.76	0.85	0.84
3	0.75	0.75	0.83	0.81
4	0.71	0.76	0.85	0.79
5	0.74	0.75	0.86	0.78

Table B.9 Experimental data of pH change for extraction L-lysine from mother liquor by ELM at various surfactant (Span 80) concentrations

Time (min)	pH			
	0.5%	1.0%	2.0%	3.0%
0	5.03	5.02	5.02	5.02
0.5	2.89	3.14	3.27	3.44
1	2.82	2.88	3.01	3.14
2	2.82	2.80	2.86	2.96
3	2.82	2.81	2.82	2.87
4	2.82	2.81	2.80	2.84
5	2.82	2.81	2.80	2.82

Part IV Carrier (D2EHPA) Concentration Variable

Experimental Conditions

W-O emulsion : external phase = 1 : 2

External phase : mother liquor adjusted pH to 5.0 by H_2SO_4)

Membrane phase : 1% span 80 , D2EHPA at various concentrations dissolved in n- dodecane

Internal phase : 2N HCl

Membrane preparation: at homogenizing speed 8000 rpm for 10 minutes

Agitation speed : 420 rpm

Table B.10 Experimental data for extraction L-lysine from mother liquor by ELM at various carrier (D2EHPA) concentrations

Time (min)	Ci (g/l)			
	5%	10%	20%	30%
0	352.00	336.52	352.00	352.00
0.5	326.82	279.38	292.05	289.65
1	318.03	277.22	284.06	275.27
2	310.83	256.73	282.06	267.67
3	304.04	252.06	278.46	267.67
4	286.85	256.37	284.06	265.27
5	307.64	252.78	274.47	267.67

Table B.11 Calculation Ci/Co for extraction L-lysine from mother liquor by ELM at various carrier (D2EHPA) concentrations

Time (min)	Ci/Co			
	5%	10%	20%	30%
0	1.00	1.00	1.00	1.00
0.5	0.93	0.83	0.83	0.82
1	0.90	0.82	0.81	0.78
2	0.88	0.76	0.80	0.76
3	0.86	0.75	0.79	0.76
4	0.81	0.76	0.81	0.75
5	0.87	0.75	0.78	0.76

Table B.12 Experimental data of pH change for extraction L-lysine from mother liquor by ELM at various carrier (D2EHPA) concentrations

Time (min)	pH			
	5%	10%	20%	30%
0	4.98	5.02	4.98	4.98
0.5	3.23	3.14	2.94	2.85
1	2.94	2.88	2.77	2.78
2	2.86	2.80	2.77	2.77
3	2.83	2.81	2.77	2.77
4	2.83	2.81	2.77	2.77
5	2.83	2.81	2.77	2.77

Part V W-O Emulsion and External Phase Volume Ratio Variable

Experimental Conditions

W-O emulsion : external phase = at various ratio

External phase : mother liquor adjusted pH to 5.0 by H_2SO_4)

Membrane phase : 1% span 80 , 10% D2EHPA dissolved in n- dodecane

Internal phase : 2N HCl

Membrane preparation: at homogenizing speed 8000 rpm for 10 minutes

Agitation speed : 420 rpm

Table B.13 Experimental data for extraction L-lysine from mother liquor by ELM at various w-o emulsion : external phase volume ratio

Batch No.	Time (min)	Ci (g/l)		
		1: 0.5	1:1	1:2
1	0	332.33	370.61	366.62
	0.5	311.42	326.0	281.31
	1	217.65	240.03	268.10
	2	198.54	238.40	272.10
2	4	161.40	173.92	198.00
	5	140.12	162.57	217.62

Table B.14 Calculation Ci/Co for extraction L-lysine from mother liquor by ELM at various w-o emulsion : external phase volume ratio

Batch No.	Time (min)	Ci/Co		
		1: 0.5	1:1	1:2
1	0	1.00	1.00	1.00
	0.5	0.94	0.88	0.77
	1	0.65	0.65	0.73
	2	0.60	0.64	0.74
2	4	0.49	0.47	0.54
	5	0.42	0.44	0.59

Table B.15 Experimental data of pH change for extraction L-lysine from mother liquor by ELM at various w-o emulsion : external phase volume ratio

Batch No.	Time (min)	pH		
		1: 0.5	1:1	1:2
1	0	5.00	5.01	5.01
	0.5	2.90	3.22	3.16
	1	1.93	2.58	2.89
	2	0.13	2.25	2.89
2	4	0.83	1.50	2.10
	5	0.46	0.63	2.04

Part VI Mother Liquor Characteristic Variable

Experimental Conditions

W-O emulsion : external phase = 1 : 2

External phase : mother liquor at various characteristic adjusted pH to 5.0 by H_2SO_4

Membrane phase : 1% span 80 , 10% D2EHPA dissolved in n- dodecane

Internal phase : 2N HCl

Membrane preparation: at homogenizing speed 8000 rpm for 10 minutes

Agitation speed : 420 rpm

Table B.16 Experimental data for extraction L-lysine from mother liquor by ELM at various mother liquor characteristic

Time	Ci (g/l)	
(min)	Filtration	No-Filtration
0	306.38	336.52
0.5	253.15	279.37
1	246.75	277.22
2	237.32	256.73
3	231.93	252.06
4	229.24	256.37
5	228.56	252.78

Table B.17 Calculation Ci/Co for extraction L-lysine from mother liquor by ELM at various mother liquor characteristic

Time (min)	Ci/Co	
	Filtration	No-Filtration
0	1.00	1.00
0.5	0.83	0.83
1	0.81	0.82
2	0.77	0.76
3	0.76	0.75
4	0.75	0.76
5	0.75	0.75

Table B.18 Experimental data of pH change for extraction L-lysine from mother liquor by ELM at various mother liquor characteristic

Time (min)	pH	
	Filtration	No-Filtration
0	6.08	5.02
0.5	3.33	3.14
1	2.98	2.88
2	2.87	2.80
3	2.87	2.81
4	2.87	2.81
5	2.87	2.81

Part VII Agitation Speed Variable

Experimental Conditions

W-O emulsion : external phase = 1 : 2

External phase : mother liquor adjusted pH to 5.0 by H_2SO_4)

Membrane phase : 1% span 80 , 10% D2EHPA dissolved in n- dodecane

Internal phase : 2N HCl

Membrane preparation: at homogenizing speed 8000 rpm for 10 minutes

Agitation speed : agitate at various speed

Table B.19 Experimental data for extraction L-lysine from mother liquor by ELM at various agitation speed

Time	Ci (g/l)			
(min)	300rpm	360 rpm	420 rpm	480 rpm
0	406.09	406.09	336.52	419.15
0.5	369.75	336.97	279.37	375.18
1	331.44	324.72	277.22	345.73
2	309.32	301.02	256.73	331.22
3	302.21	296.28	252.06	322.68
4	301.02	293.12	256.37	323.11
5	299.84	284.43	252.78	323.11

Table B.20 Calculation Ci/Co for extraction L-lysine from mother liquor by ELM at various agitation speed

Time (min)	Ci/Co			
	300rpm	360 rpm	420 rpm	480 rpm
0	1.00	1.00	1.00	1.00
0.5	0.91	0.83	0.83	0.90
1	0.82	0.80	0.82	0.82
2	0.76	0.74	0.76	0.79
3	0.74	0.73	0.75	0.77
4	0.74	0.72	0.76	0.77
5	0.74	0.70	0.75	0.77

Table B.21 Experimental data of pH change for extraction L-lysine from mother liquor by ELM at various agitation speed

Time (min)	pH			
	300rpm	360 rpm	420 rpm	480 rpm
0	5.02	5.02	5.02	5.02
0.5	3.17	3.39	3.14	3.12
1	3.06	2.97	2.88	2.78
2	2.71	2.69	2.80	2.65
3	2.60	2.64	2.81	2.65
4	2.59	2.63	2.81	2.65
5	2.58	2.65	2.81	2.64

Part VIII Source of L-lysine Variable

Experimental Conditions

W-O emulsion : external phase = 1 : 2

External phase : L-lysine at various source adjusted pH to 5.0 by H_2SO_4

Membrane phase : 1% span 80 , 10% D2EHPA dissolved in n- dodecane

Internal phase : 2N HCl

Membrane preparation: at homogenizing speed 8000 rpm for 10 minutes

Agitation speed : 360 rpm

Table B.22 Experimental data for extraction L-lysine from mother liquor by ELM at various source of L-lysine.

Time	Ci (g/l)	
(min)	Concentrated ML	Synthetic L-lysine
0	406.09	446.47
0.5	336.97	344.74
1	324.72	341.23
2	301.02	341.23
3	296.28	338.11
4	293.12	337.33
5	284.43	360.72

Table B.23 Calculation Ci/Co for extraction L-lysine from mother liquor by ELM at various source of L-lysine.

Time (min)	Ci/Co	
	Mother Liquor	Synthetic Solution
0	1.00	1.00
0.5	0.83	0.77
1	0.80	0.76
2	0.74	0.76
3	0.73	0.76
4	0.72	0.76
5	0.70	0.81

Table B.24 Experimental data of pH change for extraction L-lysine from mother liquor by ELM at various source of L-lysine.

Time (min)	pH	
	Mother Liquor	Synthetic Solution
0	5.02	5.00
0.5	3.39	2.17
1	2.97	2.02
2	2.69	1.88
3	2.64	1.83
4	2.63	1.76
5	2.65	1.74

VITA

Miss Wanwisa Thawisaeng was born on 26 September,1971 in Bangkok, Thailand. She received a Bachelor's Degree of Science in Biotechnology from Faculty of Applied Science, King Mongkut's Institute of Technology Ladkrabang in 1993. After then she subsequently completed the requirements for a Master's Degree in Chemical Engineering at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in 1999.

A part of this thesis is used to present in "Regional Symposium on Chemical Engineering 1999" on November 22-24th, 1999 at Simila Beach Hotel, Songkla in the title " L-Lysine Extraction from Mother Liquor by Emulsion Liquid Membrane Process"