

**EXTRACTION OF METAL IONS BY COUPLED
TRANSPORT MECHANISM USING SUPPORTED
LIQUID MEMBRANES**

BY

GUL AKHTAR



**DOCTOR OF PHILOSOPHY
IN
CHEMISTRY**

**INSTITUTE OF CHEMICAL SCIENCES
UNIVERSITY OF PESHAWAR
PAKISTAN
2012**

EXTRACTION OF METAL IONS BY COUPLED TRANSPORT MECHANISM USING SUPPORTED LIQUID MEMBRANES

By

GUL AKHTAR



DISSERTATION

**SUBMITTED TO THE UNIVERSITY OF PESHAWAR IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY**

**INSTITUTE OF CHEMICAL SCIENCES
UNIVERSITY OF PESHAWAR
PAKISTAN
2012**

APPROVAL SHEET

It is recommended that the thesis prepared by Gul Akhtar, entitled “Extraction of Metal Ions by Coupled Transport Mechanism using Supported Liquid Membranes” be accepted as fulfilling the partial requirement for the degree of

DOCTOR OF PHILOSOPHY IN CHEMISTRY

Supervisor
Prof. Dr. Saeed ur Rehman
Institute of Chemical Sciences
University of Peshawar

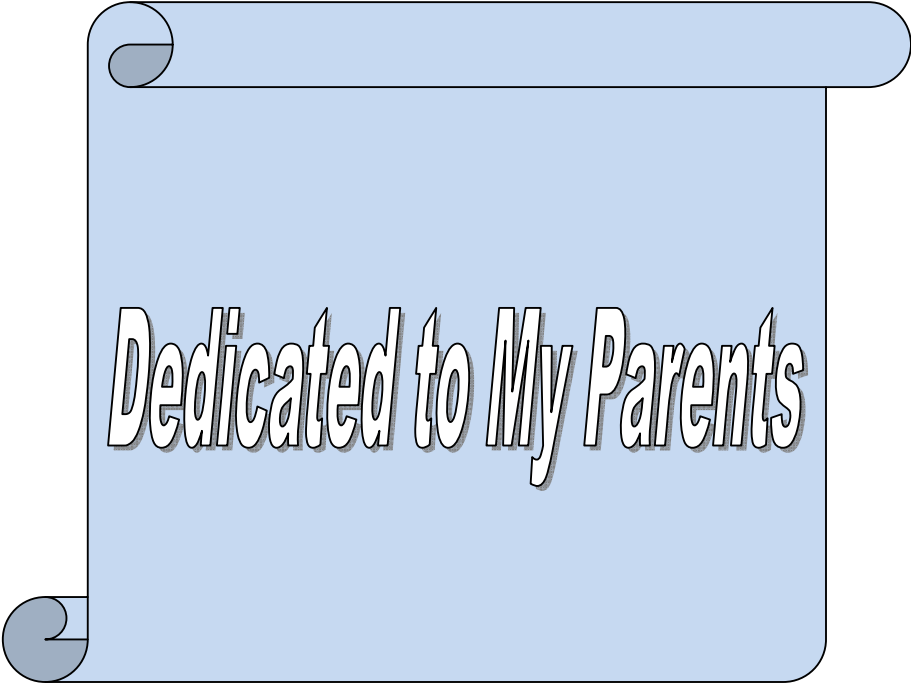
Co-Supervisor
Dr. M. Ashraf Chaudry

Examiner

Director
Prof. Dr. Imdad Ullah
Mohammadzai
Institute of Chemical Sciences
University of Peshawar

INSTITUTE OF CHEMICAL SCIENCES
UNIVERSITY OF PESHAWAR
PAKISTAN
2012

DEDICATION



Dedicated to My Parents

CONTENTS

Acknowledgements	i
Abbreviations	ii
Abstract	iv

CHAPTER-1

	INTRODUCTION	1-20
1.0	Membrane Extraction Technique	1
1.1	Types of Membranes	2
1.1.1	Microporous Membranes	2
1.1.2	Non-Porous, Dense Membranes	2
1.1.3	Electrically-Charged Membranes	2
1.1.4	Asymmetric or Anisotropic Membranes	3
1.1.5	Ceramic and Metal Membranes	3
1.1.6	Liquid Membranes	4
1.2	Supported Liquid Membrane (SLM)	4
1.2.1	Principle of SLM	7
1.2.2	Supporting Medium in SLM	8
1.2.3	Carriers and Diluents in SLM	10
1.2.4	Membrane Stability	12
1.2.5	Extraction of Metal Ions by SLM	13
1.2.5.1	Manganese (II)	14
1.2.5.2	Thallium (III)	15
1.2.5.3	Lead (II)	16
1.2.5.4	Silver (I)	18
1.2.6	Aims and Objectives	20

CHAPTER-2

LITERATURE REVIEW	21-34
-------------------	-------

CHAPTER-3

	EXPERIMENTAL	35-44
3.1	Chemicals and Reagents	35
3.2	Glassware	36
3.3	Apparatus and Instruments	36
3.3.1	Membrane Cell	36
3.3.2	Analytical Instruments	36
3.3.3	Membranes and Preparation of SLM	38
3.4	Permeation Study	39
3.5	Solvent Extraction Study	40
3.6	Formation of Metal-Carrier Complexes	41
3.6.1	Synthesis of TEA-Mn (VII) (C ₂ H ₄ OH) ₃ NH.MnO ₄	41
3.6.2	Synthesis of TEA-Tl (III) [(C ₂ H ₄ OH) ₃ NH] ₃ .TlCl ₆	41
3.6.3	Synthesis of TDDA-Ag (I) (LH).Ag(NO ₃) ₂	41
3.6.4	Synthesis of TOA-Pb (II) Pb (NO ₃) ₄ (HNR ₃) ₂	42
3.7	Experimental Conditions for Permeation of Various Metal Ions	42
3.7.1	Mn (II)	42
3.7.2	Tl (III)	43
3.7.3	Ag (I)	43
3.7.4	Pb (II)	43

CHAPTER-4

	RESULTS AND DISCUSSION	45-109
4.1	Mn (VII) Ions Transport by Triethanolamine Cyclohexanone based Supported Liquid Membrane and Recovery as Mn (II)	45

4.1.1	Theoretical	45
4.1.2	Influence of Carrier Concentration on Extraction of Mn (II)	48
4.1.3	Influence of H ₂ SO ₄ Concentration in Feed on Extraction of Mn (II)	49
4.1.4	Influence of Stripping Phase on Extraction of Mn (II)	50
4.1.5	Influence of Stirring Rate on Extraction of Mn (II)	51
4.1.6	Effect of Mn Ions in Feed on Extraction of Mn (II)	51
4.1.7	Stability of SLM	52
4.1.8	Mechanism of Mn Ions Transport	53
4.1.9	Extraction of Mn (II) Ion from Discharged Zinc Carbon Dry Battery Cell waste	53
4.2	Coupled Transport of Tl (III) through Triethanolamine-Xylene-Polypropylene Supported Liquid Membranes	54
4.2.1	Theory	54
4.2.2	Influence of HCl Concentration on Extraction of Tl (III)	58
4.2.3	Influence of TEA Concentration on Extraction of Tl (III)	59
4.2.4	Influence of NaOH Concentration on Extraction of Tl (III)	60
4.2.5	Influence of Tl (III) Concentration in Feed on Extraction of Tl (III)	61
4.2.6	Influence of Stirring Speed on Extraction of Tl (III)	61
4.2.7	Influence of Temperature on Extraction of Tl (III)	62
4.2.8	Residence Time of Tl (III)	62
4.2.9	Membrane System Constraints	62
4.2.10	SLM Stability	63
4.2.11	Recovery of Tl (III) from Coal Ash	63
4.3	Transport of Ag (I) through Tri-n-dodecylamine Supported Liquid Membranes	64
4.3.1	Theory	64

4.3.2	Effect of TDDA Concentration	67
4.3.3	Effect of HNO ₃ Concentration in Feed Solution	68
4.3.4	Effect of Stripping Phase Concentration	69
4.3.5	Effect of Ag (I) Concentration in Feed Solution	70
4.3.6	Effect of Membrane Thickness on Transport of Ag (I)	70
4.3.7	SLM Stability	71
4.3.8	Recovery of Silver from Silver Plating and Photographic Waste Solution	71
4.4	Coupled Transport of Pb (II) through TOA-Xylene-Polypropylene-Supported Liquid Membranes	72
4.4.1	Theory	72
4.4.2	Effect of TOA Concentration on Extraction of Pb (II)	74
4.4.3	Effect of HNO ₃ Concentration in Feed Solution on Extraction of Pb (II)	75
4.4.4	Effect of Stripping Phase Composition on Extraction of Pb (II)	76
4.4.5	Effect of Pb (II) concentration in Feed Solution on Extraction of Pb (II)	77
4.4.6	SLM Stability	77
4.4.7	Extraction of Pb (II) from Paint and Industrial Stream Water	78
	CONCLUSIONS	110-111
	REFERENCES	112-128
	LIST OF PUBLICATIONS	129

LIST OF FIGURES

Figure	Title	Page
1.1	Schematic representation of major types of membranes	3
1.2	Schematic representation of liquid membranes	5
1.3	Hollow fiber-supported liquid membrane	7
1.4	Schematic representation of coupled co-transport and counter transport	9
3.1	Supported liquid membrane cell	37
4.1	Transport mechanism of Mn (II)	79
4.2	Transport of Mn (II) ion from feed solution with time at various concentrations of TEA	79
4.3	Extraction of Mn (II) ion into stripping phase with time at various concentrations of TEA	80
4.4	Viscosity of triethanolamine-cyclohexanone solutions	80
4.5	Flux of Mn (II) ion at various concentrations of TEA	81
4.6	$\log J_{\eta}$ versus $\log [\text{TEA}]$	81
4.7	Concentration variation of Mn ions in feed and stripping solution against time at various H_2SO_4 concentrations in feed	82
4.8	Influence of concentration of H_2SO_4 in feed on flux of Mn	82
4.9	$\log J_{\eta}$ versus $\log [\text{H}_2\text{SO}_4]$	83
4.10	Concentration variation of Mn ions in feed and stripping phase against time at different concentrations of H_2SO_4 in strip	83
4.11	Extraction of Mn (II) ion in stripping versus different concentrations of FeSO_4	84
4.12	Extraction of Mn (II) ion in stripping versus stirring speed in feed and stripping solution	84
4.13	Influence of metal ion concentration in feed on Mn ion flux	85
4.14a	Stability of SLM: Flux versus time	85
4.14b	Durability of polypropylene support after treatment for	86

30 days in 3.75 M TEA-Cyclohexanone

4.15	Variation in Mn ions concentration in feed and stripping solution vs. time	86
4.16	Schematic diagram of membrane cell with transport mechanism of Tl(III)	87
4.17	Concentration gradient of Tl(III) ion inside the membrane	88
4.18	Positively-charged species of TEA	88
4.19	Influence of concentration of HCl on recovery of Tl(III) in stripping phase	89
4.20	Tl(III) concentration variation (decrease) in feed solution with time using various HCl concentrations	89
4.21	Tl(III) concentration variation (increase) in stripping solution with time using various concentrations of HCl	90
4.22	Plot of $\log J_{\eta}$ against $\log [\text{HCl}]$	90
4.23	Influence of TEA concentration on extraction of Tl(III) in stripping phase with time	91
4.24	Influence of TEA concentration on Tl(III) flux	91
4.25	$\log J_{\eta}$ versus $\log [\text{TEA}]$	92
4.26	Effect of NaOH concentration on Tl(III) flux	92
4.27	Influence of Tl(III) concentration in feed on its flux	93
4.28	Extraction of Tl(III) in stripping solution versus stirring speed in feed and stripping solution	93
4.29	Effect of temperature on flux of Tl(III)	94
4.30	Residence time of Tl(III)	94
4.31	Stability of SLM, Tl(III) concentration in stripping phase versus number of runs	95
4.32	Durability of polypropylene support after treatment for 60 days with 5.26 mol/dm ³ TEA-xylene solution	95
4.33	Schematic diagram showing Ag(I) transport	96
4.34	Influence of concentration of TDDA on extraction of Ag(I)	96

	in stripping phase with time	
4.35	Flux (J) and permeability (p) variation at various concentrations of TDDA in membrane phase	97
4.36	Viscosity of TDDA-cyclohexane solutions	97
4.37	Plot of $\log J\eta$ against $\log [\text{TDDA}]$	98
4.38	Influence of HNO_3 concentration in feed solution on flux (J) of Ag (I)	98
4.39	Plot of $\log J\eta$ against $\log [\text{HNO}_3]$	99
4.40	pH variation in the feed solution	99
4.41	Effect of $\text{NH}_{3(\text{aq})}$ concentration on permeability of Ag (I)	100
4.42	Effect of Ag (I) concentration in feed solution on its flux	100
4.43	Stability of SLM; permeability versus number of runs	101
4.44	Schematic representation of Pb (II) transport	102
4.45	Effect of TOA concentration on extraction of Pb (II) in feed solution with time	102
4.46	Effect of TOA concentration on extraction of Pb (II) in stripping phase with time	103
4.47	Effect of TOA concentration on flux of Pb (II)	103
4.48	Viscosity of TOA-Xylene solutions	104
4.49	Plot of $\log J\eta$ versus $\log [\text{TOA}]$	104
4.50	Extraction of Pb (II) in stripping solution vs. various concentrations of HNO_3 in feed solution	105
4.51	Plot of $\log J\eta$ versus $\log [\text{HNO}_3]$	105
4.52	pH variation in the feed solution	106
4.53	Effect of Pb (II) concentration in feed solution on its flux	106

LIST OF TABLES

Table	Title	page
3.1	Parameters of Microporous Polymeric Support	39
4.1	Analysis of Discharged Zinc Carbon Dry Battery Cell Solution	107
4.2	Recovery of Tl (III) from Coal Ash	107
4.3	Effect of Membrane Thickness on Flux of Ag (I)	108
4.4	Composition of Silver Plating and Photographic Waste Solutions	108
4.5	Effect of Strippant Composition on the Transport of Pb (II) in Stripping Phase	109
4.6	Recovery of Pb (II) from Paint and Industrial Stream Water	109

ACKNOWLEDGEMENTS

First and foremost, all the gratitude be to Almighty Allah, the most powerful and merciful, who blessed me with the stamina to accomplish this project.

I am really thankful, from the core of my heart, to my learned co-supervisor, Dr. M. Ashraf Chaudry, for his deep interest in research work, useful suggestions, technical guidance and sincere encouragement.

I would like to express thanks to my supervisor, Dr. Saeed ur Rehman, meritorious Professor, for his kind supervision, guidance, valuable advices and inspiring attitude enabling me to complete this work.

Special thanks are due to Dr. Khurshid Ali and Dr. Imtiaz Ahmed for their guidance during thesis write-up.

Thanks are also due to Dr. Naheed Bukhari for her cooperation in research work.

I would like to express my appreciation to Prof. Dr. Imdad Ullah Mohammadzai, Director Institute of Chemical Sciences University of Peshawar, for his encouraging attitude and providing all research facilities in the Institute.

I gratefully acknowledge all my respected teachers in the Institute of Chemical Sciences for their valuable guidance during the research studies.

Thanks are also due to all my lab fellows and colleagues for their moral and technical support.

I am thankful to all my family members who showed great patience and prayed all the time for the accomplishment of this task.

Gul Akhtar

LIST OF SYMBOLS AND ABBREVIATIONS

C_f	Concentration of metal ions in the bulk feed solution (mol/dm^3)
C_s	Concentration of metal ions in the stripping solution (mol/dm^3)
C_{fm}	Metal ions concentration in the membrane phase on feed side of membrane
C_{sm}	Metal ions concentration in the membrane phase on strip side of membrane
D	Diffusion coefficient (m.s^{-1})
D2EHPA	bis-(2-ethylhexyl) phosphoric acid
ELM	Emulsion liquid membrane
BLM	Bulk liquid membrane
J	Flux ($\text{mol/m}^2.\text{s}$)
K	Boltzmann constant
K_{Mn}	Equilibrium constant of manganese ion
K_{Tl}	Equilibrium constant of thallium ion
K_{pb}	Equilibrium constant of lead ion
K_{Ag}	Equilibrium constant of silver ion
ℓ	Membrane thickness
$[M]$	Metal ion concentration
LM	Liquid membrane
n	Number of moles of MnO_4^- , TEA, TOA, TDDA, NO_3^- , NH_3 or H^+ associated in the complex
p	Permeability (m/s)
r	Ionic radius of solute
A	Area of the membrane
T	Time (s)
R	$\text{C}_8\text{H}_{17}-$
SLM	Supported liquid membrane
T	Absolute temperature (K)
TEA, L	Trietanolamine
TOA, R_3N	Tri-n-octylamine

TDDA,L Tri-n-dodecylamine

Greek Symbols

η Viscosity (centipoise)

λ_{Pb} Distribution coefficient of lead ion

λ_{Mn} Distribution coefficient of manganese ion

λ_{Tl} Distribution coefficient of thallium ion

λ_{Ag} Distribution coefficient of silver ion

λ_f Distribution coefficient of the complex into membrane from feed solution

λ_s Distribution coefficient of the complex into membrane from strip solution

ε Porosity of membranes

Subscripts

m membrane

f feed

s strip

aq Aqueous

org Organic

ABSTRACT

This work elucidates the transport study of Mn (II), Tl (III), Ag (I) and Pb (II) ions through supported liquid membranes. The triethanolamine (TEA) dissolved in cyclohexanone and TEA dissolved in xylene were used as carrier, incorporated in microporous polypropylene membranes, for transport of Mn (II) and Tl (III), respectively. The Pb (II) and Ag (I) transport was carried out through tri-n-octylamine (TOA)-xylene-polypropylene and tri-n-dodecylamine (TDDA)-cyclohexane-polypropylene supported liquid membrane, respectively. The purpose of this study is as follows: (I) Optimization of the various conditions (acid concentration in feed solution, carrier concentration in membrane phase, stripping phase composition and stirring speed, etc.) for transport of the given metal ions from feed solution into strip solution, (II) derivation of theoretical equations for transport of these metal ions and their use to investigate the stoichiometry and mechanism of transport of the complexes formed inside the organic membrane phase, (III) characterization of the supported liquid membranes in term of flux, permeability and diffusion coefficient and (IV) the investigation of the stability of supported liquid membranes to evaluate the chances of their applications in industry.

The optimum conditions investigated for transport of Mn (II) are: 3.75 M TEA in cyclohexanone, 1.0 M H₂SO₄ in feed solution, 9.25×10^{-3} mol/dm³ FeSO₄ in 0.5 M H₂SO₄ in strip solution and stirring speed of 1500 rpm, for Tl (III), 5.26 mol/dm³ of TEA in xylene in membrane phase, 1.0 mol/dm³ of HCl in feed solution and 1.0 mol/dm³ of NaOH in stripping phase, for transport of Pb (II), 0.2 mol/dm³ of HNO₃ in feed solution, 0.872 M of TOA in xylene in membrane phase and 0.2 mol/dm³ of NaOH in stripping phase, and for transport of Ag (I), 0.75 mol/dm³ of HNO₃ in feed solution, 0.788 M of TDDA in cyclohexane in membrane phase and 1.0 mol/dm³ of NH_{3(aq)} in stripping phase.

The species or complexes extracted into organic membrane phase have been investigated as: (C₂H₄OH)₃NH.MnO₄ for extraction of Mn (II) and [(C₂H₄OH)₃NH]₃.TlCl₆ for transport of Tl (III). Furthermore it is also confirmed that addition of proton (H⁺) in these species target at the $\text{—}\overset{\text{N}}{\text{—}}$ site and not the —OH sites of TEA. The species Pb (NO₃)₄(HNR₃)₂ was found responsible for transport of Pb (II) where

R stands for octyl group and $(\text{LH})\text{Ag}(\text{NO}_3)_2$ for transport of Ag (I), where L stands for tri-n-dodecylamine.

The stability and durability of TEA-cyclohexanone membrane was studied for Mn (II) extraction and found quite stable for 168 hours. The TEA-xylene SLM stability for transport of Tl (III) was investigated up to 192 hours and extraction found for each run was greater than 99%. The stability of tri-n-dodecylamine-cyclohexane and tri-n-octylamine-xylene SLMs for transport of Ag (I) and Pb (II) were investigated and found stable for 120 and 240 hours respectively. The stability studies indicate that these SLMs can be used comfortably for removal of these metal ions on industrial scale.

To show practical utilization of these SLMs, these were used for extraction of aforementioned metal ions from industrial wastes, effluents and their other toxic sources. Almost all Mn (II) was extracted from a discharged zinc carbon dry battery cell solution using TEA-cyclohexanone SLM; similarly, up to 99% Tl (III) was recovered from coal ash leach liquors. The tri-n-dodecylamine-cyclohexane SLM was successfully used for extraction of Ag (I) from silver plating and photographic waste solution. Approximately all Pb (II) was transported from aqueous acidic leached solution of paint and industrial effluents, while using tri-n-octylamine-xylene SLM.

It has also been confirmed in the case of transport of Ag (I), that flux of Ag (I) decreases as the thickness of membrane film increases. Furthermore, it was observed in Tl (III) transport that diffusion of the metal complex increased with increasing temperature.

CHAPTER - 1

INTRODUCTION

1. Membrane Extraction Technique

The different types of chemicals from process industries need purification, concentration and separation of a number of constituents from each other. These include reactants and reagents used in manufacturing process, the resulting products and intermediate compounds, salts and the undesirable by-products in the waste streams. Various techniques like ion exchange, distillation, evaporation, filtration, adsorption, chromatography and crystallization have been used for separation, extraction and recovery of these species. However, these classical systems do possess some shortcomings, e.g., incomplete separation, enhanced capital cost due to costly equipment and solvents and generation of voluminous toxic effluents. Membrane separation technology has replaced these techniques due to a number of advantages like that of operational simplicity, high selectivity, simple technology and low energy requirements [1-3].

A membrane is a permeable or semi-permeable barrier like a thin polymeric film, which allows the mobility of some species and restricts the others. The membrane can be charged or neutral, porous or non-porous and acts as a permselective solid or liquid phase [1]. The membrane can be used for extraction of mixtures of vapors and gases, miscible liquids, liquids/solid and liquid/liquid dispersions and dissolved solids and solutes from liquids. Thus, all recovery and extraction requirements in industry may be achieved with membrane separation technique [1, 3].

Separation of selected species via membrane is obtained by the use of a driving force across the membrane. This provides a wide range classification of membrane extraction processes by which material is transported through the membrane. The various types of membranes are discussed briefly below [1, 4].

1.1 Types of Membranes

The major types of membranes are indicated in Fig. 1.1, with a brief description about each.

1.1.1 Microporous Membranes

It is like conventional filter and is used for removing solids from a gas or a liquid by the sieving mechanical system. The membrane is a stiff, highly porous configuration, with irregular distributed interconnected pores. The fluid-flow across the membrane is obtained by pressure gradient. During this process, the permeate or filtrate passing through the membrane should be free of suspended solids. The technique of particle separation is characterized as sieving mechanism, though the extraction is effected by the interaction of membrane-solution interface [4].

1.1.2 Non-Porous, Dense Membranes

This type of membranes consists of compact film across that species are separated by the diffusion process using the driving force of electrical potential gradient, concentration and pressure. The effectiveness of the membrane is associated to its relative transport rate within the membrane, which is investigated by their diffusion and solubility inside the membrane. Hence, non-porous membrane can extract permeates of same size if their solubility and concentration in the membrane phase differs significantly. Such membranes are mostly used in gas separation, pervaporation and separation by reverse osmosis. Generally, this type of membranes has anisotropic morphology to enhance the flux [1, 4].

1.1.3 Electrically-Charged Membranes

These membranes can be compact or microporous, although mostly they are translucently microporous. The pore walls of these membranes contain fixed negatively or positively-charged species, called anion exchange and cation exchange membranes, respectively. The extraction with the charged membrane is achieved mostly by the exclusion of ions of the similar charge due to fixed ions of the membrane configuration, and also to some extent by the pore size. The concentration of ions in solution and their charge influence the extraction process. For the

processing of the electrolytic solutions these membranes are generally used. An example of such membrane use can be found in electrodialysis process [4, 5].

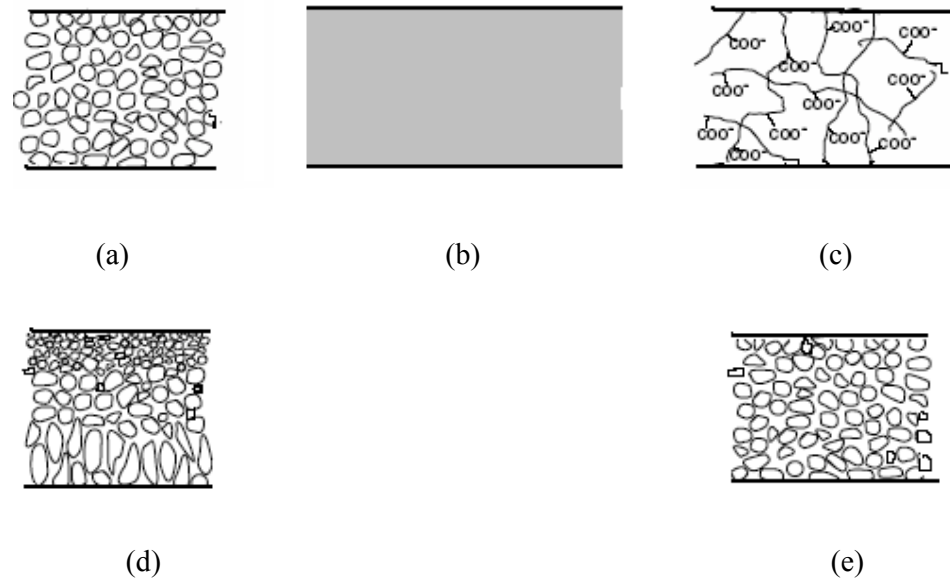


Fig.1.1 Schematic representation of major types of membranes: (a) microporous membrane (b) non-porous dense membrane (c) electrically-charged membrane, (d) anisotropic membrane (e) anisotropic membrane [5].

1.1.4 Asymmetric or Anisotropic Membranes

These membranes consist of thin microporous film supported on a much thicker, porous sub-structure. The transport separation of flow across the membrane is inversely related to membrane thickness, the thinner the membrane the higher the extraction rate. Previous membrane fabrication techniques limit up to $20\mu\text{m}$ thickness film, which are mechanically strong and without defects. The surface layer determines the permeation rates of the membrane and the sub-structure functions as a mechanical support. Due to high transport rate and high fluxes, mostly all commercial processes utilize asymmetric membranes [4].

1.1.5 Ceramic and Metal Membranes

These are microporous membranes and used in microfiltration and ultrafiltration applications, usable in acidic, basic and organic phases and possess thermal stability.

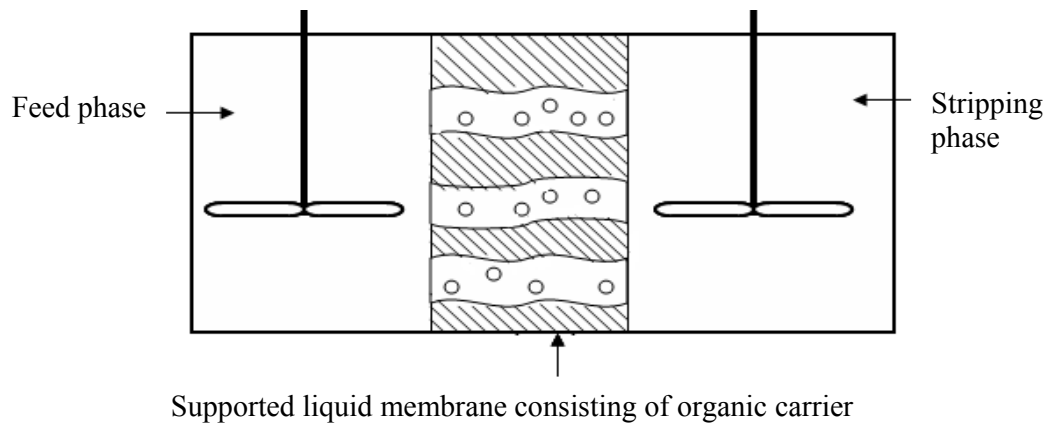
Dense metal membranes, especially palladium membranes, are used for the recovery of hydrogen from gas mixture [4, 5].

1.1.6 Liquid Membranes

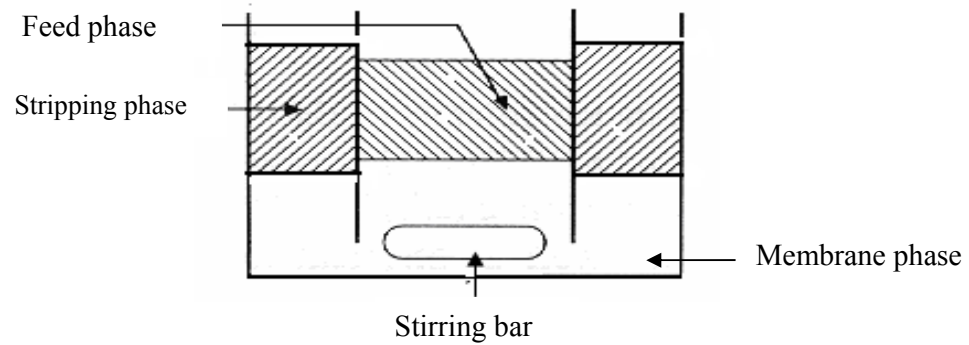
Liquid membrane (LM) techniques are recently developed and have attracted the world as these yield active and selective transport of inorganic ionic and organic species in pure form. A liquid membrane, in general, is a non-porous, homogeneous, hydrophobic, thin film, typically of organic liquid held between two aqueous phases of different compositions. Due to the concentration gradient, the solute is transferred through the LM from one phase to the other. Liquid membranes are usually of three types (Fig.1.2), i.e., supported liquid membrane (SLM), bulk liquid membrane (BLM) and emulsion liquid membrane (ELM). All other types of liquid membranes can be categorized under these classes. When the hydrophobic organic liquid phase is supported in microporous solid support by capillary action and placed between the two aqueous phases then this arrangement is usually called a supported liquid membrane. Through the diffusional process, components of the aqueous phases can travel across this SLM from one phase to another. In BLM, the liquid membrane is placed over the feed and strip solutions, separated with solid barrier, thus in contact with both of these solutions. In ELM, the principle of separation is that feed species is dispersed in the organic phase into emulsion. By different reactions, the emulsion is then broken up to release the species transported, and the emulsion components are then re-transported to the feed phase to be re-emulsified. The emulsion droplets usually comprise an oil phase and the continuous feed phase being usually an aqueous solution from which a specified solute is removed [1]. BLMs are limited to the theoretical studies due to their low mass transfer rates and interfacial surface areas, while, in the ELM, the main problem is the emulsion stability and breakage [5-7].

1.2 Supported Liquid Membrane (SLM)

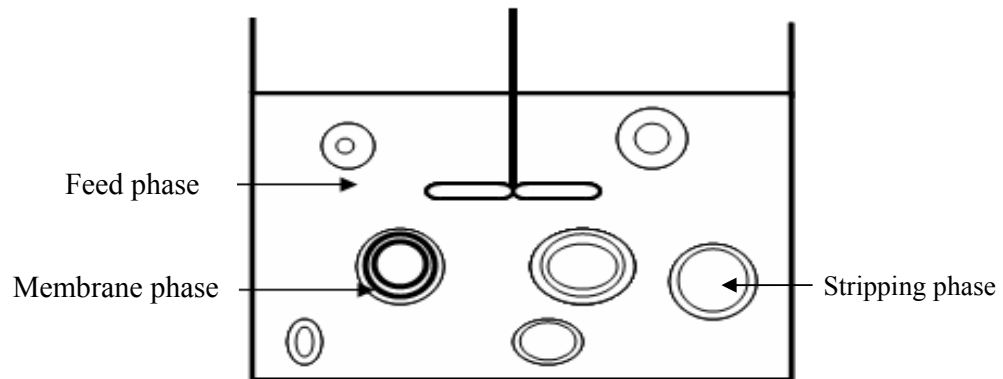
Amongst the three liquid membrane systems, the supported liquid membrane consists of organic carrier impregnated in the microporous structure of the solid inorganic or polymeric support by capillary action. Generally, the supported liquid membranes are composed of hydrophobic organic carrier and solvents immobilized in a porous solid support separating the donor and receiving solutions. A special type of



(a)



(b)



(c)

Fig.1.2 Schematic representation of liquid membranes :(a) SLM (b) BLM (c) ELM [5].

SLM can be constructed by immobilizing the organic carrier between two non-porous support which allows the transported species. This type of SLM is more effective but less appropriate due to a higher mass-transfer resistance of the non-porous layer. To enhance the stability of SLM, gelled liquid membranes and polymer inclusion membranes (PIM) have also been explored. The above-mentioned membranes can be fabricated using polymeric solution, usually polyvinyl chloride or cellulose triacetate, and plasticizer to form a stable thin film [2-4].

Supported liquid membrane was first reported by Scholander [3], who studied the transport of oxygen using aqueous hemoglobin solution supported in thin films of cellulose acetate. The concept of the emulsion liquid membrane was used for liquid membrane during 1960s and 1970s. However, the simplicity and continuous flow system of SLM attracted attention of many scientists around the world in 1980s. Since then supported liquid membranes (SLMs) have been utilized on large scale for recovery and transport of organic compounds and metal ions. The SLM has been used in the field of biotechnology, hydrometallurgy, the capture of green house gases, wastewater treatment, undesirable gases components in natural gas, pharmaceutical industry, environmental and analytical chemistry. This technique has high mass transfer and interfacial rate and has no problem of emulsification or de-emulsification as encountered in ELM systems. The preference of SLM over conventional solvent or other extraction techniques is due to: ease of operation, minimum amount of solvent or carrier, continuous operation, relatively high fluxes and low capital and operating costs. The common configurations of supported liquid membrane are: (a) hollow-fiber supported liquid membrane (HF-SLM) and (b) flat-sheet supported liquid membrane (FS-SLM) [3]. In HF-SLMs, as shown in Fig. 1.3, the carrier is incorporated in the microporous walls of polymeric support, shaped as very low diameter hollow tubes. In this process, the feed solution is diffused across the lumen and the strip solution on the shell side of the hollow fiber, and the extraction with back extraction takes place at the same time. The common configuration of FS-SLM usually consists of two-compartment cell. The carrier and diluent are contained in microporous polymeric film, which is then fixed in-between the donor and receiving phases. The complex formation takes place at feed-membrane interface which is broken at strip-membrane interface due to various prevailing conditions [7, 8].

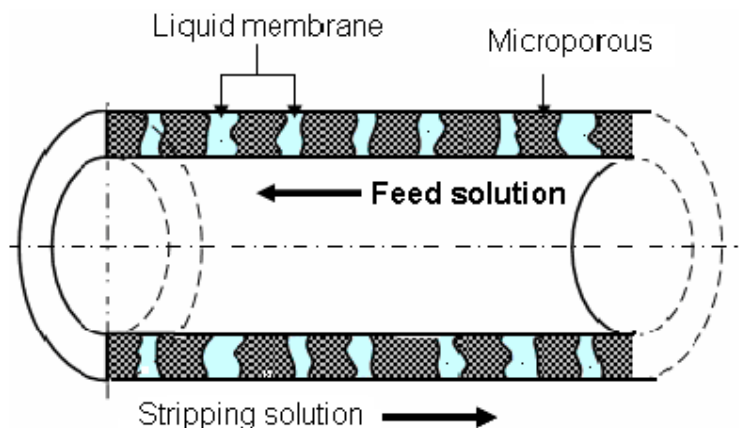


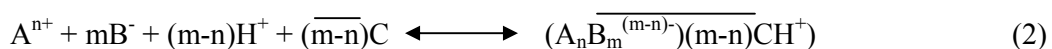
Fig.1.3 Hollow-fiber supported liquid membrane [6].

1.2.1 Principle of SLM

Supported liquid membrane combines the stripping processes and solvent extraction in a single step. The carriers or complexing agents, hydrophobic in nature are incorporated in the microporous structure of the solid support. The species on feed side of membrane come in contact with the carrier molecules and form a complex extractable into organic phase. The carriers are selected on the basis of large distribution coefficients for the component to be extracted. The complex diffuses across the membrane phase and when comes in contact with the strippant at the membrane-strip interface, it decomposes. The species are released into stripping or product solution due to high distribution coefficient. The carrier molecule becomes free and passes backward towards the feed-membrane interface and repeats the reaction cycle continuously and, thus, it shuttles in-between the feed- and strip-membrane interfaces [8, 9]. The diffusion coefficient of the forward transported complex should be less than the rearward transported free carrier molecules. Due to this reason, the free carrier molecules concentration at the feed membrane interface will always be high as compared to complex [10]. During this process, other ions involved in complex formation also travel from one side of the membrane to another side. Examples of such ions are: Cl^- , H^+ , NO_3^- , etc. As the metal ion is coupled with such energy providing ions, so the process is called coupled transport process. Depending on the nature of carrier, coupled transport can be of two types: co-transport and counter transport. Coupled co-transport takes place when the carrier

exhibits neutral or basic properties. During this transport, the species under transport and the coupling ions travel in the same direction inside the liquid membrane.

The interaction of metal ions (A), co-ions (B), and the carrier (C) forms a complex (ABC). This complex then passes across liquid membrane phase towards the stripping membrane interface where complex is broken and it releases component (A) and co-ions in stripping phase as indicated in Fig.1.4. The coupled co-ion transport is shown in Eqs. (1) and (2) for neutral and basic organic extractants, respectively. The overbar shown represents the species in liquid membrane organic phase.



When the complexing agent is acidic in nature, coupled counter transport takes place. The coupled counter transport has reverse mechanism from the co-transport. During this process, the co-ions (B) move from receiving phase to donor phase, against the transport direction of the target component. The complex (AC) formation takes place by interaction of (A) with the carrier (C) molecule. This complex then passes across the liquid membrane to strip-membrane interface, where complex is broken due to unfavorable conditions and releases (A) in stripping phase, and co-ion (B) is recovered to organic extractant.

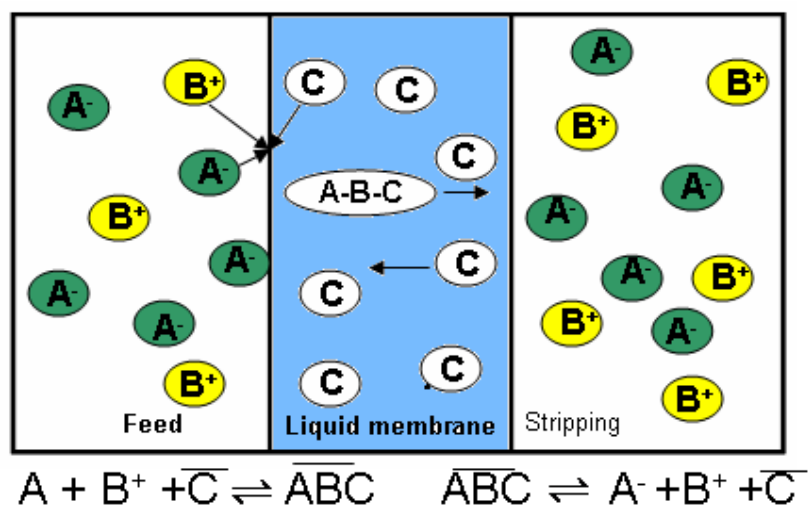
The general reaction mechanism of counter transport is shown in the Eq. (3).



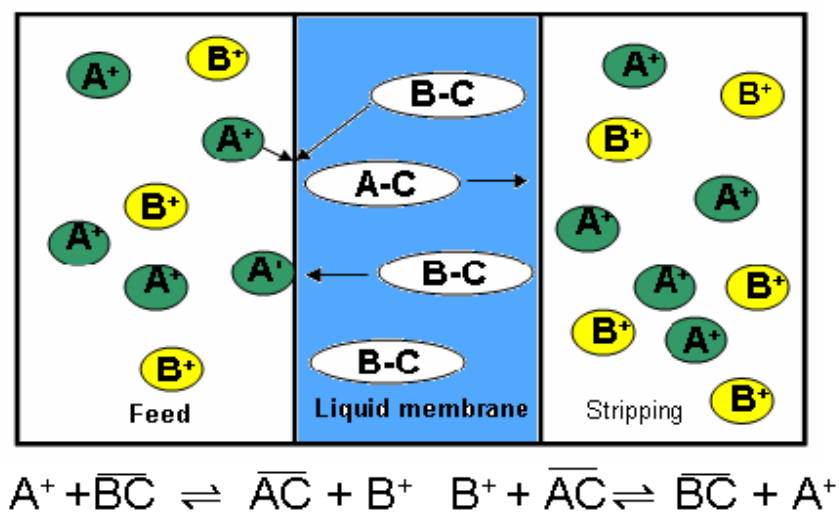
Counter-ion concentration and pH are used as driving forces for co-transport and counter transport, respectively.

1.2.2 Supporting Medium in SLM

The supporting materials used in supported liquid membrane are of two types, i.e, polymeric or ceramic, which hold the carrier with diluent and separate the donor and receiving phases. The micropores of solid support are completely filled with organic



(a)



(b)

Fig.1.4 Schematic representation of (a) coupled co-transport and (b) counter transport [6].

extractant by capillary action. The solid supports are often hydrophobic in nature, which enhance the wetting by organic carrier. The support, which is commonly used in SLM, consists of microporous polymeric film, made of cellulose acetate,

polypropylene, etc. with various trade names. These films are then converted into thin films or sheets with different pore size, porosity and thickness.

The second type of supporting membrane may be made of inorganic materials, such as glass or porous stainless steel. The porosity of both types of membrane is very important as the carrier and diluent are supported within the pores of the membrane. The function of these membranes is to support the organic extractant and diluent in the pores of the membrane [7].

1.2.3 Carriers and Diluents in SLM

The carriers or extractants in supported liquid membrane are usually organic compounds that are non-miscible in water. During the separation and extraction process of supported liquid membrane, the carrier molecules shuttle in-between feed and strip-membrane interfaces. The carrier molecule forms complex at feed-membrane interface, due to the presence of a nucleophilic center, and due to this reason the carrier molecule may have one or more lone pairs of electrons or presence of excess electron density on central atom. The carriers, thus, studied usually contain nitrogen, oxygen, phosphorus and sulphur or any other atom of similar properties.

The carriers can be broadly classified as acidic, basic or neutral on the type of reaction responsible for metal ion extraction.

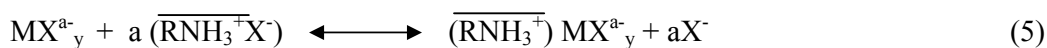
a) Acid type carriers: This type of carriers extracts metal ions by a cationic exchange reaction as:



This type of carriers can be further classified into two sub-groups: normally non-chelating and chelating extractants. Non-chelating acid extractants are further divided into two groups: carboxylic acids and organic derivatives of phosphorous acids. The latter acids consist of esters of phosphoric, phosphonic acids and similar compounds having polyfunctional groups, the most common of them is DEHPA [di (2-ethylhexyl) phosphoric acid]. The other type of non-chelating carriers includes versatic acids and naphthenic acids obtained from distillation of crude petroleum.

The chelating carriers are those containing a group with an easily dissociated proton, capable to synthesise bidendate complexes with the metal ions. The most commonly used extractants of this type are ketoximes, salicylaldoximes or mixtures.

b) Basic type carriers: This type of extractants transport or extract anionic metal complexes by an anionic exchange reaction.



To get this anionic exchange reaction, the amine should be first converted to its salt to carry the anion exchange with the metal cations:



In the above equations, (5) and (6), X indicates the counter ion for M^{n+} , H^+ , or the cationic ammonium ion. Although, in some cases, the amines can transport metallic neutral species by donation of a free electron pair of the nitrogen atom.

c) Neutral or solvation type carriers: These carriers are based on the solvation of neutral inorganic molecules or complexes by electron donor atoms contained in the extractant molecule. Due to this solvation process, the dissociation rate of the inorganic species in organic medium is enhanced. In neutral extractants, normally the oxygen is bonded to a phosphorus atom and is grouped in three sub-types: phosphate esters, phosphonic esters and phosphine oxides. However, in some neutral extractants, the sulphur is bonded to a phosphorus atom like cyanex 471 X, whose active substance is a trialkylphosphine sulphide.

A good carrier must have the properties of high diffusion and distribution coefficients, nonvolatility on a wide range of temperatures, resistance to chemicals such as acids, bases, oxidizing agents and stability to irradiation and hydrophobic in nature.

The diluents are normally nonpolar organic solvents, which are used in various proportions with almost all the carriers in supported liquid membrane. The carriers are usually large molecular weights and highly viscous organic liquids and, therefore, after making complex with metal ions, their diffusion decreases due to friction of highly viscous liquid membrane. The function of diluents is to decrease the viscosity

of liquid membrane in supported liquid membrane so that the metal-carrier-complex can diffuse with enhanced speed. For this purpose, the optimum concentration of the carrier in the diluent is to be determined to find maximum values of flux for metal ion transport. The commonly used diluents are n-butane, kerosene oil, cyclohexanone, etc. [2, 4, 6-8].

1.2.4 Membrane Stability

Supported liquid membranes have been usually used in metal ions extraction due to their selectivity, low cost and low energy. However, in some cases the applications of supported liquid membranes have been limited due to instability problems. The most common degradation problems are as:

- a) Pressure variation across the membrane due to osmotic pressure.
- b) Dissolution of species from the feed and strip phases and organic membrane phase.
- c) The regular wetting of pores in the membrane support by both donor and receiving solutions causing the removal of carrier and diluent filling the pores of solid membrane.
- d) The obstruction of membrane pores by the complex precipitation.
- e) Emulsion formation in the organic phase.
- f) Solid support thickness and its pore diameter.
- g) Flow rate of the feed and strip solutions, the lower the stirring rate, the longer the life time of supported liquid membranes due to low shear force.
- h) The solubility of organic phase in aqueous phases increases with the increasing of operating temperature and usually reduces the life time of membrane.
- i) Sometimes it has been observed that by reducing the salt and solute concentration in aqueous phases, the life time of SLM is also reduced due to carrier leaching and larger emulsification.

Whatsoever is the degradation mechanism, it is usually observed that SLM failure takes place gradually. In order to improve the lifetime of SLM, several ways have been proposed in literature which are given below:

- I) Synthesis of selective, hydrophobic extractants and development of dispositives for membrane refilling with fresh organic carrier when it is leaking or losing its properties.
- II) Gelation of supported liquid membranes: a gel is formed to stop the flow of the organic phase away from the gelled membrane.
- III) Keeping of an interface-immobilizing pressure across a membrane in a direction to oppose the tendency of leakage.
- IV) Improving the degrees of binding of the extractant to the membrane support. It has been reported that polymeric plasticizer membrane (PM) or polymeric inclusion membrane (PIM) has shown excellent durability and selectivity as in this type of membranes the solid support is created with the organic carrier and is free of solvents.
- V) Reducing the emulsion formation by decreasing the surface shear, gelling of immobilized carrier, or by using a protective coating. Some workers have shown that using an uncoated SLM shows no flux after one day due to degradation problems. However, the coated membranes with this technique show no decrease in flux for 350-hour continuous operation [2, 3, 7].

1.2.5 Extraction of Metal Ions by SLM

Metals have been used throughout much of human history to make machinery, buildings, utensils and chemicals. Metals are introduced into the environment through different routes like that of mining, smelting and processing activities. These can also contaminate the biosphere by their industrial and consumer products, used in homes, e.g., nickel/cadmium batteries, paints, plastics, antifungal agents, creams, consumer electronics, toiletries, etc. Despite their wide scale applications, metals toxicity is a challenge to almost all living organisms. These include enzyme inhibition/activation, disruption of function and structure of a number of organelle, carcinogenic effect,

nervous system disordering, endocrine and reproductive effects and failure of respiratory system. Some precious metals such as gold, silver and platinum, are toxic in nature. Therefore, the separation of metal ions from environment is essential for their safe disposal or reuse. Metal ions present in organic as well as in inorganic effluents from the industries pose another threat and so their recovery and removal from effluents is of great importance [11-13].

Liquid membranes for extraction and separation of metal ions have attained significant attention during the past three decades due to their uniqueness such as low cost operation, selectivity and ease of operation. The applications include industrial hydrometallurgy [14-16], analytical [17, 18], biomedical [19-21], waste water treatment [22, 23] and separation of gases [24, 25]. Supported liquid membrane-based technique is an effective unit process in hydrometallurgy for various metal ions separation. Due to chemical potential difference, the metal ions can be extracted from the aqueous feed solution into strip solution across the supported liquid membrane.

In the present study, the transport and separation of Mn (II), Tl (III), Pb (II) and Ag (I) was carried out. The brief introduction as well as their extraction by various techniques is discussed below.

1.2.5.1 Manganese (II)

The concentration of manganese in the Earth's crust is about 0.1% making it 12th most abundant element [26]. Manganese is the most essential part of steel due to its deoxidizing, alloying and sulfur-fixing properties. Due to its application in steel, its present demand has increased in the range of 85% to 90% of the total demand. The second largest application of manganese is in the production of aluminium alloy. Aluminium, with a manganese content of roughly 1-5%, has increased its corrosion resistance property [27, 28]. Manganese (IV) oxide is used in zinc carbon dry battery cell [29].

A considerable amount of work has been done for extraction of manganese by solvent extraction technique using various extractants, i.e., tributyl phosphate [30], thiocyanate and pyridine [31], thenoyltrifluoroacetone and bidentate ligands [32], 8-mercaptoquinoline, 8-quinolinol and its analogues [33], calixarene with acetyl group [34], hydroxyoxime with 5-nonyl salicylic acid [35], 2-hydroxyl-1-(2-hydroxy-4-

sulfo-1-naphthylazo)-3-naphthoic acid [36], 5, 10, 15, 20-tetraphenyl-21H, 23H-porphine (TPP) [37], 1 M H₂SO₄ [38] and triphenylmethane dye crystal violet [39].

There are few papers related with the extraction of manganese by using supported liquid membrane technique. Lorraine et al. [40] reported the recovery of manganese from biological fluids (blood serum, milk and water) using SLM containing di-2-ethylhexyl phosphoric acid dissolved in kerosene as a metal ion carrier. Various parameters were investigated for optimization of manganese (II) ion transport such as pH of the feed and stripping solutions, dilution factor and feed flow rate. The images of scanning electron microscope of the membrane have shown that precipitation of matrix compounds on the membrane surface have restricted the transport process. The optimum conditions investigated for this SLM system were as: the feed solution pH was of 0.3, nitric acid concentration in stripping solution was of 0.2 M, the feed flow rate was in the range of 1.0 to 0.3 mL/min, DEHPA concentration was of 15% (w/v) in organic phase and dilution factors of 30 times for milk and 20 times for blood serum. Molinari et al. [41] extracted manganese by SLM using 2-hydroxy-5-dodecylbenzaldehyde in kerosene as carrier.

Millions of dry battery cells are used each year in Pakistan that are thrown as wastes after discharging, which cause a serious environmental problem. Total worldwide dry battery cell demand was estimated to be round about 4.6 billion by year 2010 [42]. The increasing demand of dry battery cell, highly pure manganese for steel production and its toxic nature ask for the separation of Mn (II) ion from discharged zinc carbon dry battery cell by using different techniques including the SLM process.

1.2.5.2 Thallium (III)

Thallium is a rare but widely distributed element. Its concentration in the Earth's crust is in the range of 0.1 to 1.7 mg/kg, mostly present in the sulfide ores of copper, zinc, lead and coal. Thallium is incorporated into the environment mainly from the combustion of coal and cement production [43]. Thallium is more lethal to living beings than mercury, copper, cadmium, or zinc, and has been responsible for therapeutic and accidental poisonings with carcinogenic and mutagenic effects [44, 45]. Acute thallium toxicity in mammals is characterized by vomiting, anorexia,

diarrhea, skin changes, dyspnea, nervous disorder, and respiratory failure leading to death [46].

Due to severe toxic effects of thallium, it is necessary to remove thallium from the environment for its safe disposal. Various complexing agents have been used for separation and concentration of thallium by solvent extraction technique, like thiooxine- CHCl_3 for extraction of Tl (I) and 1-(2-pyridylazo)-2-naphthol (PAN)- CHCl_3 for Tl (III) [47], isoamyl acetate [48], hexaacetyl calix[6]arene [49], 18-crown-6 [50], tribenzylamine [51], calix[4]arene dansylcarboxamide [52], 2-octylamino-pyridine chloroform [53], diethylhexyl phosphoric acid [54], and dicyclohexano-18-crown-6 [55].

There is limited data available for extraction of thallium by supported liquid membrane. Trtic et al. [56] extracted trace amounts of thallium by two-step hollow fiber contactors from $\text{NaCl}/\text{H}_2\text{SO}_4$ solution with butyl acetate as carrier. Zolgharnein et al. [57] extracted thallium (III) by bulk liquid membrane system with potassium-dicyclohexyl-18-crown-6 as a specific metal ion carrier and oxalate anion as a metal ion acceptor in the stripping solution. The interfering effect of Pb (II) ion was diminished drastically at 0.01 M of Na_3PO_4 and at pH 3.00 in feed solution. The transport efficiency of the membrane for thallium (III) was about 96%.

1.2.5.3 Lead (II)

Lead is present in the Earth's crust at 13 ppm by weight [58]. Its contaminations in the environment are mostly anthropogenic; largely due to use of leaded gasoline, paints, battery recycling, smelters, explosive manufacturing, cosmetics, toys and photographic materials [59]. It is one of the elemental contaminants and has been shown to cause severe damage to human health such as anemia, encephalopathy, high blood pressure, reproductive abnormalities, behavior problems and malfunctioning of kidney, liver, brain and central nervous system [60]. Advanced countries such as U.S.A. and Australia have banned leaded gasoline and lead based paints. In developing countries, such as Pakistan, leaded gasoline and paints are used in large quantities. In most of the big cities of Pakistan, the conditions of houses, especially in slum areas, are miserable and paint and plaster chipping off the walls is a common problem [59, 61]. Higher blood lead level in children in Pakistan has been reported

due to eating dirt and paint chips [62]. Another major source of lead contamination in the environment in Pakistan is due to careless disposal of industrial and municipal wastes and effluents into fresh water streams. All these result in surface and ground water contamination and affect the life and the ecosystem [63].

Due to severe toxic effects of lead, it is necessary to eliminate lead from the environment for its safe removal. Various researchers have studied the extraction of lead by different techniques, like ion exchange [64, 65], solvent extraction [66, 67], cloud point methodology [68, 69], and sorption [70-72]. However, these given processes have some shortcomings, e.g., incomplete metal ion removal, enhanced capital cost due to costly equipment and solvents and generation of toxic sludge [2, 3].

Apart from these techniques, liquid membrane (LM) separation process is one of the promising techniques for extraction of metal ions [73, 74]. Minhas et al. [75] studied the extraction of Pb (II) using calix[6]arene hexaester as a metal ion extractant in bulk liquid membrane. The influence of different factors like type of solvent, carrier concentration, temperature and stirring rate were evaluated for transport of Pb (II). They reported that the membrane exit rate and entrance rate constant increased with increasing carrier concentration and stirring rate, and decreased with increasing temperature. Lead extraction of 80.1% has been achieved. Kazemi et al. [76] investigated the selective recovery of Pb (II) through BLM consisting of benzylaza-12-crown-4 and oleic acid as a metal ion carrier. It has been found that in the presence of $S_2O_3^{2-}$ in the stripping solution, the quantity of Pb (II) transported after 150 minutes across the liquid membrane was about 95%. Sabry et al. [77] reported the transport of lead (II) across an emulsion liquid membrane consisting of di (2-ethyl hexyl) phosphoric acid as a metal ion carrier dissolved in kerosene, span 80 as emulsifying agent and sulfuric acid as a strippant. The parameters influencing the ELM stability and recovery of Pb (II) were found as: emulsification speed (1000 to 3000rpm), emulsification time (5 to 30minutes) and concentration of surfactant (2-12%V/V). Lead recovery of 99-99.5% was obtained at optimum experimental conditions. Competitive recovery of Pb (II), Zn (II), and Cd (II) across polymer inclusion membrane consisting of calix[4]-crown-6-derivative as a metal ion carrier was examined by Ulewicz et al. [78]. It has been found that the efficiency and selectivity of Zn (II), Pb (II) and Cd (II) extraction have been affected by the group attached to

the calix[4]-crown-6 molecule. The transport selectivity order for polymer inclusion membrane (PIMS) was found as $\text{Pb (II)} > \text{Zn (II)} > \text{Cd (II)}$. Escobar et al. [79] investigated the effect of composition of feed solution, stripping phase and carrier concentration in supported liquid membrane on extraction of Pb (II) in the presence of Cd (II) ions using D2EHPA as a metal ion carrier. The extraction yield was found to be 97% at optimum experimental conditions (source solution pH=2.2, strip solution pH= 2.2, D2EHPA concentration in membrane phase = 0.2 M). Selective removal of Pb (II) across liquid membrane consisting of aza-18-crown-6 and palmitic acid was performed by Akhond et al [80]. It was observed that composition and nature of the liquid membrane phase and stripping phase had a significant influence on lead ion transport. The amount of Pb (II) extracted was about 89.1%.

1.2.5.4 Silver (I)

Silver is one of the earliest metals used in arts and jewellery. The various types of alloys, normally used in dentistry, contain silver with a trace amount of palladium and platinum [81]. It is also used in conventional photographic emulsion in the form of AgCl and AgBr. Furthermore, silver has been reported to be used in some medicines [81]. It is believed that approximately 12% of the world's silver resources are used in the manufacturing of light sensitive devices. Several tons of silver are lost throughout the world annually in the wastes from photographic and galvanizing industries. Silver can be incorporated into the environment through industrial water because it is normally present as an impurity in Cu, Zn, As, and Sb ores [82]. Being precious and toxic, silver must be recovered and separated from industrial effluents [83].

Different techniques have been used for the extraction of silver such as solvent extraction [84-86], adsorption [87, 88], cloud point extraction [69], emulsion liquid membrane (ELM) [89, 90], bulk liquid membrane (BLM) [91, 92]. Traditional solvent extraction and other conventional methods may not be appropriate for large scale processes due to their major shortcomings such as time consuming, requiring costly solvents and equipments and generating toxic sludge [93].

There is a limited study for extraction of Ag (I) by SLM. Gherrou et al. [94] have investigated the extraction of Ag (I) via SLM consisting of D2EHPA as ion carrier from acidic thiourea feed solution. It has been found that Ag (I) species predominate

at very low thiourea concentration (10^{-5} - 10^{-4} M). Saito [95] reported the transport of Ag (I) across a supported liquid membrane consisting of bathocuproine (4, 7-diphenyl-2, 9-dimethyl-1, 10-phenanthroline) as a metal ion carrier. The effect of Ag (I) concentration in feed solution, NO_2^- ions (pairing ions) and carrier concentration was investigated on the extraction of Ag (I). It has been found that selective transport of Ag (I) can be achieved using NO_2^- ions as the pairing ions species with bathocuproine as the carrier. It has also been observed that the magnitude of the permeation velocity through SLM was in the order of $\text{Ag}^+ > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$. Shamsipur et al. [96] have reported the transport of Ag (I) across SLM composed of aza-thioether crown containing 1, 10-phenanthroline as a specific ion carrier. It has been observed that the presence of thiosulfate, as Ag (I) strippant in the receiving phase, increased the extraction of silver ion and approximately all the silver was recovered after 3 hours. Shamsipur et al. [83] reported the selective extraction of Ag (I) and Hg (II) with a mixed donor macrocycle aza-thioether crown having 1, 10-phenanthroline sub unit and terathia-12-crown-4 carriers, respectively, loaded in two composite SLMs. EDTA disodium salt and sodium thiosulfate were used as strippants for Hg (II) and Ag (I) ions respectively. Amiri et al. [82] investigated the selective extraction of Ag (I) across SLM consisting of calix [4]pyrroles as a metal ion carrier. The influence of different factors like picric acid concentration in the feed phase, thiosulfate concentration in stripping phase, concentration of carrier in the organic phase, stirring rate and the type of solvent was studied for transport rate of silver ion. Altin et al. [97] studied the extraction of silver ions across SLM consisting of DC18C6 (Dicyclohexano 18crown6) in toluene as a metal ion carrier. The influence of different parameters such as donor phase concentration, concentration of carrier, flow rates of feed and stripping phases, the nature and concentration of strippant in the receiving phase was studied for silver ion transport. The maximum extraction of Ag (I) was achieved at: flow rates of 50mL/min in both feed and stripping phases, DC18C6 carrier concentration of 0.05 M in toluene, HNO_3 concentration in feed solution of 0.015 M and $\text{Na}_2\text{S}_2\text{O}_3$ concentration in stripping solution of 0.08 M. The maximum extraction of silver ion found at optimum conditions was about 94%.

The present work done for the transport and recovery of Mn (II), Tl (III), Ag (I) and Pb (II) is based on the hydrophobic flat sheet supported liquid membrane using various carriers. The data obtained in the form of membrane characterization

coefficients, flux and permeability have been presented and used for stoichiometry of the chemical reactions taking place during this process. The influence of various parameters that affects the transport of metal ions such as feed concentration, pH variation in feed and stripping solution, carrier concentration in membrane phase, membrane thickness, temperature and stirring rate, have been investigated and optimized conditions for specific metal ion transport have been determined. Membrane stability as well as integrity and membrane constraints have also been studied in some cases. To show practical utilization of these SLMs, the optimized supported liquid membranes were then used for extraction and recovery of these metal ions from industrial waste effluents.

1.2.6 Aims and Objectives

The objectives of the study are as follows:

- To study the extraction and separation of various metal ions by using different organic complexing agents as mobile carrier dissolved in solvents.
- To design a theoretical model and mechanism for extraction of various metal ions using the above carriers.
- To investigate the influence of various factors on the transport of different metal ions across supported liquid membrane.
- To characterize the supported liquid membrane based on the mobile carrier for specific metal ion.
- To investigate the optimum conditions for extraction of various metal ions across SLM and to utilize these optimum conditions for practical applications.
- To use these SLMs for recovery and extraction of toxic as well as precious metal ions from wastes, industrial effluents, or other hazardous materials.
- To classify the species formed during transport of metal ion through the SLM.
- To develop equations for stoichiometric study of complexes formed during transport of metal ions and to elucidate the mechanism of transport.
- To study the chemical durability/stability of SLM.
- To study the mutual separation of various metal ions.
- To calculate the flux for specific metal ion, and to use the data for stoichiometry of the complex.

CHAPTER - 2

LITERATURE REVIEW

Bhattacharya et al. [98] investigated the separation behavior as well as transport of trivalent actinides through a hollow fiber supported liquid membrane containing cyanex-301 (bis (2, 4, 4-tri methyl pentyl) dithiophosphoric acid dissolved in n-dodecane as a metal ion carrier. It has been observed that the trivalent actinides extraction rate was faster than those of the trivalent lanthanides. Furthermore, it has been observed that carrier concentration also affects the metal ions extraction rate.

Zaghbani et al. [99] studied the transport of Cd (II) across supported liquid membrane impregnated with thiacalix[4]arene as a metal ion carrier. It has been found that carrier thiacalix[4]arene shows higher flux of Cd(II) than that of lipophilic carrier lasalocide.

Shuxiang et al. [100] reported the comparative extraction study of Cd (II) via supported liquid membrane having tri-n-octylamine dissolved in kerosene and through dispersion hybrid liquid membrane. It has been found that dispersion hybrid liquid membrane has superiority over supported liquid membrane in terms of percentage extraction of solute in receiving solution, permeability coefficient, loss of carrier, separation efficiency and transport flux.

The transport of Co (II) through triethanolamine-cyclohexanone SLM has been investigated by Bukhari et al [101]. It has been observed that the concentration of HCl in feed solution and concentration of triethanolamine in membrane phase has pronounced effect on extraction of Co (II). The optimum conditions found for the extraction of Co (II) were: 1M of HCl in feed phase and 3.75M of triethanolamine in membrane phase. It was further suggested that 80% of Co (II) is transported with complex $\text{LH} \cdot \text{CoCl}_3$ and 20% with $(\text{LH})_2 \cdot \text{CoCl}_4$.

Molinari et al. [102] studied the efficiency of a stagnant liquid film named as stagnant sandwich liquid membrane (SSWLM) and a SLM in terms of stability and flux for copper (II) transport. In both configurations, D2EHPA in n-dodecane was used as a metal ion carrier. It has been observed that hydroxide formation can be

affected by the carrier concentration. The SSWLM has shown higher stability and flux as compared to supported liquid membrane. It has been found that SSWLM has lower overall resistance for copper ion extraction than supported liquid membrane.

Liquid membrane containing cyclic and acyclic tetrathiazaalkanes bearing a hydrazone moiety as a proton dissociable group has been reported for the up hill transport of silver ion by Ishikawa et al. [103]. Excellent selective transport of silver ion was observed, when citric acid was used for adjusting pH and for preventing hydrolysis of several metal ions in the feed solution. Complete selective recovery of silver was achieved from silver solder sample using this liquid membrane system.

Yaftian et al. [104] investigated the extraction of rare-earth metal ions across a SLM consisting of 5, 11, 17, 23-tetra-tert-butyl - 25, 26, 27, 28-tetrakis (diphenyl phosphinoyl methoxy) calix[4]arene 1 as a metal ion carrier. The influence of salting out agent, concentration of metal ion in the feed solution, temperature and concentration of carrier in the membrane phase on the flux was investigated. It was observed that calixarene (1) exhibits improved intra-group separation efficiency as compared to non-macrocyclic carrier tri-n-octyl phosphine oxide.

The permeation of Co (II) from sulphate feed solution across a SLM consisting of the mixture of DP8R and Acorga M5640 as metal ion extractants was investigated by Alguacil et al [105]. Various factors affecting the transport of Co (II) like hydrodynamic conditions, pH variation and concentration of cobalt (II) in the feed solution, carrier concentration in liquid membrane phase and strippant concentration in the stripping phase were studied. To illustrate the transport study of Co (II), a model was presented consisting of interaction between the carrier and metal ion and diffusion of the complex across the liquid membrane phase. The aqueous diffusion layer thickness was determined as 1.9×10^{-3} cm. The mass transfer resistance in the feed solution was calculated as 188 s/cm, although it has been found that the rate-controlling step of the transport of metal ions mainly depends upon experimental conditions.

Sriram et al. [106] observed the extraction of Am (III) via SLM impregnated with dimethyldibutyltetradecyl-1, 3-malonamide as a carrier in n-dodecane. The feed phase was of nitrate medium of Am (III) and the stripping phase was of 0.01M nitric acid.

The diffusional parameters and chemical conditions affecting the transport have been studied. It was also found that permeability of Fe (III) was considerably lower than that of Am (III) under same experimental conditions.

Prakorn et al. [107] investigated the synergistic transport and recovery of the mixture of neodymium and lanthanum through a hollow fiber SLM containing thenoyltrifluoro acetone (HTTA) and tri-octylamine (TOA) in benzene as a mobile carrier. It has been reported that extraction was highly dependant on feed solution pH and liquid membrane phase concentration. Furthermore, it was found that lanthanum can be extracted more than neodymium, because of the adduct formation.

Marchese et al. [108] reported the transport of molybdenum (VI) across alamine 336 supported liquid membrane. The molybdenum flux has been investigated in terms of Na_2CO_3 concentration in receiving phase, the acidity of the feed solution and the carrier concentration in the organic membrane phase. It was found that effective transport of Mo (VI) ion can be achieved at pH 2 with H_2SO_4 in the feed solution and at pH 11.5 with Na_2CO_3 in the receiving phase. Moreover, the maximum transport of Mo (VI) ion was obtained at 0.02 M of alamine 336 in liquid membrane phase.

Alguacil et al. [109] observed the extraction of chromium (VI) across SLM having cyanex 921 as a metal ion carrier. The recovery of chromium (VI) was studied in terms of different factors like concentration of chromium (VI) and HCl in feed solution, hydrodynamic conditions, carrier concentration in liquid membrane phase and strippant concentration in receiving phase. Furthermore, the selectivity of this SLM towards various metal ions and behavior of the system against other organic carriers has also been presented.

The selective transport of bismuth across diisooctyldithiophosphonic acid (cyanex 301) SLM was studied by Madaeni et al. [110]. It has been reported that cyanex 301 works as a selective carrier for the extraction of bismuth ions across supported liquid membrane. It was also observed that interfering effect of other metal ions could be eliminated in the presence of $\text{P}_2\text{O}_7^{2-}$ ions as suitable masking agent in feed solution.

Rosell et al. [111] developed and characterized a hollow-fiber SLM for recovery of vanadium (V) consisting of tricaprylmethylammonium chloride (Aliquat 336) in dodecane as a metal ion carrier. The selective extraction study of vanadium (V) was

observed at low concentration (mg/L) of vanadium (V) in feed solution. It has been found that by increasing the flow rate of the feed phase the transport of vanadium (V) also increased. It has also been shown in this module that the membrane area increases by increasing the fibers' number. It has been reported that the transport process of vanadium (V) is scarcely affected by the the length of fibers.

Harnandez et al. [112] investigated the permeation of Gd (III) and Eu (III) across supported liquid membrane consisting of di-(2ethylhexyl) phosphate in kerosene as a metal ion carrier. It was observed that with the increase in feed solution pH in the range of 0.5 to 2.5, the permeability coefficient of metal ions increased while keeping the receiving solution concentration constant at 0.1 mol/L of HNO₃.

Swain et al. [113] reported the transport of Li (I) and Co (II) by SLM consisting of cyanex 272 as a metal ion carrier. For the extraction of Li (I) and Co (II), various factors influencing the transport rate, e.g., pH and metal ion concentration in feed solution, carrier concentration in liquid membrane phase, strippant concentration in stripping phase and stirring speed were investigated. It was found that with the increase in the feed solution pH in the range of 4.0 to 6.0, the flux of Co (II) increased, and on further increasing the pH up to 6.75, the flux of metal ion decreased. The flux reported of Li (I) and Co (II) was 0.918×10^{-6} mol/m².s and 82.20×10^{-6} mol/m².s, respectively, at optimum conditions.

Swain et al. [114] studied the extraction of Co (II) across supported liquid membrane and solvent extraction (SX) from dilute sulfate feed solution using cyanex 272 as a metal ion carrier. H₂SO₄ was used as a stripping agent and PVDF film as a solid support for liquid membrane. Complete removal of cobalt (II) was obtained at pH 6.0 of feed solution, 25 mol/m³ of H₂SO₄ in stripping phase and 750 mol/dm³ of cyanex 272 in membrane phase. The distribution coefficient of 1136 and flux of 63.79×10^{-6} mol/m².s was investigated for SX and SLM, respectively, at optimum conditions.

Guell et al. [115] studied the extraction of Cr (VI) across a SLM consisting of aliquat 336 as a metal ion carrier. The efficiency of the membrane system has been studied in terms of organic solvent and the stripping phase composition. Among the various stripping agents, 0.5 M of HNO₃ has been observed the most efficient for

removal of Cr (VI) from organic membrane phase. This SLM system has been successfully applied for removal of chromium from spiked natural water and industrial water at $\mu\text{g/L}$ level. Furthermore, it was observed that this SLM system is quite stable for continuous 8 days operation at a flow rate of 1 mL/min.

Chakrabarty et al. [116] reported the recovery of lignosulfonate across a flat sheet SLM consisting of trioctylamine (TOA) dissolved in dichloroethane as a metal ion carrier. The effect of various supporting materials for liquid membrane and operating conditions such as strippant and feed solution concentration and concentration of carrier in membrane phase was investigated for transport of lignosulfonate. It has been found that lignosulfonate transport increases with increasing of NaOH concentration in stripping phase up to 0.5 M. The stability of SLM was studied and found stable for 10 hours. The extraction of lignosulfonate was about 90% at optimum conditions.

Weidong et al. [117] observed the transport of Cu (II) from aqueous feed solution into hydrochloric stripping solution across a hollow fiber SLM consisting of di (2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene as a metal ion carrier. It has been found that the recovery of Cu (II) is affected by pH and the concentration of feed solution, tube side and shell side velocity, buffer media concentration and D2EHPA concentration in membrane. The results have indicated that the mass transfer coefficient of Cu (II) increased by increasing flow rates on the tube side and carrier concentration in membrane phase and decreased with increasing Cu (II) concentration in the donor solution. The optimum conditions found for this HFSLM system were: carrier volume fraction of about 10% in kerosene as organic phase, acetic ion concentration of 0.1 mol/L in feed phase and pH value of 4.4.

Gaikwad et al. [118] investigated the recovery of yttrium ions from feed solution into strip solution across micro fiber supported liquid membrane solvent extraction technique. It has been observed that the pH and concentration of yttrium ions in source solution, stirring of bulk phases and concentration of PC-88A in membrane phase affect the transport of yttrium ion. It was further noted that the two-channel fibers SLM solvent extraction enhances the yttrium ion extraction as compared to that of single channel fibers SLM solvent extraction.

The separation of mercury ion from aqueous feed solution through PVDF-TOA-coconut oil supported liquid membrane has been investigated by Chakrabarty et al. [119]. It has been observed that extraction of mercury ion increases with increasing concentration of NaOH in receiving solution, and becomes steady at 0.3 M of NaOH. It was further examined that the transport process depends on the feed solution pH and becomes maximum at pH 1.0. The SLM was found stable for 98 hours. It was also observed that 95% mercury was transported at optimum conditions.

The extraction study of W (VI) via supported liquid membrane has been reported by Chaudry et al. [120]. The tri-n-octylamine was used as a metal ion carrier in microporous polypropylene support. The optimum conditions found for transport of W (VI) were: TOA concentration of 0.66 mol/dm^3 in membrane phase, HF concentration of 0.01 mol/dm^3 in feed solution and NaOH concentration of 2.5 mol/dm^3 in stripping phase. It was also observed that with the increase of temperature, the flux of W (VI) also increased.

Danesi et al. [121] investigated the transport rate of Zn (II) and Cd (II) from aqueous feed chloride solution into ammonium acetate receiving solution across a SLM having trilaurylammonium chloride solution in triethylbenzene as a metal ion carrier. The carrier was adsorbed on a microporous polypropylene support. The effect of stirring speed of bulk solutions, carrier concentration and feed chloride concentration were investigated for extraction study. The transport study of metal ions was explained in terms of complex formation chemistry, aqueous film diffusion and membrane diffusion.

Danesi et al. [122] investigated the permeation of Eu (III) and Am (III) across two composite SLMs. These SLMs were separated through an aqueous solution; the first one was a neutral while the second was an acidic, i.e., a solution of bis (2-ethylhexyl) phosphoric acid in n-dodecane. It has been observed that by repeating the composite SLM arrangement number of times, a single stage character of SLM extraction of metal ions in solution is overcome. It was also observed that the permeability of these SLMs, for a given cation, is a function of the SLM area, the volumes of the aqueous solutions and single membrane permeability.

Parthasarathy et al. [123] reported the extraction of Cd, Cu, and Pb ions across a hollow fiber SLM containing 1, 10-didecyldiaza 18-crown-6, fatty acid and a mixture of toluene and phenyl hexane (1+1) as a mobile carrier. For metal ions, extraction flow and non flow system of single hollow fiber module were studied. In case of the flow system for a given receiver solution, volume (ca 50-60 μ L) kept in the lumen of the membrane, the influence of target elements, the volume of sample, metal ions concentration and flow rates of sample solution on the preconcentration factor have been investigated. The preconcentration factors of 100-3000 for Pb, Cd and Cu for preconcentration times in the range of 5-20 minutes have been observed for sample and receiver solution volumes of 250 mL and 60 μ L, respectively. It has been observed that preconcentration factors were dependant on the initial sample volume and independent of the initial concentration of target elements in the feed solution [123].

Yaftian et al. [124] investigated the extraction of rare-earth metal ions across a supported liquid membrane consisting of 5, 11, 17, 23-tetra-tert-butyl-25, 26, 27, 28-tetrakis (diphenylphosphinoylmethoxy) calix[4]arene (1) (cone conformation) in *o*-nitrophenyl hexyl ether (NPHE) as a metal ion carrier. The influence of concentration of salting-out agent and initial metal ion concentration in feed phase, temperature and the carrier concentration in membrane phase on the metal ions flux has been evaluated. It has been investigated that flux of metal ions differs in the order of Al (NO₃)₃ > NaNO₃ > HNO₃ and depends mainly on the salting-out agent. Furthermore, the maximum flux has been observed for Nd and Pr metal ions. The carrier calixarene 1 showed improved intra-group transport efficiency with that of non-macrocyclic carrier tri-*n*-octylphosphine oxide.

Campderros et al. [125] reported the transport of Ta (V) and Nb (V) across a SLM consisting of tributyl phosphate as a metal ion carrier. The extraction process was performed in a two-compartment cell with a continuous agitation of bulk solutions and continuous flow system. It has been found that the HCl concentration, in feed solution, has a profound influence on Nb (V) transport. Maximum flux of Nb (V) was obtained at 6 and 9 M of HCl in feed solution and below 6 M of HCl, the transport of Nb (V) was less. It has been reported that mechanism of coupled transport of Ta (V) and Nb (V) through SLM was a function of HCl concentration.

Voorde et al. [126] reported the extraction of nickel ions across a supported liquid membrane consisting of cyanex 302 and LIX 860-1 from effluents of metal ions finishing industry. During this process, in the first stage, commercial extractants were separated through conventional extractions. The effect of the type of the extractant and other critical factors like pH and concentration of the feed solution has been investigated for extraction of nickel ions. In the second stage of extraction of nickel ions, the SLM technology was tested with most promising combinations in a lab-scale environment. Transport rate was calculated for various concentrations of carrier and experimental runs were undertaken for real effluents for separation of nickel ions.

Transport of copper, cadmium, and lead via supported liquid membrane consisting of alamine 304-i for cadmium and lead transport and LIX 84-i for copper transport has been reported by Breembroek et al. [127]. It has been observed that for the copper extraction, the transport rate was restricted by the diffusion across the aqueous stagnant films in the module. The measured mass transfer rates of metal ions were compared to generally accepted mass transfer correlations. It has been found that these correlations were three times higher mass transfer rate than measured ones for a feed flowing on the tube side of the membrane, while the mass transfer rate predicted from these accepted correlations, up to a factor of 8 was lower than the measured ones for feed flowing on the shell side of the membrane. Furthermore, it has been examined that high mass transfer rate for cadmium can be achieved from a feed solution containing mixtures of sulfuric and phosphoric acid. The recovery rate of cadmium was a factor of 20 higher than that of lead.

Venkateswaran et al. [128] studied the separation of chromium (VI) ions from an aqueous feed solution across a flat sheet SLM consisting of tri-n-butyl phosphate (TBP) as a mobile carrier supported in polytetrafluoroethylene (PTFE). The different factors which affect the extraction of Cr (VI) ion such as initial Cr (VI) concentration and pH in feed solution, stirring speed, concentration of receiving phase, feed to stripping proportion and characteristics of support were investigated. The polytetrafluoroethylene having 1.0 μm pore size showed higher flux than 0.5 μm . The complete extraction of Cr (VI) was achieved at 9.6×10^{-4} M of initial Cr (VI) concentration in feed phase, 0.5 M of NaOH concentration in stripping solution and stirring rate of 500 rpm. The stability of this SLM system was also determined and it

has been found that TBP carrier showed no significant loss for continuous ten runs with one impregnation of carrier and retained the same transport efficiency.

Ansari et al. [129] studied the performance of various extractants viz. TRUEX (trans uranium extraction), DIAMEX (diamide extraction) and TODGA in hollow fiber SLM for transport of trivalent actinides and lanthanides. It has been investigated that from 500 mL of feed solution at 0.6 g/L Nd in 3 M HNO₃ and from pressurized heavy water reactor quantitative recovery of Am (III) and Nd (III) was obtained in 30 minutes using TODGA solvent (0.5 M DHOA + 0.1 M TODGA) as an extractant. In case of TRUEX solvent comprising 0.2 M octyl (phenyl)-N, N-diisobutylcarbamoyl methylphosphine oxide as the complexing agent + 1.2 M tri-n-butyl as the modifier has shown only 50% extraction. This deficiency in transport was ascribed to the major amount of acid transport that affected the dissociation of complex. The DIAMEX solvent (1 M N, N'-dimethyl-N, N'-dibutyl tetradecyl malonamide) has shown 85% transport.

Reyes-Aguilera et al. [130] investigated the transport of Bi (III) through supported liquid membranes impregnated with tri-*n*-octylphosphine oxide (cyanex 921) as a metal ion carrier from synthetic feed solution of 0.5 M of HCl and 2 M of H₂SO₄. It has been observed that the solvate BiCl₃·2cyanex 921 is formed as a result of interaction of 2 molecules of cyanex 921 with that of a Bi (III) ion. The influence of different parameters on extraction of Bi (III) including: support, feed solution concentration, carrier concentration in the organic phase and the nature of strippant in stripping phase has been evaluated. No transport of Bi (III) was observed from H₂SO₄ media, although the transport of Bi (III) occurs by addition of HCl in feed solution. The maximum transport of Bi (III) was investigated at 0.5 M of HCl in feed solution, 0.2 M of H₂SO₄ as a stripping solution and at 0.3 M of cyanex 921 in membrane phase.

Sastre et al. [131] studied the extraction of Au (I), across supported liquid membrane consisting of LIX 79 (guanidine derivative) in cumene as a mobile carrier. For the transport mechanism, a model has been reported describing the interfacial chemical reaction, diffusion across the liquid membrane phase and process of diffusion via the feed aqueous diffusion layer. A mathematical equation was also derived to correlate the equilibrium and diffusional parameters with the membrane

permeability coefficient. The mass transfer coefficient of Au (I) was found as 5.5×10^{-3} cm/s, while the aqueous boundary thickness was calculated as 1.3×10^{-3} cm. It has been found that gold ions can be selectively transported in the presence of different metallic-cyano complexes.

Junwen et al. [132] reported the permeation study of cadmium with the three types of carriers, kelex 100, LIX 54 and aliquat 336 impregnated in supported liquid membranes. The fluxes found were: 7.9×10^{-11} , 1.5×10^{-10} and 1.12×10^{-9} mol/cm².s for LIX 54, kelex 100 and aliquat 336, respectively. The extraction capabilities of these three carriers for cadmium have also been calculated using the quantum chemical computation. The computational results have shown that for cadmium transport, the aliquat 336 was the excellent carrier followed by kelex 100 and LIX 54. It has also been found that the heavy metal transmembrane flux can be enhanced effectively by addition of small amount of anions with less negative free energy of hydration. The optimum conditions found for this supported liquid membrane were: 50% v/v of aliquat 336 in liquid membrane phase, 1mM of EDTA in stripping phase and stirring speed of 400 rpm.

Gill et al. [133] investigated the simultaneous separation of Ni (II), Cu (II) and Fe (III) from dilute feed solution with two PTFE supported liquid membranes impregnated with LIX 84 and alamine 336. The alamine 336 impregnated membrane was positioned in-between the first and 2nd compartments while LIX 84 membrane was positioned in-between the 2nd and 3rd compartments of the permeation cell. It has been reported that Fe (III) was separated with the alamine 336 impregnated membrane, whereas Cu (II) was extracted with the LIX 84 membrane and Ni (II) remained in the central feed compartment (2nd compartment) of the permeation cell.

The extraction of copper through supported liquid membrane consisting of LIX 984N as a carrier, impregnated in Celgard and Accurel, was studied by Fane et al. [134]. It has been found that LIX 984N produces good extraction results for copper from dilute acidic copper feed solution. It has been reported that at the initial stage of extraction, the liquid loss from membrane phase leading to membrane instability was due to surface shear forces created by stirring the solutions in feed and stripping compartment of the cell. The instability of long-term operation was investigated for

surface shear forces, Marangoni effects, membrane morphology and membrane preparation protocol.

Rathore et al. [135] studied the permeation of plutonium (Pu) from acidic waste solution with hollow fiber SLM containing tri-n-butyl phosphate in dodecane as an extractant. The hollow fiber membrane was operated on recycling mode with acidic waste donor solution of 3 M of HNO_3 containing $\text{Pu} = 8 \text{ mg/dm}^3$ and $\text{U} = 15 \text{ mg/dm}^3$ at a flow rate of 3 mL/min. The selective recovery of Pu (IV) was observed from various fission products across the bundle of hollow fiber test module into stripping phase consisting of 0.1 M of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.3 M of HNO_3 . The membrane reported has been found stable against radiation up to the level of 1M rad.

The concurrent extraction of arsenic and mercury from natural-gas-co-produced water via hollow fiber supported liquid membrane was studied by Lothongkum et al. [136]. The effect of various parameters such as, types of extractants (bromo-PADAP, cyanex 923, cyanex 471 and aliquat 336) dissolved in toluene, H_2SO_4 concentration in feed solution, the number of separation cycles and types of strippants (NaOH , de-ionized water, HNO_3 , H_2SO_4 , and thiourea) have been investigated for transport of these metal ions. By adding cyanex 471 in aliquat 336 resulted in the synergistic coefficient of 2.8 that demonstrated the synergistic effect on arsenic extraction. Thiourea was observed to be the excellent strippant. The optimized conditions found for extraction of mercury and arsenic were : 0.2 M of H_2SO_4 in feed solution, 0.1 M of thiourea as the stripping solution at 4 cycle separation and 0.22 M of aliquat 336 mixed with 0.06 M of cyanex 471 in membrane phase.

Parhi et al. [137] have reported the transport efficiencies of the three phosphoric acid extractants (cyanex 272, PC-88A and D2EHPA) for cadmium extraction through supported liquid membrane. The equilibrium study has indicated that the adduct complex responsible for transport of cadmium ion consists of two moles of H^+ ions, two moles of the extractants and one mole of cadmium ion. The influence of various parameters like flow rate, extractants concentration in the membrane phase, pH and cadmium concentration in the feed solution and H_2SO_4 concentration in stripping solution on cadmium flux has been studied. The maximum extraction of cadmium ion was observed at pH 7.5 of the feed solution, 600 mol/m³ of PC-88A and D2EHPA,

800 mol/m³ of cyanex 272 and 900 mol/m³ of H₂SO₄. The extraction efficiencies for three phosphoric acids found in the order of D2EHPA > PC-88A > Cyanex 272.

The extraction of americium (III) from aqueous nitrate feed solution into formic acid aqueous stripping solution across supported liquid membrane has been described by Danesi et al. [138]. The mobile carrier used in this system was carbamoylmethylphosphine oxide dissolved in diethylbenzene and supported into a 48µm thick microporous polypropylene film. The extraction mechanism found consisted of a diffusion process across an aqueous diffusion film, diffusion through the liquid membrane and a fast interfacial chemical reaction. Equations have been derived to correlate chemical composition of the system to membrane permeability coefficient and to the diffusional parameters. Furthermore, the diffusion coefficients of the permeating species as well as the equilibrium constant of the fast interfacial reactions have also been evaluated.

Dreher et al. [139] investigated the extraction of copper ion across supported liquid membrane impregnated with Acorga P5 100 (salicyladoxime and 4-nonyl phenol with small amount of kerosene). The influence of membrane liquid rheology and its composition on mass transfer and membrane stability was modeled and discussed. It has been found that by increasing the viscosity of membrane fluid, the flux of copper ion decreased but enhanced the membrane stability. Furthermore, it has been found that destabilization of the membrane occurred as a result of two mechanisms: hydrodynamic instabilities due to stirring effects and the interfacial turbulence owing to mass transfer, termed as the Marangoni effect.

Alpoguz et al. [140] studied the extraction behavior of Hg (II) from an aqueous feed solution across a flat sheet SLM consisting of calix[4]arene derivatives as metal ion extractant loaded in Celgard 2400 and 2500 solid films. The effect of the nature of solvent and anions like nitrate and chloride ions were studied for the transport of Hg (II). The permeability coefficients for various parameters studied were calculated with the Danesi model. The highest values of permeability were studied for 2-nitrophenyloctylether (NPOE) solvent and the effect observed was in the order of NPOE > chloroform > xylene.

Juang et al. [141] analyzed the extraction rates of europium (III) across supported liquid membrane consisting of di (2, 4, 4-trimethyl pentyl) phosphinic acid as a metal ion extractant. The equilibrium constants for the formation of the extracted complexes were studied and the transport model was also presented considering the interaction of metal ions with carrier at feed membrane interface, diffusion of the carrier and its metal complex in the liquid membrane phase and diffusion of metal ions across the feed stagnant layer. The kinetic parameters of metal-carrier complex were studied from the supported liquid membrane extraction data.

The compound N-benzoyl-N', N'-diheptadecylthiourea has been studied as a mobile carrier in supported liquid membrane for transport of mercury from acidic nitrate solution into thiourea as a stripping agent by Claudia et al. [142]. They observed that, in the pH range of 2 to 6, only lead was transported from nitrate feed solution containing Pb (II) and Cd (II). Various parameters affecting the extraction were evaluated like the organic solvent, the feed solution composition and the length of alkyl chains in the carrier. This membrane system has shown 100% efficiency for mercury extraction from spiked sea water sample having concentration of 10 mg/L at pH 2, thiourea concentration of 0.3 M in stripping phase and solvent mixture of decaline/cumene at 80:20 ratio.

Kubota et al. [143] performed the transport of three rare earth metal ions (Y, Ho and Er) through hollow fiber supported liquid membrane impregnated with calix[4]arene carboxyl derivatives in toluene as a metal ion extractant. It has been observed that with calix[4]arene carboxyl derivatives, permeation rate of metal ions was relatively slow, while by the addition of small amount of sodium ions into the feed solution, the transport rate drastically increased and also enhanced the selectivity between rare earth metal ions (Y, Ho and Er). The developed model explained well the permeation behavior of the rare earth metal ions and also the role of addition of sodium ion on the high transport rate.

The selective transport of copper ions from chalcopyrite leach liquor solution having zinc, copper, magnesium and iron through supported liquid membrane consisting of LIX841 as the metal ion extractant was studied by Adebayo et al. [144]. It has been found that the copper flux increases from 1.79×10^{-5} to 4.72×10^{-5} mol/m².s with increase in flow rate from 20 to 120 mL/min. Furthermore, it has been

studied that flux of copper ion increases by increasing feed solution pH up to 2.5, and concentration of LIX 841 in membrane phase up to 950 mol/m^3 . The co-permeations of iron, zinc and magnesium along with copper were found as 0.107, 0.152 and 1.09 mol/m^3 , respectively.

Ren et al. [145] presented a new liquid membrane technique, hollow fiber renewal liquid membrane (HFRLM) for transport of Cu (II). The system reported was based on the liquid film transport, surface renewal theory and other liquid membrane processes. The liquid membrane has been renewed continuously by the direct contact of aqueous phase and organic droplets provide large mass transfer area and considerably decrease the mass transfer resistance in the lumen side of the membrane. It has been observed that the higher mass transfer rate can be obtained by flowing a mixture of feed phase and organic phase across the lumen side of membrane as compared to that of stripping phase and organic phase. It has also been found that transport rate of Cu (II) increases with increasing flow rates and carrier concentration in the membrane phase and decreases with decreasing initial copper concentration in the feed solution.

Kunungo et al. [146] examined the extraction of Zn (II) from aqueous feed solution across supported liquid membrane loaded with bis (2, 4, 4-trimethyl pentyl) phosphinic acid (cyanex 272) in kerosene as an extractant. It has been observed that flux of Zn (II) across membrane was dependant upon the H^+ and Zn (II) concentrations in the feed solution and carrier concentration in the membrane phase. The species $\text{ZnL}_2(\text{HL})$ and $\text{ZnL}_2(\text{HL})_2$ were observed to be responsible for transport of Zn (II). The overall flux studied was first order with respect to Zn (II) concentration up to 4.0 mol/m^3 in feed solution and 0.75 order with respect to dimeric carrier concentration.

CHAPTER - 3

EXPERIMENTAL

3.1 Chemicals and Reagents

For transport of Mn (II) triethanolamine (AR grade BDH) dissolved in cyclohexanone (AR grade BDH) was used as a carrier in liquid membrane phase. Potassium permanganate (99.5% Merck) in H_2SO_4 (98% Merck) was used as feed solution and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (AR grade BDH) was used as a strippant for Mn (II) recovery.

To study the extraction of Tl (III), TlI (99.999% Aldrich) dissolved in HCl (37% Merck) and NaOH (99-100% Sigma Aldrich) in various compositions were used as a feed and stripping solution, respectively. Triethanolamine (> 98% Merck) dissolved in xylene (96% Riedel-de Haen) was used as metal ion extractant in liquid membrane phase.

For transport of silver, silver nitrate (Scharlau 99.99%) in HNO_3 (Fisher Scientific 69-72%) was used as feed in given concentration. The liquid membrane was composed of tri-n-dodecylamine (Merck $\geq 95\%$) in cyclohexane (Panreac 99.5%) as a diluent to get various compositions of metal ion carrier. The stripping solutions were made of $\text{NH}_3(\text{aq})$ (35% BDH) in given concentrations. All metal ions permeation studies were carried out in double-distilled deionized water. All other chemicals were of analytical grade.

Analytical grade $\text{Pb}(\text{NO}_3)_2$ (99.5% BDH) in HNO_3 (69-72% Fisher Scientific) was used as feed solution, tri-n-octylamine (>98% Fluka) and xylene (96% Riedel-de Haen) was used as liquid membrane phase with various compositions for transport of Pb (II). NaOH (99-100% Sigma Aldrich), Na_2SO_4 (99-100% Merck) and $\text{CH}_3\text{COONH}_4$ (98% Merck) were used as a strippant in different compositions for recovery of Pb (II) from liquid membrane phase.

The standard solutions (1000 ppm), for calibration of atomic absorption spectrophotometer for analysis of trace metal, were stored in non-humid atmosphere to ensure the shelf life and chemical stability. For preparation of the working

standards, the spectroscopic purity grade reagents were used. To avoid possible photo-degradation, all the reagents were stored in the dark.

3.2 Glassware

The glassware used in this work was of high quality Pyrex glass (borosilicate). As the cleanliness of the glassware is of the utmost importance, so for this purpose all glassware was washed with chromic acid then with warm detergent solution and rinsed with dilute nitric acid. The glassware was then thoroughly rinsed with tap water followed by three or four washings of distilled water. For removing organic contaminations, final rinse was given with acetone or benzene. The glassware was then dried in an electric oven at 90°C for six hours. All volumetric glassware was calibrated before use.

3.3 Apparatus and Instruments

3.3.1 Membrane Cell

All the metal ions transport experiments were carried out in a two-compartment cell, fabricated from Perspex material as shown in Fig. 3.1. Each half-cell of permeation cell had a cross-sectional hole area of 23.79 cm² for Mn (II), Tl (III) and Pb (II) transport and 23.75 cm² for Ag (I) transport. The volume capacity of each compartment of the cell was 250 cm³. To fix the membrane film between the cell compartments, each cell was equipped with flanges. A thin cork sheet of 4 mm thickness was inserted on both sides of the membrane film at the position holding the frame to ensure strong sealing of the membrane between the compartments. Feed and stripping solutions in both the compartment of the cell were agitated with synchronous motors at about 1500 rpm and at 25±1 °C. To study the influence of temperature on transport of Tl (III), the permeation cell was kept in an isothermal chamber. The cell was covered with a lid having ports for sampling, pH electrode and stirring rods.

3.3.2 Analytical Instruments

Atomic absorption spectrometer, Perkin Elmer 400 with graphite furnace (resolution 0.001 ppm, accuracy ± 0.1 ppm), was used for the determination of

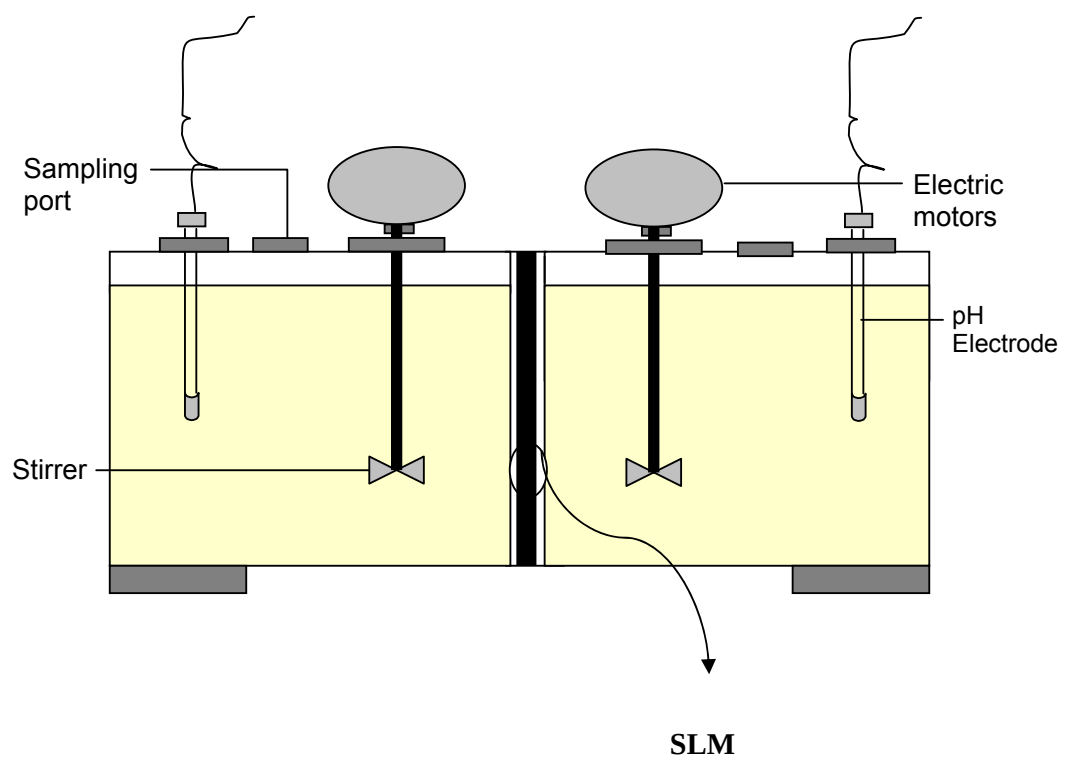


Fig. 3.1 Supported liquid membrane cell.

various metal ions concentration in aqueous phases. The wave length and slit width were adjusted as follows: for Mn (II) 279.48 nm, 1.8/1.05 mm, Tl (III) 276.79 nm, 2.7/1.05 mm, Ag (I) 328.07 nm, 2.7/0.8 mm and for Pb (II) 283.31 nm and 2.7/1.05 mm. Specific hollow cathode lamps were used for particular metal analysis.

The elemental CHN and S analysis of metal-carrier complex was performed with CHNS/O analyzer 2400 series of Perkin Elmer (resolution 0.01%, accuracy $\pm 0.2\%$ for each element). In this analysis method, the sample is combusted in ultrapure oxygen environment (99.999%) to simple gases, i.e., CO₂, H₂O, N₂, and SO₂ at 975 °C. Through the scrubbing reagents in the reduction zone, the interfering elements like halogens are eliminated. The resulting gases (CO₂, H₂O, N₂, and SO₂) in the combustion zone are homogenized and controlled to exact conditions of temperature, volume and pressure. These gases are then separated in a stepwise steady state method and analyzed as a function of their thermal conductivities [147].

The pH of the feed and stripping solution was measured with Metrohm 827 pH meter (resolution 0.001 pH, accuracy ± 0.003 pH). Muffle furnace, Thermolyne 47900 (resolution 0.1 °C, accuracy ± 0.5 °C), was used for ignition of coal and local paint. Isothermal chamber (resolution 0.1 °C, accuracy ± 0.05 °C) was used for permeation study of metal ion at various temperatures. The viscosity of organic carriers in various solvents was measured by Brookfield viscometer/rheometer LVDV-III (resolution 0.1 cP, accuracy $\pm 1.0\%$ of the range). The Sartorius balance, BP 221 S (resolution 0.0001 g, accuracy ± 0.001 g), was used for weighing. The sodium and potassium metal ions were analyzed with industrial flame photometer, JENWAY, model PFP7 UK.

3.3.3 Membranes and Preparation of SLM

Celgard 2500 hydrophobic, polypropylene film was used as a solid support for liquid membrane phase for transport of Mn (II) and Pb (II), while for the extraction of Tl (III) Celgard 2400 and for Ag (I) extraction, three types of Celgard membranes, i.e., 2500, 2502 and 4400 were used. The membranes were supplied by Hoechst Celanese Corporation NC., USA. The characteristics of all these membranes are given in Table 3.1.

The supported liquid membranes for the extraction of Mn (II) and Tl (III) were prepared by soaking the microporous polypropylene membranes in (TEA)/cyclohexanone solution (0.75 M-7.51 M) and TEA/xylene solution (0.75 M-6.75 M), respectively, for 24 hours. For Pb (II) extraction, the SLM was prepared by

Table 3.1

Parameters of Microporous Polymeric Support

Membrane	Thickness (μm)	Porosity (%)	Material
Celgard 2400	25	38	Polypropylene
Celgard 2500	25	45	Polypropylene
Celgard 2502	50	45	Polypropylene
Celgard 4400	175	68	Polypropylene

soaking the polypropylene membranes in (TOA)/xylene solution (0.174 M-1.395 M) and for transport of Ag (I), the membranes were soaked in tri-n-dodecylamine (TDDA) dissolved in cyclohexane solution (0.158 M-1.261 M) for 24 hours. The carrier solution was loaded in the membrane film by capillary action. The membranes were taken out from the organic carrier solution after soaking for specific time and allowing to drain off for 5 minutes to remove excess amount of carrier and diluent.

3.4 Permeation Study

The supported liquid membranes prepared for specific metal ions were mounted between the two compartments of the cell (Fig. 3.1). The feed and stripping solutions (250 cm^3 each) were added simultaneously to both the compartments of the permeation cell, covered and agitated continuously to avoid concentration polarization at membrane faces. One cm^3 samples, each from feed and stripping solution, were drawn after regular intervals of time and analyzed for specific metal ion concentration.

The flux (J) and permeability (p) were calculated with the following formulae [148]:

$$\text{Flux} = \frac{\text{Concentration change of metal ion} \left(\text{mol/dm}^3 \right) \times \text{solution volume in feed or strip} \left(\text{dm}^3 \right)}{\text{Effective membrane area} \left(\text{m}^2 \right) \times dt} \quad (1)$$

$$p = \frac{\left[\ln \left(\text{initial feed concentration / feed concentration at time } (t) \right) \right] \times \text{volume in feed phase}}{\text{Effective membrane area} \times \Delta t} \quad (2)$$

where, Δt indicates the total permeation time interval in seconds.

3.5 Solvent Extraction Study

The solvent extraction study was carried out by shaking 20 cm³ of 4.826 × 10⁻⁴ mol/dm³ of Pb (II) in 0.2 mol/dm³ of HNO₃ with equal volume of 0.872 M of TOA for 30 minutes in separatory funnel. The mixture after shaking was allowed to stand for one hour. The aqueous layer after separation was analyzed for Pb (II) ion concentration and the diffusion coefficient (D) was calculated using the following equation [81].

$$D = \frac{p}{\lambda_{pb}} \quad (3)$$

Where p is permeability and λ_{pb} , distribution coefficient of Pb (II).

The method of solvent extraction for Mn (II), Tl (III) and Ag (I) was the same as described above for Pb (II), however, the conditions were different which are as follows:

For Mn (II), 1.82 × 10⁻³ mol/dm³ of Mn (II) in 1.0 mol/dm³ of H₂SO₄ and 3.75 mol/dm³ of TEA in cyclohexanone.

For Tl (III), 1.95 × 10⁻⁴ mol/dm³ of Tl (III) in 1.0 mol/dm³ of HCl and 5.26 mol/dm³ of TEA in xylene.

For Ag (I), 7.42 × 10⁻⁴ mol/dm³ of Ag (I) in 0.75 mol/dm³ of HNO₃ and 0.788 M of TDCA in cyclohexane.

3.6 Formation of Metal-Carrier Complexes

3.6.1 Synthesis of TEA-Mn (VII) $(C_2H_4OH)_3NH.MnO_4$

The complex $(C_2H_4OH)_3NH.MnO_4$ was synthesized by dropwise addition of 3.75 M of TEA to 1.82×10^{-3} mol/dm³ of Mn (VII) in 1.0 M H₂SO₄ with regular stirring until clear precipitate of the complex was obtained. The precipitate of the manganese complex formed was washed four to five times with ethanol, re-crystallized from aqueous solution and dried under vacuum. The yield of the complex was 91%. The percentage of C, H and N analysed was: C 26.80%, H 5.889% and N 5.185%, whereas theoretical results were calculated as: C 26.776%, H 5.992% and N 5.204%.

3.6.2 Synthesis of TEA-Tl (III) $[(C_2H_4OH)_3NH]_3.TlCl_6$

Thallium iodide solution having 1.95×10^{-4} mol/dm³ concentration of thallium in 1.0 mol/dm³ HCl was evaporated on a hot plate at 100 °C to obtain thallium chloride, which was then dissolved in xylene and a few drops of bromine water were added to oxidize Tl^+ to Tl^{3+} . TEA of 5.26 mol/dm³ concentration in xylene was added under constant stirring for a period of an hour at room temperature. White crystals of a complex were formed which were washed four to five times with ethanol. The complex was re-crystallized from aqueous solution. The solid crystals were then dried under vacuum. The yield of the complex was 85%. The dried solid was preserved in glass stoppered bottles. According to experimental results, there were 25.02% C, 5.62% H and 4.89% N, whereas theoretically there were 24.91% C, 5.53% H and 4.84% N.

3.6.3 Synthesis of TDDA-Ag (I) $(LH).Ag(NO_3)_2$

The complex of Ag (I) with tri-n-dodecylamine (TDDA) was formed by dropwise addition of 0.788 M of TDDA in cyclohexane from burette to 7.42×10^{-4} mol/dm³ of Ag (I) in 0.75 mol/dm³ of HNO₃ with constant stirring. When the clear precipitate of the complex was formed, it was separated from mother liquor by filtration. The precipitate was washed several times with ethanol. The crystals of solid complex were dried under vacuum and preserved in glass stoppered bottles. The yield of the complex was 68%. The percentage of C, H and N analysed was: C 57.33%, H 10.17%

and N 5.60%, whereas theoretical results were calculated as: C 57.279%, H 10.147% and N 5.566%.

3.6.4 Synthesis of TOA-Pb (II) $\text{Pb}(\text{NO}_3)_4(\text{HNR}_3)_2$

To synthesize lead (II) complex with tri-n-octylamine, 250 cm³ of 4.826×10^{-4} mol/dm³ of Pb (II) in 0.2 mol/dm³ of HNO₃ was taken in 500-mL beaker. TOA of 0.872 M in xylene was added dropwise under constant stirring to the solution of Pb (II) at room temperature until clear precipitate was formed. The precipitate was washed four to five times with ethanol and re-crystallized from water solution. The crystals of Pb (II) complex were then dried under vacuum and preserved in glass stoppered bottles. The yield of the complex was 77%. The percentage of C, H and N analysed was: C 49.78%, H 9.22% and N 7.27%, whereas the theoretical results were calculated as: C 49.505%, H 9.001% and N 7.216%.

3.7 Experimental Conditions for Permeation of Various Metal Ions

For the permeation, different conditions, e.g., acid concentration in feed solution, stripping concentration in stripping phase, carrier concentration in membrane phase, etc. were optimized for each specific metal ion. The detail is as follows:

3.7.1 Mn (II)

- I)** Permeation cell of $12 \times 8 \times 7$ cm³ size.
- II)** Celgard 2500 polypropylene film with effective membrane area of 23.79 cm².
- III)** Mn (II) of 0.91×10^{-3} to 6.37×10^{-3} mol/dm³ in 1 M H₂SO₄ in feed solution.
- IV)** TEA of 3.75 M in cyclohexanone was used as a carrier in membrane phase.
- V)** FeSO₄ of 9.25×10^{-3} mol/dm³ in 0.5 M H₂SO₄ was used as a stripping.
- VI)** The feed and stripping solutions were stirred at 1500 rpm.
- VII)** To determine the Mn (II) concentration in feed and stripping solutions, wavelength of 279.48 nm and slit width of 1.8/1.05 mm of atomic absorption spectrophotometer was used.

3.7.2 Tl (III)

- I) Celgard 2400 polypropylene film with effective membrane area of 23.79 cm².
- II) Permeation cell of 12 × 8 × 7 cm³ size.
- III) Tl (III) of 0.978 × 10⁻⁴ to 4.893 × 10⁻⁴ mol/dm³ in 1.0 mol/dm³ of HCl was used as feed solution.
- IV) NaOH of 1.0 mol/dm³ was used as a strippant.
- V) TEA of 5.26 mol/dm³ in xylene was used as a carrier in membrane phase.
- VI) The wavelength of 276.79 nm and slit width of 2.7/1.05 mm of atomic absorption spectrophotometer was used.
- VII) The stirring speed of 1500 rpm was used in feed and stripping solutions.

3.7.3 Ag (I)

- I) Permeation cell of 13 × 8 × 7 cm³ size.
- II) Celgard 2500 polypropylene sheet with effective membrane area of 23.79 cm².
- III) 0.788 M of TDDA in cyclohexane was used as a metal ion carrier in membrane phases.
- IV) Feed and stripping solutions were stirred with 1500 rpm.
- V) The Ag (I) of 3.71 × 10⁻⁴ to 22.26 × 10⁻⁴ mol/dm³ in 0.75 mol/dm³ of HNO₃ were used as a feed solution.
- VI) The wavelength and slit width of 328.07 nm and 2.7/0.8 mm, respectively, of atomic absorption spectrophotometer were used.
- VII) 1.0 mol/dm³ of NH_{3(aq)} was used as a strippant.

3.7.4 Pb (II)

- I) Celgard 2500 polypropylene film with effective membrane area of 23.79 cm².
- II) Permeation cell of 13 × 8 × 7 cm³ size.
- III) Pb (II) of 0.965 × 10⁻⁴ to 14.47 × 10⁻⁴ mol/dm³ in 0.2 mol/dm³ of HNO₃ were used as a feed solution.
- IV) The stirring speed of 1500 rpm was used in feed as well as in stripping solution.

- V)** TOA of 0.872 M in xylene was used as a mobile carrier for Pb (II) extraction.
- VI)** The NaOH of 0.2 mol/dm³ was found to be a better and more suitable stripping agent than CH₃COONH₄ and Na₂SO₄.
- VII)** The wavelength of 283.31 nm and slit width of 2.7/1.05 mm of atomic absorption spectrophotometer were used.

CHAPTER - 4

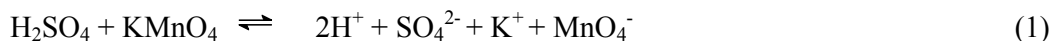
RESULTS AND DISCUSSION

In this chapter, theoretical equations, combining flux, distribution and diffusion coefficients have been derived to study the effect of metal ion concentration in feed, the H^+ concentration in feed and the carrier concentration in membrane phases. Effect of viscosity is also included in these equations. Different parameters studied have been described and the results obtained are presented in the following sections and are discussed with respect to the stoichiometry of the chemical reactions involved, the species formed in these reactions and the applications of the optimized conditions for the recovery or removal from waste aqueous solutions.

4.1 Mn (VII) Ions Transport by Triethanolamine Cyclohexanone based Supported Liquid Membrane and Recovery as Mn (II)

4.1.1 Theoretical

It is reported that when $KMnO_4$ is dissolved in H_2SO_4 , manganese ion exists as MnO_4^- [149].



If triethanolamine (TEA) is represented by L, the following possibility of protonation of triethanolamine occurs in acidic medium:



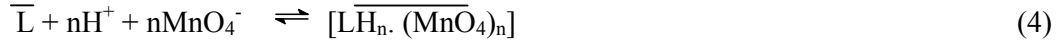
Or in general form:



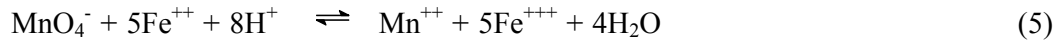
Where $n = 1$ to 4 and as triethanolamine molecule has one nitrogen and three oxygen atoms, therefore, maximum protonation of four protons can take place. The species produced in Eq. (2b) will interact with MnO_4^- ions on the feed membrane solution interface as shown in Eq. (3). The overbar represents the species in organic phase of membrane and brackets indicate the activities.



Therefore the over-all reaction is:



The complex $[\overline{\text{LH}}_n \cdot (\text{MnO}_4)_n]$ formed will immediately dissociate on the stripping membrane interface due to redox reaction with Fe (II) in the stripping solution in acidic medium, and will release Mn (II) ion in the stripping phase. The transport mechanism of Mn (VII) ion therefore is supposed to be coupled co-ion transport type, in which both H^+ and MnO_4^- ions are moving towards the stripping phase. The excessive amount of FeSO_4 in H_2SO_4 on the stripping side reduces MnO_4^- to Mn^{++} as per following reaction mechanism [149]:



Keeping in view the reaction (4), the extraction constant for Mn (II) ion is given by K_{Mn} .

$$K_{\text{Mn}} = \frac{[\overline{\text{LH}}_n \cdot (\text{MnO}_4)_n]}{[\overline{\text{L}}] \cdot [\text{H}^+]^n \cdot [\text{MnO}_4^-]^n} \quad (6)$$

The distribution coefficient λ_{Mn} , is the ratio of the concentration of the Mn (II) in the aqueous phase to that in the organic phase. So, the distribution coefficient for Mn (II) can be represented as:

$$\lambda_{\text{Mn}} = \frac{[\overline{\text{LH}}_n \cdot (\text{MnO}_4)_n]}{[\text{MnO}_4^-]^n} \quad (7)$$

From Eq. (6) and (7)

$$K_{\text{Mn}} = \frac{\lambda_{\text{Mn}} \cdot G}{[\overline{\text{L}}] \cdot [\text{H}^+]^n} \quad (8)$$

Where G is a factor that collectively presents activity coefficients of all the species involved. The Eq. (8) can be re-written as:

$$\lambda_{\text{Mn}} = \frac{K_{\text{Mn}} \cdot [\overline{\text{L}}] \cdot [\text{H}^+]^n}{G} \quad (9)$$

The activity of the species involved in Eq. (9) for dilute solutions approaches to unity, so, the factor G may be considered to be nearly equal to 1.

$$\text{and } \lambda_{\text{Mn}} = K_{\text{Mn}} \cdot [\overline{\text{L}}] \cdot [\text{H}^+]^n \quad (10)$$

As per Fick's law, the flux (J) of the given species is directly related to the concentration gradient, that is $\frac{dc}{dx}$, hence,

$$J \propto \frac{dc}{dx} \quad (11)$$

$$\text{or } J \propto \frac{C_f - C_s}{\ell} \quad (12)$$

If C_{fm} and C_{sm} stand for membrane phase concentration of manganese ion on feed and stripping solution inside the membrane, respectively, and ℓ indicates the thickness of membrane. If D stands for the diffusion coefficient of the complex (I), then Eq. (12) becomes:

$$J = \frac{D (C_{\text{fm}} - C_{\text{sm}})}{\ell} \quad (13)$$

Taking into consideration the porosity ε , λ_f and λ_s that represent the distribution coefficients of the complex into the membrane from feed and stripping side, respectively, the Eq. (13) becomes:

$$J = \frac{D \cdot \varepsilon (\lambda_f C_f - \lambda_s C_s)}{\ell} \quad (14)$$

C_f and C_s are the concentrations of Mn ions in the bulk feed and stripping solutions.

According to Wilke–Chang relation, the diffusion coefficient D is shown as:

$$D = \frac{K \cdot T}{\eta} \quad (15)$$

Where T is the absolute temperature, K is constant and η is the viscosity of liquid membrane. As on stripping membrane interface, the complex immediately dissociates and releases Mn (II) ions in the stripping phase, therefore $\lambda_s \rightarrow 0$ and $\lambda_f = \lambda_{\text{Mn}}$. By putting these values in Eq. (14):

$$J = \frac{K.T.\varepsilon.\lambda_{Mn}.C_f}{\eta.\ell} \quad (16)$$

By putting the value of λ_{Mn} from Eq. (10), the Eq. (16) becomes:

$$J = \frac{K.T.\varepsilon.K_{Mn}.[\bar{L}].[H^+]^n.C_f}{\eta.\ell} \quad (17)$$

If $\frac{K.T.\varepsilon.K_{Mn}}{\ell} = Y$, another constant

$$J = \frac{Y.[\bar{L}].[H^+]^n.C_f}{\eta} \quad (18)$$

Taking log on both sides and on re-arranging, equation (18) becomes:

$$\log J\eta = \log Y + \log[\bar{L}] + n\log[H^+] + \log C_f \quad (19)$$

From (19), we can determine the stoichiometry of the complex formed at the feed membrane interface. As $\log Y$ is constant, therefore, by plotting $\log J\eta$ versus $\log [H^+]$, keeping absolute temperature (T), carrier concentration (L) and also C_f constant, it will give the number of protons associated with carrier from the slope of this plot. Similarly, by plotting $\log J\eta$ versus C_f (manganese concentration in feed solution), keeping T, carrier concentration and acid concentration constant, it will give the number of MnO_4^- ions taking part in complexation.

4.1.2 Influence of Carrier Concentration on Extraction of Mn (II)

In this study, the concentration of the TEA was varied from 0.75 M to 6.75 M with an interval of 0.75 M, while the manganese ion concentration in the feed solution was kept at 1.82×10^{-3} mol/dm³ in 1 M H₂SO₄, and FeSO₄ was maintained at 9.25×10^{-3} mol/dm³ in 0.5 M H₂SO₄ in the stripping phase.

The triethanolamine carrier plays a significant role in the extraction of Mn (II) ion as protonated triethanolamine which is produced as per Eqs. (2a) and (2b), forms a complex with MnO_4^- on the feed membrane interface. The complex then diffuses to

stripping membrane interface where it decomposes and liberates Mn (II) ion into the stripping solution as per reaction mechanism shown in Fig. 4.1. The triethanolamine diffuses backside towards the feed SLM interface and repeats the reaction cycle continuously and, thus, it shuttles between the feed and stripping solutions SLM interfaces. The diffusion coefficient of the rearward transported bare ligand (TEA) molecules should be high as compared to the diffusion coefficient of the forward transported metal ligand complex $(C_2H_4OH)_3NHMnO_4$ [129]. Due to this reason, the TEA concentration at feed membrane interface will always be higher as compared to complex.

By increasing carrier concentration from 0.75 M to 3.75 M in membrane phase, the extraction of Mn (II) ion increases from $0.355 \times 10^{-3} \text{ mol/dm}^3$ to $1.817 \times 10^{-3} \text{ mol/dm}^3$ and the extraction of Mn (II) ion varies from 19.50% to 99.83%, however, exceeding the concentration of TEA beyond 3.75 M, the extraction gradually decreases as shown in Figs. 4.2 and 4.3. This decrease in extraction of Mn (II) ion can be explained as: by increasing TEA concentration in cyclohexanone diluents, viscosity of the membrane phase also increases (Fig. 4.4), by which diffusion of the complex from feed membrane interface into the stripping membrane interface decreases, as shown by decrease in flux (Fig. 4.5).

The plot of $\log J_{\eta}$ versus $\log \text{TEA}$ (Fig. 4.6), keeping feed concentration (C_f) and acid concentration $[H^+]$ in feed solution constant, gives a slope of 1.0077, which indicates that only one molecule of TEA is involved in complex formation.

4.1.3 Influence of H_2SO_4 Concentration in Feed on Extraction of Mn (II)

The various concentrations of H_2SO_4 studied for extraction of Mn (II) ion in feed solution were 0.75 M, 1.0 M, 1.5 M, 2.0 M and 2.5 M, while keeping the concentration of TEA in SLM at 3.75 M in cyclohexanone and concentration of $FeSO_4$ in stripping phase at $9.25 \times 10^{-3} \text{ mol/dm}^3$ in 0.5 M H_2SO_4 .

Fig. 4.7 shows that as the concentration of H_2SO_4 increases from 0.75 M to 1.0 M in feed solution, extraction of Mn (II) ion also increases from $1.31 \times 10^{-3} \text{ mol/dm}^3$ to $1.87 \times 10^{-3} \text{ mol/dm}^3$. This increase in transport may be due to excess of hydrogen ions that are produced due to ionization of sulfuric acid in feed solution that associate with

TEA, leading to increase in the concentration of $[LH_n]^{+n}$ species as per Eq. (2b). This results in an increase in the concentration of the complex $(C_2H_4OH)_3NH.MnO_4$ as well as extraction of Mn (II) ion by dissociation of complex at stripping membrane interface. Further, by exceeding the concentration of H_2SO_4 beyond 1.0 M in feed solution, the extraction of Mn (II) ions decreased, which may be due to formation of $HMnO_4$ type species shown by the following reaction:



These species ($HMnO_4$) are difficult to ionize to form complex and ultimately result in decrease in extraction of Mn (II) ion as well as flux (Fig. 4.8) [150].

The number (n) of hydrogen ions involved in extraction of Mn (II) ions was determined from Eq. (19) in section 4.1.1, i.e., by plotting $\log J_n$ versus $\log H^+$ (Fig.4.9), keeping feed concentration (C_f) and carrier concentration (L) constant. This provided straight line plot with slope of 1.0021 indicating that one proton is involved in complex formation.

As in the complex formation, one TEA and one proton are involved, therefore, the proposed formula of the complex will be $(C_2H_4OH)_3NH.MnO_4$ or $LH.MnO_4$.

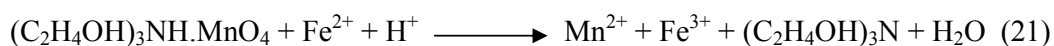
4.1.4 Influence of Stripping Phase on Extraction of Mn (II)

In this study, the concentrations of H_2SO_4 and $FeSO_4$ in stripping solution were varied from 0.25 M to 0.75 M and $1.58 \times 10^{-3} \text{ mol/dm}^3$ to $11.1 \times 10^{-3} \text{ mol/dm}^3$, respectively, while keeping the concentration of manganese ion in feed solution at $1.82 \times 10^{-3} \text{ mol/dm}^3$ in 1 M H_2SO_4 and TEA concentration in SLM at 3.75 M.

As shown in Eq. (5) that reduction of Mn^{7+} to Mn^{2+} takes place in acidic medium (H_2SO_4), that is why as the concentration of H^+ ion increases in stripping phase by increasing concentration of H_2SO_4 from 0.25 M to 0.50 M, the extraction of Mn (II) ions also increases as shown in Fig. 4.10. However, by increasing the concentration of H_2SO_4 beyond 0.5 M in stripping solution, the extraction of Mn (II) ions decreases. This decrease in extraction of Mn (II) ions may be due to the fact that transport of Mn (II) ions is by coupled transport mechanism (Fig. 4.1) and the driving force for transport is proton gradient across the membrane. That is why as the H_2SO_4

concentration in stripping solution increases, the pH gradient across the membrane decreases which ultimately decreases the extraction of Mn (II) ions.

Ferrous ion (Fe^{2+}) reduces MnO_4^- to Mn^{2+} in acidic medium and it may be due to this reason that in stripping phase the concentration of ferrous ions increases gradually, it enhances the dissociation of complex $(\text{C}_2\text{H}_4\text{OH})_3\text{NH.MnO}_4$ species by redox reaction at stripping membrane interface and releases Mn (II) ions in stripping phase as shown in Eq. (21). 99.83% of Mn (II) ions are extracted at 9.25×10^{-3} mol/dm³ of FeSO_4 in 0.5 M H_2SO_4 as shown in Fig. 4.11. The dissociation of complex at the stripping SLM interface will take place as follows:



4.1.5 Influence of Stirring Rate on Extraction of Mn (II)

To study the effect of stirring rate on extraction of Mn (II) ions, both the feed and stripping solutions were stirred at 1000-1800 rpm, while keeping manganese ion concentration in feed at 1.82×10^{-3} mol/dm³ in 1 M H_2SO_4 , TEA concentration in SLM at 3.75 M in cyclohexanone and FeSO_4 concentration in stripping phase at 9.25×10^{-3} mol/dm³ in 0.5 M H_2SO_4 . Fig. 4.12 exhibits that as the stirring rate increases from 1000 rpm to 1500 rpm, extraction of Mn (II) ions also increases from 1.423×10^{-3} mol/dm³ to 1.817×10^{-3} mol/dm³, but exceeding 1500 rpm, extraction of Mn (II) ions decreases. This can be explained that as the stirring speed of feed and stripping solutions increases, the diffusion layer thickness on feed and stripping membrane interfaces decreases and enhances the transport of Mn (II), but on further increasing the stirring rate, there is a possibility that some TEA molecules may escape from the pores of microporous film due to high turbulence caused by high stirring rates. This indicates that stirring speed has direct effect on the efficiency as well as life time of SLM. The optimum stirring speed for this SLM was considered to be 1500 rpm and further studies were performed with this stirring rate.

4.1.6 Effect of Mn Ions in Feed on Extraction of Mn (II)

To investigate the influence of feed concentration on recovery of Mn (II) ions in stripping phase, concentration range of manganese ions of 0.91×10^{-3} mol/dm³ to 6.37×10^{-3} mol/dm³ in 1.0 M H_2SO_4 in feed solution was used. During this study, the

concentration of TEA concentration in SLM was kept at 3.75 M in cyclohexanone, FeSO_4 concentration in stripping phase at $9.25 \times 10^{-3} \text{ mol/dm}^3$ in 0.5 M H_2SO_4 with stirring rate of 1500 rpm. Fig. 4.13 shows that the flux of Mn (II) ions increases as the concentration of manganese ions increases from $0.91 \times 10^{-3} \text{ mol/dm}^3$ to $4.55 \times 10^{-3} \text{ mol/dm}^3$ in feed solution that is in accordance with Eq. (19) in section 4.1.1. Nevertheless, on further increasing the concentration of Mn (II) ions in the feed solution, the extraction becomes constant shown by the plateau of plot 4.13. This could be due to that TEA is saturated with manganese ions and extraction is restricted by diffusion of Mn-carrier complexes across the membrane phase [3].

4.1.7 Stability of SLM

One of the drawbacks of SLM is that its efficiency and life time decrease with time; the probable causes may be pore blocking, loss of membrane carrier or solvent by dissolution, formation of emulsion, and osmotic pressure etc. [7, 151-153]. To show durability and stability of polypropylene-TEA-cyclohexanone SLM, it was subjected to a prolonged study up to 168 hours of 7 runs for extraction of Mn (II) ions at optimum experimental conditions, i.e., 1.0 M of H_2SO_4 in feed solution, TEA concentration in SLM at 3.75 M in cyclohexanone, FeSO_4 concentration at $9.25 \times 10^{-3} \text{ mol/dm}^3$ in 0.5 M H_2SO_4 in stripping phase with stirring rate of 1500 rpm. Each run was of 5-hour duration with SLM remained the same one as in the first run and both feed and stripping solutions were replaced with fresh ones after 24 hours before each run. The results show (Fig. 4.14a) that the aforementioned SLM is quite stable and extraction of Mn (II) ions is more than 98% for 168 hours with flux of $2.604 \times 10^{-9} \text{ mol/m}^2\text{s}$. The study was replicated thrice with relative standard deviation $\pm 2\%$.

The chemical stability of polypropylene solid support against TEA-cyclohexanone was confirmed by dipping the support in 3.75 M TEA in cyclohexanone solution for 30 days at 25°C . This solid support was then used for extraction of Mn (II) ions at optimum experimental conditions. The results show (Fig. 4.14b) 99.89% extraction of Mn (II) ions. This experiment was repeated twice with relative standard deviation of $\pm 1.0\%$. This study indicates the stability of liquid membrane (LM) phase as well as integrity and durability of polypropylene film support against TEA-cyclohexanone for 30 days.

4.1.8 Mechanism of Mn Ions Transport

The mechanism of Mn ions transport in the present work is shown in Fig. 4.1. It indicates that association of MnO_4^- and H^+ with TEA molecules to form $(\text{C}_2\text{H}_4\text{OH})_3\text{NH.MnO}_4$ complex at feed membrane interface, which extracts into organic liquid membrane phase. The complex diffuses through the membrane phase to the stripping side and decomposes to release triethanolamine molecules to come back and react again at feed face. The Mn (VII) ions get reduced to break the complex at membrane stripping phase to release Mn (II) ions. H^+ ions also travel in the direction of Mn ions and so the process is coupled co-ion transport system.

4.1.9 Extraction of Mn (II) Ions from Discharged Zinc Carbon Dry Battery Cell Waste

The SLM designed for Mn (II) ion extraction shows efficient transport ability. One of the major applications of manganese is its use in zinc carbon dry battery cell [154]. The optimized SLM was used for recovery of manganese from discharged zinc carbon dry battery cell. Heavy duty 1.5 V, size D, power flash zinc carbon dry battery cell was opened and black powder adjacent to carbon rod was separated. The powder was digested in 1.0 M H_2SO_4 for two hours at room temperature and filtered with Whatman[®]-41 filter paper to remove the residue (carbon powder). 250 cm³ solution of the filtrate was taken as feed solution and oxidized with sodium bismuthate (10% solution) by dropwise addition until pink color was obtained [149], while all other conditions were kept the optimum ones as have already been discussed. The study shows that almost all Mn (II) ions were recovered (Fig. 4.15) from feed solution having flux of $4.998 \times 10^{-9} \text{ mol/m}^2 \cdot \text{s}$.

The stripping results also show that there is no extraction of zinc ions. In stripping phase, both Mn (II) and Fe (III) can be further separated by precipitation. $\text{Fe}(\text{OH})_3$ is precipitated at pH 3 by addition of NaOH, whereas Mn (II) is not precipitated as Mn $(\text{OH})_2$ at this pH [149, 155]. $\text{Fe}(\text{OH})_3$ precipitate can be separated from Mn (II) solution by filtration. Analysis of discharged zinc carbon dry battery cell is shown in Table 4.1.

4.2 Coupled Transport of Tl (III) through Triethanolamine-Xylene-Polypropylene Supported Liquid Membranes

4.2.1 Theory

The supported liquid membrane designed for Tl (III) transport is composed of triethanolamine in xylene loaded in hydrophobic, microporous polypropylene polymeric film.

The thallium iodide, dissolved in hydrochloric acid, ionizes as follows:



TlCl is present in the solution in the ionic form as:



By adding a few drops of bromine water, Tl^+ is oxidized to Tl^{3+} [156].

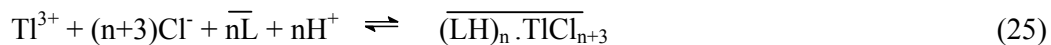


In the presence of hydrochloric acid, the TEA (represented as L) molecules get protonated at the feed membrane interface as indicated below.



Where $n = 1$ to 4 indicating the numbers of proton associated with triethanolamine. Since the triethanolamine molecule has one nitrogen and three oxygen atoms, therefore, maximum protonation up to four protons can occur.

At the feed membrane interface, the following reaction takes place to produce a neutral species extractable into the hydrophobic organic liquid membrane phase:



The “n” represents the numbers of triethanolamine, protons and chloride ions on the reactant side as well as in the complex. The “n” gives the stoichiometry of the complex. The visualized transport mechanism of Ti (III) is shown in Fig. 4.16.

The equilibrium constant of Eq. (25) can be presented as:

$$K_{\text{Ti}} = \frac{[\overline{(\text{LH})_n \cdot \text{TiCl}_{n+3}}]}{[\text{Ti}^{3+}] [\text{Cl}^-]^{n+3} \cdot [\text{H}^+]^n \cdot [\overline{\text{L}}]^n} \quad (26)$$

The distribution coefficient of Ti (III), λ_{Ti} , for distribution between the aqueous and membrane phase can be indicated as:

$$\lambda_{\text{Ti}} = \frac{[\overline{(\text{LH})_n \cdot \text{TiCl}_{n+3}}]}{[\text{Ti}^{3+}]} \quad (27)$$

and Eq. (26) can be written as:

$$K_{\text{Ti}} = \frac{\lambda_{\text{Ti}}}{[\text{Cl}^-]^{n+3} \cdot [\text{H}^+]^n \cdot [\overline{\text{L}}]^n} \quad (28)$$

and on re-arranging Eq. (28), we obtain:

$$\lambda_{\text{Ti}} = K_{\text{Ti}} \cdot [\text{Cl}^-]^{n+3} \cdot [\text{H}^+]^n \cdot [\overline{\text{L}}]^n \quad (29)$$

In the above equations, the brackets indicate the concentration of the given species and overbar represents the species in organic phase.

As per Fick's law, the rate of diffusion of a solute $\frac{dN}{dt}$ (where N is amount of substance and t stands for time), through an area A is known as diffusion flux and given by the symbol J .

$$J = \frac{(1/A) dN}{dt} \quad (30)$$

J is proportional to the concentration gradient $\frac{dc}{dx}$. Since the concentration gradient is

negative in the direction of flux, i.e., $-\frac{dc}{dx}$, thus,

$$J = -D \frac{dc}{dx} \quad (31)$$

Where D represents the diffusion coefficient, dc stands for the concentration difference of the species through a very small section of the membrane thickness, dx , and J represents the flux of species.

It is supposed that the x -axis is perpendicular to the face boundaries of the membrane. Then, at the feed side boundary of the membrane $x = 0$, at the stripping side boundary of the membrane $x = \ell$, and C_{fm} and C_{sm} are the membrane phase concentrations of Tl (III) at feed and stripping side, respectively, as shown in Fig. 4.17. Assuming a linear concentration gradient for Tl (III) within the membrane, one can write:

$$J \propto \frac{C_{fm} - C_{sm}}{\ell} \quad (32)$$

$$\text{Hence, } \frac{C_{fm} - C_{sm}}{\ell} = -\frac{dc}{dx} \quad (33)$$

Eq. (31) then becomes:

$$J = D \frac{C_{fm} - C_{sm}}{\ell} \quad (34)$$

Where, as mentioned earlier, D is the diffusion coefficient. Since distribution coefficient of Tl (III) at the feed membrane interface and stripping membrane interface can be given by λ_f and λ_s respectively, so

$$\lambda_f = \frac{C_{fm}}{C_f} \quad \text{and} \quad \lambda_s = \frac{C_{sm}}{C_s} \quad (35)$$

Where C_f and C_s represent bulk feed and stripping concentrations of Tl (III), respectively.

And on re-arranging Eq. (35), we get:

$$C_{fm} = \lambda_f \cdot C_f \quad \text{and} \quad C_{sm} = \lambda_s \cdot C_s \quad (36)$$

with the help of Eq. (36), Eq. (34) becomes:

$$J = \frac{D (\lambda_f \cdot C_f - \lambda_s \cdot C_s)}{\ell} \quad (37)$$

As there is no transport of metal ions from the stripping solution towards the membrane phase, so $\lambda_s \longrightarrow 0$ and as a result, $\lambda_s C_s \approx 0$ and Eq. (37) is modified to:

$$J = \frac{D \cdot \lambda_f \cdot C_f}{\ell} \quad (38)$$

Here $\lambda_f = \lambda_{TI}$ as given by Eq. (29), thus, Eq. (38) becomes:

$$J = \frac{D \cdot K_{TI} \cdot [Cl^-]^{n+3} \cdot [H^+]^n \cdot [\bar{L}]^n \cdot C_f}{\ell} \quad (39)$$

The diffusion coefficient as per Wilke-Chang:

$$D = \frac{k' \cdot T}{\eta} \quad (40)$$

Where k' is constant, η is the viscosity and T is the absolute temperature, and so,

$$J = \frac{k' \cdot T \cdot K_{TI} \cdot [Cl^-]^{n+3} \cdot [H^+]^n \cdot [\bar{L}]^n \cdot C_f}{\eta \cdot \ell} \quad (41)$$

Since k' and K_{TI} are constants equal to Y , a new constant.

$$\text{Therefore, } J = \frac{Y \cdot T \cdot [Cl^-]^{n+3} \cdot [H^+]^n \cdot [\bar{L}]^n \cdot C_f}{\eta \cdot \ell} \quad (42)$$

Nevertheless, if the concentration of the feed solution does not vary rapidly, then C_f may be taken approximately constant for a short interval.

Taking log of Eq. (42):

$$\log J\eta = \log Y + \log T + (n+3) \log [Cl^-] + n \log [H^+] + n \log [\bar{L}] + \log C_f - \log \ell \quad (43)$$

As Y , T and the thickness (ℓ) of the membrane are constant, so Eq. (43) becomes:

$$\log J\eta = \text{constant} + (n+3) \log [Cl^-] + n \log [H^+] + n \log [\bar{L}] + \log C_f \quad (44)$$

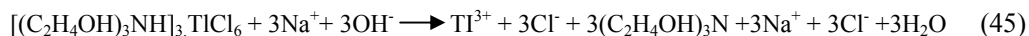
This Eq. (44) shows that flux (J) of metal ions is directly related to feed concentration C_f , $[Cl^-]$, $[H^+]$ and $[L]$ at constant temperature. Eq. (44) can be used to determine “ n ”, the number of H^+ associated with L as LH^{n+} and also that of Cl^- ions as $n+3$. This can be done in different ways; one way for calculating the number of hydrogen ions, is keeping $[Cl^-]$, $[L]$ and C_f constant and plotting $\log J\eta$ versus $\log [H^+]$, the slope of the curve will give the “ n ” value.

4.2.2 Influence of HCl Concentration on Extraction of Tl (III)

$(C_2H_4OH)_3N$ (TEA) possesses lone pairs of electrons at N and O. So there is a possibility of addition of one H^+ on the nitrogen and three protons on oxygen atoms in hydroxyl groups. There are more chances of addition of a proton on N rather than on O atoms, as the electronic charge on latter atoms is attracted by carbon atoms as well. So in $(H\ddot{O}-C_2H_4)_3N^+$ molecule of TEA, the first proton addition may be on N and the molecule becomes positively charged as shown in Fig. 4.18 by charged species I. The second, third and fourth protons, addition will be on $-O-$ atoms and there are possibilities of the charged species II, III, IV of TEA (Fig. 4.18) after attracting acid protons from the feed solution. These charged species (I, II, III & IV) will then associate with thallium anions, formed in Eq. (23f), to form a complex which diffuses to stripping membrane interface and decomposes thus resulting in the transport of Tl (III) ions. The results are presented and discussed in the following paragraph:

To study the influence of HCl concentration on the recovery of Tl (III), concentration range of 0.25 mol/dm^3 to 2.0 mol/dm^3 of HCl was used while keeping the concentration of NaOH in stripping phase at 1.0 mol/dm^3 and that of TEA in membrane phase at 5.26 mol/dm^3 in xylene. Fig. 4.19 indicates that as HCl concentration increases from 0.25 mol/dm^3 to 1.0 mol/dm^3 in feed solution, the extraction of Tl (III) gradually increases from 34.87% to 99.74%. However, by increasing concentration of HCl beyond 1.0 mol/dm^3 , the transport of Tl (III) decreases. The mass balance of Tl (III) was obeyed all the times in feed and stripping solutions (Fig. 4.20 and 4.21), indicating no accumulation of Tl (III) complex in membrane phase. The increase in extraction of Tl (III) may be explained that as the HCl concentration increases from 0.25 mol/dm^3 to 1.0 mol/dm^3 in feed solution, the concentrations of H^+ and Cl^- also increase which enhance the formation of $[TlCl_{n+3}]^{n-}$ and $[LH]^{n+}$ species as per Eq. (23f) and (24), respectively. Due to increased

concentrations of these species, the formation of complex $[(C_2H_4OH)_3NH]_3.TlCl_6$ also increases at the feed membrane interface as per Eq. (25). Due to concentration gradient, the complex then diffuses to stripping membrane interface, where it decomposes due to NaOH in stripping phase releasing Tl (III) in stripping solution. The decomposition reaction of complex will take place as follows:



The decrease in transport of Tl (III) beyond 1.0 mol/dm³ of HCl may be due to the formation of H_nTlCl_{n+3} type species in feed solution (preferentially due to excessive availability of H^+ as well as Cl^-) which inhibited the Eq. (25). Hence, 1.0 mol/dm³ of HCl was found to be the optimum concentration for extraction and transport studies of Tl (III) for the subsequent evaluation of different parameters.

If [TEA] and C_f are kept constant in Eq. (44), a graph of $\log J_n$ against $\log [H]^+$ should be straight line giving the slope equal to “n”, i.e., number of protons associated with TEA. Fig. 4.22 gives a slope of 3.0074, which indicates that three protons are taking part in complexation. The association of three protons with TEA may be either $[(HO-H_4C_2)_3N^+H]_3$ or $[H_2O^+-H_4C_2]_3N$, but due to electronic effects the charge on -OH ions is lowered and so the species $[(HOH_4C_2)_3N^+H]_3$ is more dominant.

4.2.3 Influence of TEA Concentration on Extraction of Tl (III)

To investigate the influence of TEA concentration on extraction of Tl (III), its concentration range from 0.75 mol/dm³ to 7.51 mol/dm³ in xylene was used while keeping the concentrations of HCl and NaOH in feed and stripping solutions at 1.0 mol/dm³, respectively. An experiment was conducted with xylene in the absence of TEA in membrane phase, and found no extraction of Tl (III) even for long time (9 hours) indicating that TEA plays a crucial role in extraction of Tl (III). Fig. 4.23 shows the extraction of Tl (III) with time and it is apparent from this plot that on increasing concentration of TEA from 0.75 mol/dm³ to 5.26 mol/dm³ in xylene, the extraction of Tl (III) increases gradually and becomes maximum, i.e., 1.945×10^{-4} mol/dm³ (99.74%) at 5.26 mol/dm³ of TEA. A further increase in concentration of TEA in xylene, decreases extraction of Tl (III). This could be attributed to reduced diffusion rate of Tl (III) complex inside the membrane due to enhanced friction of the

liquid membrane phase, as with the increase of carrier concentration in diluent, the membrane phase viscosity increases [9].

Similarly the flux variation (Fig. 4.24) indicates that as the concentration of TEA increases, the flux of Tl (III) increases and reaches maximum at 5.26 mol/dm³ of TEA in xylene. Hence, the optimum concentration of carrier for Tl (III) transport is 5.26 mol/dm³ in xylene.

The Eq. (44) was used in plotting of log J_{η} against log [TEA] (Fig.4.25) for determining the number (n) of TEA molecules involved in complexation by using viscosity and flux data of various concentrations of TEA while keeping feed and acid concentrations constant in feed phase. Slope of 3.0057 was calculated, which indicates that three molecules of TEA are involved in transport of Tl (III) ion.

As three protons (discussed in section 4.2.2) and three molecules of triethanolamine are involved in complexation, therefore, it is concluded that complex species of type $[(C_2H_4OH)_3NH]_3.TlCl_6$ is involved in transport of Tl (III). This is also supported by C, H, and N analysis of the complex prepared. According to experimental results, there are 25.02% C, 5.62% H and 4.89% N, whereas theoretically there are 24.91% C, 5.53% H and 4.84% N.

4.2.4 Influence of NaOH Concentration on Extraction of Tl (III)

Strippant plays a significant role at membrane stripping solution interface in the extraction of Tl (III) in the stripping phase as given in Eq. (45). To study the effect of strippant on extraction of Tl (III), concentration range of 0.25 mol/dm³ to 1.75 mol/dm³ of NaOH was used while keeping the concentration of TEA in membrane phase at 5.26 mol/dm³ in xylene and concentration of HCl in feed solution at 1.0 mol/dm³. Fig. 4.26 indicates that flux (J) of Tl (III) increases from 2.262×10^{-10} mol/m².s to 3.548×10^{-10} mol/m².s, as concentration of NaOH increases from 0.25 mol/dm³ to 1.0 mol/dm³. By further increasing the NaOH concentration beyond 1.0 mol/dm³, the transport of Tl (III) decreases. This can be explained that as the NaOH concentration in stripping solution increases, the amount of OH⁻ also increases which enhances the dissociation of the complex, due to stripping of protons from the complex by OH⁻ released from NaOH solution as per Eq. (45). The decrease in transport of Tl (III) beyond 1.0 mol/dm³ of NaOH may be due to Tl (OH)₃ formation,

which is insoluble in excess of NaOH solution [155]. This precipitate may block the pores of membrane and extraction of Tl (III) in stripping phase decreases. By visual inspection of membrane at higher concentration of NaOH ($>1.0 \text{ mol/dm}^3$), brown precipitate was observed on the membrane surface on stripping side. This study reveals that 1.0 mol/dm^3 of NaOH produces sufficient amount of OH^- to remove protons from transported complex, thus, releasing Tl (III) in stripping solution. Hence, the optimum concentration of NaOH as stripping agent is 1.0 mol/dm^3 .

4.2.5 Influence of Tl (III) Concentration in Feed on Extraction of Tl (III)

To investigate the influence of Tl (III) concentration in feed solution on transport of Tl (III) in stripping phase, various concentrations of Tl (III) ranging from $0.978 \times 10^{-4} \text{ mol/dm}^3$ to $4.893 \times 10^{-4} \text{ mol/dm}^3$ in feed solution were used. During this particular study, the concentration of TEA was kept constant at 5.26 mol/dm^3 , the concentrations of HCl and NaOH in feed and stripping phase were fixed at 1.0 mol/dm^3 . Fig. 4.27 shows that flux of Tl (III) increases as concentration of Tl (III) increases in feed solution. This is as per Eq. (44), where flux is directly related to concentration of feed solution. This study shows that for concentration range of $0.978 \times 10^{-4} \text{ mol/dm}^3$ to $4.893 \times 10^{-4} \text{ mol/dm}^3$ of Tl (III) in feed solution, no saturation of the carrier with Tl (III) was observed, by which permeation of metal ion is limited as observed in our previous study for transport of Mn (II) [9].

4.2.6 Influence of Stirring Speed on Extraction of Tl (III)

To study the influence of stirring speed on extraction of Tl (III), stirring speed was varied from 800 rpm to 2000 rpm while other experimental conditions were kept at the optimum values. The Fig. 4.28 indicates that the recovery of Tl (III) increases as stirring speeds in bulk feed and stripping solutions increase from 800 rpm to 1500 rpm. Though, the extraction becomes constant at stirring speed of 1500 rpm to 1600 rpm and then it decreases as stirring speed increases beyond 1600 rpm. This can be explained that as stirring speed increases, the diffusion layer thickness on membrane feed and stripping faces decreases and results in increase in transport of Tl (III). However, by increasing stirring speed ($>1600 \text{ rpm}$), some carrier molecules may come out from pores of membrane decreasing transport of Tl (III). Hence, 1500 rpm

was considered the suitable stirring speed for this SLM system and subsequent studies were performed with this stirring speed.

4.2.7 Influence of Temperature on Extraction of Tl(III)

To study the influence of temperature on recovery of Tl(III), temperature was varied from 17 °C to 31 °C and during this study all other conditions were kept at the optimum values as already mentioned. It is observed (Fig. 4.29) that as the temperature increases, the flux of Tl(III) also increases. As per kinetic theory, with the increase in temperature, the molecules move faster and so the diffusion of Tl(III) complex increases [150]. This is also as per Eq. (43), where flux is directly related to temperature (T). This study reveals that temperature increases the flux of Tl(III).

4.2.8 Residence Time of Tl(III)

To study the residence time of Tl(III), an experiment was performed at optimum experimental conditions, i.e., concentration of triethanolamine in membrane phase at 5.26 mol/dm³, concentration of HCl and NaOH in feed and stripping solutions, respectively, at 1.0 mol/dm³ and stirring rate at 1500 rpm. Fig. 4.30 shows that Tl(III) has very low residence time and, after 5 seconds, its concentration starts decreasing in feed solution. It indicates that complex formation reaction at the feed membrane face is very fast. This study shows that this SLM system is very efficient and effective for transport of Tl(III).

4.2.9 Membrane System Constraints

In most of the SLM systems, membrane stability has been considered a major problem [151]. In the present case, the membrane was found reasonably stable for low concentration of Tl(III). The other constraint, in the present process, is precipitation of Tl(III) as Tl(OH)₃ beyond a concentration of 1.0 mol/dm³ of NaOH. Decrease in the extraction of Tl(III) was observed at concentration greater than 5.26 mol/dm³ of TEA due to high viscosity of liquid membrane phase. Boundary layer may be formed at the membrane faces if stirring speed is less than 1500 rpm. To overcome these constraints, this SLM system should be run at optimized conditions.

4.2.10 SLM Stability

To investigate durability and stability of TEA-xylene-propylene SLM, an experiment was performed for 192 hours of 8 runs at optimum experimental conditions. An extraction was carried out after every 24-hours period keeping the SLM as the same as in first run, but the feed and stripping solutions were replaced before every run. Each run was of 4-hour duration. The results were reproducible even after 192 hours and extraction capability was greater than 99% (Fig. 4.31) for each run. The study was replicated thrice with relative standard deviation of $\pm 3\%$.

To study the chemical durability and stability of polypropylene solid support against TEA-xylene, it was dipped in 5.26 mol/dm^3 of TEA in xylene for 60 days at 25°C . The support was then used for transport of Tl (III) at optimum experimental conditions. The results of this study are presented in Fig. 4.32. It can be noted from this figure that the extraction of Tl (III) is $1.939 \times 10^{-4} \text{ mol/dm}^3$ which is 99.43% of the original amount of Tl (III). The experiment was replicated twice with relative standard deviation of $\pm 1\%$. These studies indicate the stability of liquid membrane (LM) phase, as well as durability of polypropylene solid support against TEA-xylene for 60 days and it can be scaled up to industrial or commercial level.

4.2.11 Recovery of Tl (III) from Coal Ash

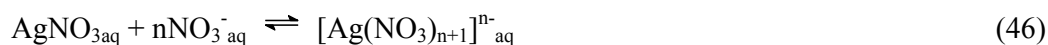
After establishing the optimum conditions for Tl (III) extraction, this SLM was used to extract Tl (III) from coal ash. The local coal was ignited in muffle furnace at $1100 \pm 5^\circ\text{C}$ and allowed to cool in a desiccator to room temperature. The ash was digested in 1.0 mol/dm^3 of HCl for 10 hours and filtered with Whatman[®]-41 filter paper to remove the residue. The filtrate was diluted up to 250 cm^3 with 1.0 mol/dm^3 of HCl and used as feed solution, keeping all other conditions at the optimum level as described earlier. The experiment shows that almost all Tl (III) along with nickel, chromium and zinc ions are transported in stripping phase in 110 minutes as shown in Table 4.2.

4.3 Transport of Ag (I) through Tri-n-dodecylamine Supported Liquid Membranes

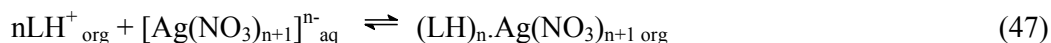
4.3.1 Theory

In this study, the liquid membrane is made of tri-n-dodecylamine (TDDA) in cyclohexane, supported in microporous polymeric polypropylene film. Being hydrophilic, Ag (I) cannot go into the liquid membrane organic phase directly and, hence, the direct transport of silver ions across the liquid membrane is impossible.

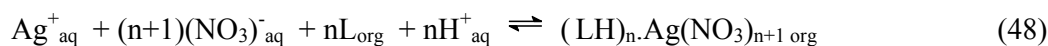
Tri-n-dodecylamine may be indicated as L. The TDDA that is basic carrier and its pK_a value is 11.3 [157]. The TDDA at the feed membrane interface may be protonated to LH^+ in acidic medium as nitrogen atom of TDDA has lone pair of electrons. It is assumed that in the presence of HNO_3 in feed phase, the silver nitrate is converted to $[Ag(NO_3)_{n+1}]^{n-}$ [81].



The species LH^+ and $[Ag(NO_3)_{n+1}]^{n-}$ then react at the feed membrane interface to form the complex as per following equation:



The subscripts org. and aq. stand for the organic and aqueous phases, respectively. To show the contribution of H^+ and NO_3^- , Eq. (47) may be indicated as:



The visualized transport mechanism of Ag (I) is shown in Fig. 4.33, in which H^+ , NO_3^- and Ag (I) move in the same direction towards stripping phase. The complex formed as per Eqs. (47/48), diffuses from feed membrane interface into liquid membrane phase and then diffuses to membrane stripping interface due to concentration gradient. The complex dissociates at membrane stripping interface due to the presence of $NH_{3(aq)}$ in stripping phase and forms $[Ag(NH_3)_2]^+$ [157]. The free carrier diffuses backside to feed membrane interface, and net result is the extraction of Ag (I) from feed solution into stripping solution.

Equilibrium constant for Eq. (48) can be written as:

$$K_{Ag} = \frac{[(LH)_n \cdot Ag(NO_3)_{n+1}]_{org}}{[Ag^+]_{aq} \cdot [NO_3^-]_{aq}^{n+1} \cdot [H^+]_{aq}^n \cdot [L]_{org}^n} \quad (49)$$

The distribution coefficient of Ag (I), (λ_{Ag}), for distribution between the membrane and aqueous phase can be given as:

$$\lambda_{Ag} = \frac{[(LH)_n \cdot Ag(NO_3)_{n+1}]_{org}}{[Ag^+]_{aq}} \quad (50)$$

Eq. (49) can be represented as:

$$K_{Ag} = \frac{\lambda_{Ag}}{[NO_3^-]_{aq}^{n+1} \cdot [H^+]_{aq}^n \cdot [L]_{org}^n} \quad (51)$$

and on re-arranging Eq. (51), we get:

$$\lambda_{Ag} = K_{Ag} \cdot [NO_3^-]_{aq}^{n+1} \cdot [H^+]_{aq}^n \cdot [L]_{org}^n \quad (52)$$

The activities of the species involved in transport are indicated by brackets. The reactions of complex formation on the feed side and complex dissociation on the stripping side are believed, to be very fast. Hence, the transport of Ag (I) through the SLM by diffusion is assumed to be the rate controlling step. According to the Fick's law:

$$J = \frac{(1/A) dN}{dt} \quad (53)$$

Where N is amount of substance and t stands for time for transport. Following the same route as that for Tl (III), the flux J is presented as:

$$J = \frac{D (\lambda_f \cdot C_f - \lambda_s \cdot C_s)}{\ell} \quad (54)$$

Where λ_f and λ_s represent the distribution coefficients of Ag (I) at the membrane surface on feed and stripping side, respectively. The C_f and C_s indicate the bulk feed and stripping concentrations of Ag (I), respectively.

The permeability coefficient p is related to the distribution coefficient and diffusion coefficient (D) as:

$$p = D\lambda \quad (55)$$

If, $\lambda_f = \lambda_s$, then

$$J = \frac{p (C_f - C_s)}{\ell} \quad (56)$$

As no transport of Ag (I) from the stripping phase into the membrane phase occurs, therefore, λ_s becomes zero and Eq. (54) transforms to:

$$J = \frac{D \cdot \lambda_f \cdot C_f}{\ell} \quad (57)$$

$\lambda_f = \lambda_{Ag}$ as given by Eq. (52), therefore,

$$J = \frac{D \cdot K_{Ag} \cdot [\text{NO}_3^-]_{\text{aq}}^{n+1} \cdot [\text{H}^+]_{\text{aq}}^n \cdot [\text{L}]_{\text{org}}^n \cdot C_f}{\ell} \quad (58)$$

The diffusion D as per Wilke - Chang relation [9]:

$$D = \frac{k' \cdot T}{\eta} \quad (59)$$

Where η is viscosity, k' is constant and T is the absolute temperature. Proceeding in the same way as for Tl(III), we get the final equation:

$$\log J\eta = \frac{\text{constant} + (n+1) \log \left[(\text{NO}_3^-)_{\text{aq}} \right] + n \log [\text{H}^+]_{\text{aq}} + n \log [\text{L}]_{\text{org}} + \log C_f}{\ell} \quad (60)$$

The Eq. (60) can be used to determine the stoichiometry of the complex formation, by studying the influence of only one parameter while keeping the others constant.

This can be done in different ways; one way is to keep $[\text{NO}_3^-]$, $[\text{L}]$, ℓ and C_f constant and plot $\log J\eta$ against $\log [\text{H}^+]$, the slope of the curve will give the “n” value, for the number of H^+ . Likewise, by keeping $[\text{NO}_3^-]$, $[\text{H}^+]$, ℓ and C_f constant, the slope of $\log J\eta$ versus $\log [\text{L}]$ will give number of molecules of tri-n-dodecylamine taking part in complexation.

4.3.2 Effect of TDDA Concentration

To study the effect of concentration of TDDA on transport of Ag (I), various concentrations of TDDA, ranging from 0.158 M to 1.261 M, were used in organic membrane phase. During this study, the concentration of AgNO_3 was kept at $7.42 \times 10^{-4} \text{ mol/dm}^3$ in 0.75 mol/dm³ of HNO_3 in feed solution and concentration of $\text{NH}_3(\text{aq})$ was fixed at 1.0 mol/dm³ in stripping solution.

Fig. 4.34 indicates the influence of carrier concentration on transport of Ag (I) into stripping phase with respect to time. This figure shows that recovery of Ag (I) increases from 46.49% to 98.65%, as the TDDA concentration increases from 0.158 M to 0.788 M in membrane phase. The extraction of Ag (I) decreases by increasing the concentration of TDDA beyond 0.788 M. Similar trend in the increase and then decrease for permeability (p) and flux (J) of Ag (I) was also observed for various concentrations of TDDA as shown in Fig. 4.35.

As expected and according to Eq. (60) that as the TDDA concentration increases in membrane phase so does the flux of Ag (I). This is because more numbers of TDDA interact with H^+ to form LH^+ , which on reacting with anions $([\text{Ag}(\text{NO}_3)_{n+1}]^{n-})$, enhances the formation of complex. The increase in metal ion transport with increasing carrier concentration has already been reported in literature for similar type of carrier [119, 120].

The decrease in transport of Ag (I) beyond 0.788 M of TDDA could be explained by the increase in the viscosity of the liquid membrane phase. As the concentration of TDDA increases in cyclohexane, viscosity of liquid membrane also increases. The viscosity of various compositions of TDDA is shown in Fig.4.36. The diffusion coefficient of the solute through the liquid membrane is given by the Stokes–Einstein equation [158] as follows:

$$D = \frac{kT}{6\eta\pi r} \quad (61)$$

Where T is the absolute temperature, k is the Boltzmann constant, r is the ionic radius of the metal ion and η is the viscosity of the organic phase in centipoise (cP) equilibrated with the aqueous phase. Since viscosity is inversely proportional to diffusivity, that is why diffusion coefficient of complex $(LH)_n \cdot Ag(NO_3)_{n+1}$ in membrane phase decreases, and results in decrease in extraction of Ag (I). The decrease in metal ion transport with increasing viscosity of liquid membrane phase has already been observed for Mn (II), W (VI) and Pd (II) transport [119, 120, 159]. Hence, 0.788 M of TDDA was considered to be the optimum concentration for extraction of Ag (I) for subsequent optimization of various parameters.

The number (n) of TDDA (L), involved in formation of complex of $(LH)_n \cdot Ag(NO_3)_{n+1}$, can be determined by plotting $\log J\eta$ against $\log [TDDA]$ as indicated in Fig.4.37. The slope of the graph was 1.0023 which means that one molecule of TDDA is involved in the complex formation.

4.3.3 Effect of HNO₃ Concentration in Feed Solution

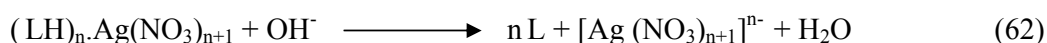
HNO₃ plays a significant role in the transport of Ag (I) as it provides H⁺ and NO₃⁻ for the formation of LH⁺ and $[Ag(NO_3)_{n+1}]^{n-}$, respectively. During this study, the HNO₃ concentration in feed solution was varied from 0.25 mol/dm³ to 1.25 mol/dm³, while concentration of TDDA in membrane phase and that of NH_{3(aq)} in stripping phase were fixed at 0.788 M and 1.0 mol/dm³, respectively. Fig. 4.38 shows that the flux of Ag (I) increases from 4.682×10^{-10} mol/m².s to 8.901×10^{-10} mol/m².s with increase in the concentration of HNO₃ from 0.25 mol/dm³ to 0.75 mol/dm³ and reaches maximum at 0.75 mol/dm³ of HNO₃. This behavior is as per Eq. (60), where flux is directly related to [H⁺]. Further increase in concentration of HNO₃ beyond 0.75 mol/dm³ results in decrease in the flux of Ag (I). This can be attributed to the formation of $H_n Ag(NO_3)_{n+1}$ instead of $(LH)_n \cdot Ag(NO_3)_{n+1}$ due to large number of H⁺ and NO₃⁻, thus, Eq. (46) is inhibited in forward direction. Therefore, 0.75 mol/dm³ of HNO₃ in feed solution was considered as the optimum concentration for transport of Ag (I) for this SLM system.

To study the number of H^+ in the proposed complex, $(LH)_n \cdot Ag(NO_3)_{n+1}$, Eq. (60) was used for plotting $\log J_\eta$ against $\log [HNO_3]$ as indicated in Fig. 4.39. The slope of 1.0013 indicates that one mole of H^+ is involved in complex formation.

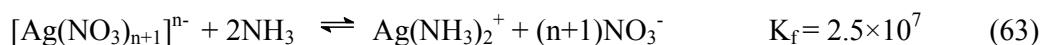
To investigate the transport of H^+ , feed solution pH was measured after regular intervals of time as shown in Fig. 4.40. Increase in the feed solution pH was observed up to 2.1, which suggests that protons of feed solution are being utilized by carrier (TDDA) molecules to form LH^+ species at feed membrane interface. An experiment was conducted to show the transport of H^+ in the absence of $Ag(NO_3)_{aq}$ in feed solution at optimum experimental conditions. Since no change in the pH of the feed and stripping solutions was observed, therefore, it could be safely said that no transport of H^+ from feed solution towards the stripping solution takes place.

4.3.4 Effect of Stripping Phase Concentration

$NH_{3(aq)}$ was used as strippant with different concentrations ranging from 0.25 mol/dm³ to 1.5 mol/dm³ whereas the concentration of HNO_3 was kept at 0.75 mol/dm³ in feed solution and that of TDDA at 0.788 M in membrane phase. It was found that in the absence of strippant, no extraction of Ag (I) was observed even after conducting the experiment for long time (8 hours). This indicates that strippant plays a very significant role in the extraction of Ag (I). The Fig. 4.41 manifests, that as the $NH_{3(aq)}$ concentration increases, the permeability of Ag (I) also increases and touches maximum at 1.0 mol/dm³ of $NH_{3(aq)}$. The extraction phenomenon with $NH_{3(aq)}$ can be explained by the following two reasons: Firstly, the OH^- of $NH_{3(aq)}$ can react with the H^+ of the complex $(LH)_n \cdot Ag(NO_3)_{n+1}$, which was formed in accordance with Eq. (48), and it results in the decomposition of complex in the reverse way as shown below.



Secondly, the free NH_3 of $NH_{3(aq)}$ can react with $[Ag(NO_3)_{n+1}]^{n-}$ and can form soluble diammine-argentate complex ion [157, 160].



To investigate the transport of H^+ towards stripping solution, the pH of the stripping solution was measured. The stripping solution pH at the start of the experiment, at optimum conditions, was 10.55 while after 4 hours the pH decreased to 9.08. This decrease in pH may be due to that OH^- ions of $NH_{3(aq)}$ are consumed in the neutralization of H^+ of the complex, $(LH)_n.Ag(NO_3)_{n+1}$, as per Eq. (62).

4.3.5 Effect of Ag (I) Concentration in Feed Solution

To investigate the effect of Ag (I) concentration on transport of Ag (I), concentration range of $3.71 \times 10^{-4} \text{ mol/dm}^3$ to 22.26×10^{-4} of Ag (I) was used in feed solution. During this study, the concentration of HNO_3 in feed solution was adjusted at 0.75 mol/dm^3 , $NH_{3(aq)}$ in stripping solution at 1.0 mol/dm^3 and TDDA in membrane phase at 0.788 M. As shown in Fig. 4.42, that flux of Ag (I) increases from $4.463 \times 10^{-10} \text{ mol/m}^2.s$ to $26.788 \times 10^{-10} \text{ mol/m}^2.s$ as the concentration of Ag (I) increases from $3.71 \times 10^{-4} \text{ mol/dm}^3$ to $22.26 \times 10^{-4} \text{ mol/dm}^3$ in feed solution. This behavior is in accordance with Eq. (60), where flux is directly proportional to feed concentration (C_f). No metal loading behavior for carrier up to the concentration of $22.26 \times 10^{-4} \text{ mol/dm}^3$ of Ag (I) in feed solution was observed. This phenomenon is contrary to our earlier observation [9] with triethanolamine SLM, where transport of Mn (VII) was limited due to carrier loading effect.

4.3.6 Effect of Membrane Thickness on Transport of Ag (I)

To study the influence of membrane thickness on transport of Ag (I), three microporous hydrophobic membranes of Celgard 2500, 2502 and 4400 were used. The specifications of the membranes are given in Table 3.1. The Table 4.3 shows that the flux of Ag (I) decreases as thickness of membrane film increases. The Celgard 4400 membrane with the highest thickness shows the lowest flux of $7.231 \times 10^{-10} \text{ mol/m}^2.s$. These results are in accordance with the proposed theoretical model shown in Eq. (60), where the flux is inversely related to the thickness of membrane. The decrease in Ag (I) transport with membrane thickness is comparable with the earlier reported results for supported liquid membranes [94, 106, 114].

4.3.7 SLM Stability

The SLM is one of the most useful techniques for transport and recovery of metal ions; nevertheless, its applications were limited for two decades due to instability problems. The major degradation causes are: shear induced emulsion formation in membrane phase, membrane pore blocking by precipitation of the complex, solubility of species from the feed and stripping solutions and organic membrane phase, osmotic pressure and wettability of support pores by aqueous phase [8, 152, 153].

To study the long term stability of this SLM, it was impregnated once with 0.788 M of TDDA in cyclohexane and used for 5 runs. Each run was of 4-hour duration and time interval between successive runs was of 24 hours. Fig.4.43 shows that flux is consistent for continuous operation of 120 hours and recovery of Ag^+ for each run was more than 98%. The study replicated twice with relative standard deviation of $\pm 1\%$. This study indicates that this SLM configuration is quite stable and can be scaled up at industrial level.

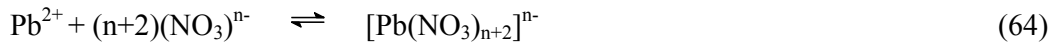
4.3.8 Recovery of Silver from Silver Plating and Photographic Waste Solution

The tri-n-dodecylamine SLM has the most effective transport ability for Ag (I). To show practical utilization of this SLM system, it was used for the extraction of Ag (I) from silver plating and photographic waste solutions. The conditions used for the recovery of Ag (I) were: 0.75 mol/dm^3 of HNO_3 in feed solution, 0.788 M of TDDA in membrane phase and 1.0 mol/dm^3 of $\text{NH}_{3(\text{aq})}$ in stripping solution. Table 4.4 shows almost complete extraction of Ag (I) from silver plating waste solution. To confirm further application of this technique, the optimized SLM was used for recovery of Ag (I) from photographic waste solution. The results indicate that only silver is transported which show the selectivity and efficiency of this method for silver recovery. The compositions of silver plating and photographic waste solutions are shown in Table 4.4.

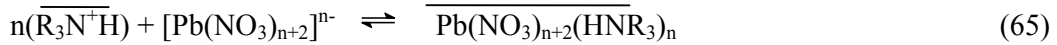
4.4 Coupled Transport of Pb (II) through TOA-Xylene-Polypropylene Supported Liquid Membranes

4.4.1 Theory

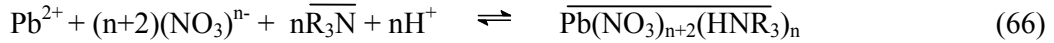
Tri-n-octylamine (TOA) may be indicated as R_3N , where R represents the octyl group. The R_3N molecules at the feed membrane interface may be protonated as R_3N^+H in the presence of HNO_3 . The Pb (II) in feed solution is converted to nitrate complex $[Pb(NO_3)_{n+2}]^{n-}$ in presence of excess nitrate ions, from nitric acid, as per following equation suggested by Inoue and Baba [161].



The species R_3N^+H and $[Pb(NO_3)_{n+2}]^{n-}$ then react at feed membrane interface to form the complex as indicated in the Eq. (65). The schematic representation of the transport mechanism of Pb (II) is shown in Fig. 4.44.



To show the contribution of NO_3^- and H^+ , the Eq. (65) may be expressed as:



Equilibrium constant, K_{pb} , using Eq. (66) for Pb (II) can be related as:

$$K_{pb} = \frac{[\overline{Pb(NO_3)_{n+2}(HNR_3)_n}]}{[Pb^{2+}] \cdot [(NO_3)^{n-}]^{n+2} \cdot [\overline{R_3N}]^n \cdot [H^+]^n} \quad (67)$$

The brackets indicate the concentration and the overbar represents the species in liquid membrane phase.

The Pb (II) distribution coefficient (λ_{pb}) for distribution between the aqueous phases and membrane can be represented as:

$$\lambda_{pb} = \frac{[\overline{Pb(NO_3)_{n+2}(HNR_3)_n}]}{[Pb^{2+}]} \quad (68)$$

Eq. (67) can be re-written as:

$$K_{Pb} = \frac{\lambda_{Pb}}{\left[\left(NO_3 \right)^{n-} \right]^{n+2} \cdot \left[\overline{R_3N} \right]^n \cdot \left[H^+ \right]^n} \quad (69)$$

$$\text{or } \lambda_{Pb} = K_{Pb} \cdot \left[\left(NO_3 \right)^{n-} \right]^{n+2} \cdot \left[\overline{R_3N} \right]^n \cdot \left[H^+ \right]^n \quad (70)$$

As the concentration of Pb (II) in this study was very low (4.826×10^{-4} mol/dm³), therefore, the concentrations were taken as activities in the calculations [81,101].

The flux J of Pb (II), assuming the Fick's law holds:

$$J = \frac{D \cdot \epsilon (\lambda_f \cdot C_f - \lambda_s \cdot C_s)}{\ell} \quad (71)$$

Where D is the diffusion coefficient, ϵ is the porosity of membrane, ℓ is the thickness of the membrane, λ_f and λ_s represent the distribution coefficients of Pb (II) at the membrane surface in the feed side and stripping side, respectively, and C_f and C_s represent bulk feed and stripping concentration of Pb (II), respectively.

$$\lambda_f = \frac{C_{fm}}{C_f} \quad \text{and} \quad \lambda_s = \frac{C_{sm}}{C_s} \quad (72)$$

The diffusion coefficient (D), temperature and the viscosity (η), are related as per Wilke-Chang relation as:

$$D = \frac{k' \cdot T}{\eta} \quad (73)$$

Following the same route as shown for the extraction of Tl (III), the final equation will be:

$$J = \frac{A' \cdot T \cdot \left[\left(NO_3 \right)^{n-} \right]^{n+2} \cdot \left[\overline{R_3N} \right]^n \cdot \left[H^+ \right]^n \cdot C_f}{\eta \cdot \ell} \quad (74)$$

However, if C_f does not change considerably during the course of the process, then it may be taken as constant for a short interval.

Taking logarithm of Eq. (74), we get,

$$\log J\eta = \log A' + \log T + (n+2) \log \left[(\text{NO}_3)^{n-} \right] + n \log [\overline{\text{R}_3\text{N}}] + n \log [\text{H}^+] + \log C_f - \log \ell \quad (75)$$

As A' , T , and the thickness ℓ of the membrane are constant, Eq. (75) can be expressed as:

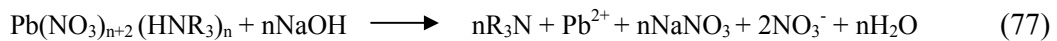
$$\log J\eta = \text{constant} + (n+2) \log \left[(\text{NO}_3)^{n-} \right] + n \log [\overline{\text{R}_3\text{N}}] + n \log [\text{H}^+] + \log C_f \quad (76)$$

The Eq. (76) indicates that flux of Pb (II) is directly related to feed concentration C_f , $[\text{NO}_3^-]$, $[\overline{\text{R}_3\text{N}}]$ and $[\text{H}^+]$ at constant temperature. The stoichiometry of the complex formation at the feed membrane interface can be calculated by using Eq. (76). The number of H^+ or triethanolamine can be calculated by plotting $\log J\eta$ versus $\log [\text{H}^+]$ or $\log J\eta$ against $\log [\text{R}_3\text{N}]$, respectively, while keeping other parameters constant.

4.4.2 Effect of TOA Concentration on Extraction of Pb (II)

To study the influence of TOA on extraction of Pb (II), various concentrations of TOA ranging from 0.174 M to 1.395 M in xylene were used. During this study, the HNO_3 concentration in feed solution was kept at 0.2 mol/dm^3 , NaOH concentration in stripping phase at 0.2 mol/dm^3 and Pb (II) concentration in feed solution at $4.826 \times 10^{-4} \text{ mol/dm}^3$.

Nitrogen atom of TOA has a lone pair of electron and it can be protonated to $\text{R}_3\text{N}^+\text{H}$ at feed membrane interface, which can then associate with $[\text{Pb}(\text{NO}_3)_{n+2}]^{n-}$ anion and form a complex of $\text{Pb}(\text{NO}_3)_{n+2}(\text{HNR}_3)_n$ as per Eq. (65). Due to the concentration gradient, this complex then diffuses into the membrane phase from where it diffuses to membrane stripping interface. The complex at membrane stripping interface dissociates, due to NaOH in stripping phase, and results in the release of Pb (II) in stripping solution according to the following reaction:



Figs. 4.45 and 4.46 indicate the recovery of Pb (II) with time, and it can be seen that the extraction increases gradually as the concentration of TOA increases from 0.174 M to 0.872 M. These results are in accordance with Eq. (66), although the extraction of Pb (II) decreases by increasing the concentration of TOA above 0.872 M. The similar trend of an increase and then decrease in flux (J) was also observed for various TOA concentrations (Fig. 4.47). The decrease in extraction of Pb (II) could be due to enhanced friction of membrane phase due to its high viscosity as viscosity of membrane phase increases with increasing carrier concentration [9, 162]. The viscosity of TOA in xylene is shown in Fig. 4.48. As viscosity is inversely proportional to diffusivity, that is why diffusion coefficient of complex, $\text{Pb}(\text{NO}_3)_{n+2}(\text{HNR}_3)_n$, in membrane phase decreases, and results in decrease in extraction of Pb (II). Hence, 0.872 M of TOA has been found to be the optimum concentration for extraction and transport study of Pb (II) for the subsequent investigations to evaluate different parameters.

The plot of $\log J\eta$ against $\log [\text{TOA}]$ (Fig. 4.49) gives a slope of 2.002, which means that in complex formation two molecules of TOA are involved. Hence, in the proposed complex, $[\text{Pb}(\text{NO}_3)_{n+2}(\text{HNR}_3)_n]$, the number “n” of TOA (R_3N) responsible for transport of Pb (II) is two.

4.4.3 Effect of HNO_3 Concentration in Feed Solution on Extraction of Pb (II)

HNO_3 plays significant role in extraction of Pb (II), because it provides H^+ for protonation of TOA and NO_3^- for formation of $[\text{Pb}(\text{NO}_3)_{n+2}]^{n+}$. To investigate the influence of HNO_3 concentration in feed solution on extraction of Pb (II), various concentrations of HNO_3 ranging from 0.05 mol/dm³ to 0.30 mol/dm³ were employed, while keeping concentration of NaOH in stripping phase at 0.2 mol/dm³, concentration of TOA in membrane phase at 0.872 M and Pb (II) concentration in feed solution at 4.826×10^{-4} mol/dm³.

Fig. 4.50 shows that extraction of Pb (II) increases as the concentration of HNO_3 increases from 0.05 to 0.2 mol/dm³; this could be due to sufficient concentrations of H^+ and NO_3^- which shift the equilibrium Eq. (66) to the right and ultimately result in increase in the flux of Pb (II). However, by further increasing in concentration of HNO_3 beyond 0.2 mol/dm³, the recovery of Pb (II) gradually decreases. This could be

due to formation of $H_n.Pb(NO_3)_{n+2}$ type species due to excessive amount of H^+ and NO_3^- in feed solution and reaction (66) is inhibited [9, 163]. This study indicates that 0.2 mol/dm^3 of HNO_3 is the optimum concentration for this SLM system for recovery of Pb (II).

To find the number of H^+ involved in complex formation, Eq. (76) was used for plotting $\log J_n$ versus $\log [HNO_3]$ while keeping feed and TOA concentrations constant. Slope calculated from Fig. 4.51 is 2.007, which indicates that two moles of H^+ are involved for one mole of complex formation.

To investigate the transfer of H^+ towards the stripping phase, the pH of feed solution was measured at regular intervals as shown in Fig. 4.52. It can be seen that feed solution pH increases with time; this is due to protonation of trioctylamine at feed membrane interface and transport of H^+ coupled with Pb (II) to the stripping phase through the membrane. Thus, the transport of Pb (II) follows proton co-ion coupled type transport mechanism.

4.4.4 Effect of Stripping Phase Composition on Extraction of Pb (II)

Strippant plays a crucial role in the extraction of metal ion from liquid membrane phase into stripping phase. Three strippants (CH_3COONH_4 , Na_2SO_4 and $NaOH$) with different compositions and similar conditions were employed to extract Pb (II) from membrane phase as shown in Table 4.5. The composition and nature of stripping phase were found to have a considerable effect on the extraction of Pb (II). The Table 4.5 shows that $NaOH$ is the most suitable strippant of these three with more than 99% recovery of Pb (II) at 0.2 mol/dm^3 . This study proves that 0.2 mol/dm^3 of $NaOH$ furnishes sufficient number of OH^- to neutralize H^+ in complex, $Pb(NO_3)_4(HNR_3)_2$, by dissociation reaction shown in Eq. (77). Thus, 0.2 mol/dm^3 of $NaOH$ was selected as the suitable strippant for transport of Pb (II). The diffusion coefficient of Pb (II), at optimum conditions for this SLM system, was found as $1.349 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$.

To investigate the pH variation of $NaOH$ stripping solution, it was measured at optimum experimental conditions. The pH of the stripping solution at the start of the experiment was 13.1 but after 4.5 hours it was decreased to 11.30. This decrease in pH indicates that OH^- of $NaOH$ have been consumed by the neutralization of H^+ of the complex.

4.4.5 Effect of Pb (II) Concentration in Feed Solution on Extraction of Pb (II)

To study the effect of Pb (II) in feed solution on recovery of Pb (II) in stripping phase, concentration range of Pb (II) from 0.963×10^{-4} mol/dm³ to 14.47×10^{-4} mol/dm³ in feed solution was used, while keeping the NaOH concentration in stripping phase at 0.2 mol/dm³, TOA concentration in membrane phase at 0.872 M in xylene and HNO₃ concentration in feed solution at 0.2 mol/dm³. Fig. 4.53 shows that flux (J) of Pb (II) increases as the concentration of Pb (II) increases from 0.965×10^{-4} mol/dm³ to 10.62×10^{-4} mol/dm³ in feed solution and that is in accordance with Eq. (76). However, extraction of Pb (II) becomes approximately constant by further increasing Pb (II) concentration in the feed solution which is shown by the plateau of plot 4.53. The limiting extraction of Pb (II) could be attributed to the saturation of TOA with Pb (II) and, thus, the transport of lead-carrier complexes becomes only diffusion-controlled through membrane phase. This effect has been reported in the literature as carrier-metal loading effect [9, 148].

4.4.6 SLM Stability

The stability of SLM is one of the most important key factors for industrial and commercial applications for long-term use. The SLM may have a limited application due to liquid membrane instability problem. The major degradation or instability causes are: pressure difference across the membrane, pore blocking of membranes by precipitation of carrier complex, possibility of emulsion formation in membrane phase, solubility of carrier or solvent in aqueous phases, and progressive wettability of the support pores by both feed and aqueous phases, causing the displacement of organic phase from membrane pores [7, 152].

To study the long term stability of this SLM configuration, the polypropylene support was impregnated with 0.872 M of TOA in xylene only once and then used for 10 runs (240 hours). All other conditions were kept at the optimum level as recorded during this study. Each run was of 4.5-hour duration and time interval between the successive runs was 24 hours. For each new run, both the feed and stripping compartments were filled with the fresh solutions. Flux for each run was almost the same and the extraction of each run was more than 99%. The study was replicated thrice with relative standard deviation of $\pm 1.5\%$.

4.4.7 Extraction of Pb (II) from Paint and Industrial Stream Water

The purpose of this study is to design and optimize SLM for transport of Pb (II) and extend its application for recovery of Pb (II) from paint and industrial water contaminated with lead. 0.5 g of typical local paint was taken in washed and dried platinum crucible and ignited in furnace at 700 °C for three hours. The ash was then allowed to cool in a desiccator up to room temperature. Ash was digested in 0.2 mol/dm³ of HNO₃ and filtered with Whatman®-41 filter paper. The filtrate was diluted up to 250 cm³ by 0.2 mol/dm³ HNO₃ and used as feed keeping all other conditions at the optimum level as already mentioned. Table 4.6 shows that almost all lead ions are extracted with chromium and zinc ions.

To show further practical utilization of this method, the optimized SLM configuration was then applied to stream water passing through an industrial area. The results (Table 4.6) indicate the complete recovery of lead along with the zinc, copper, and chromium ions.

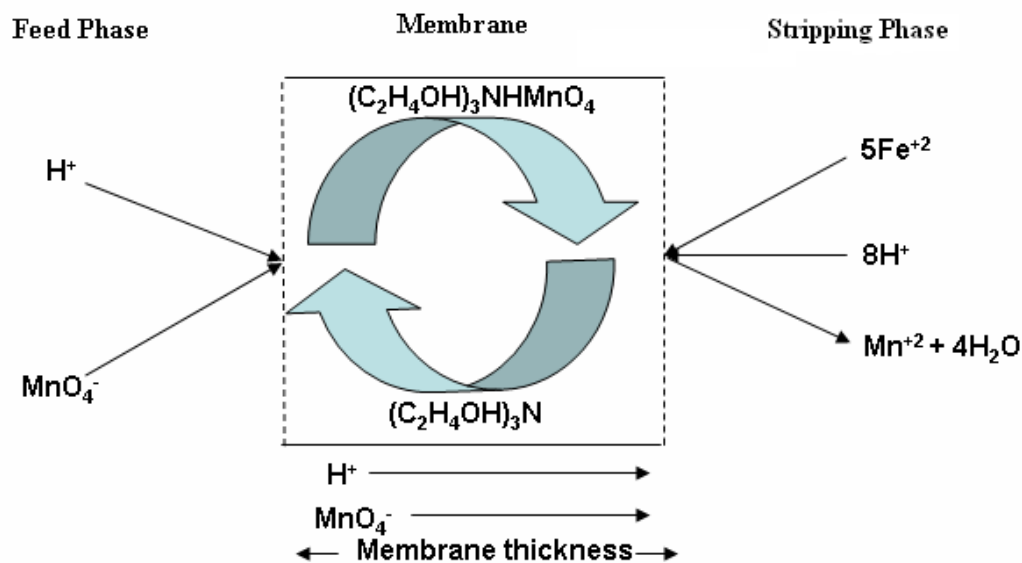


Fig. 4.1 Transport mechanism of Mn (II).

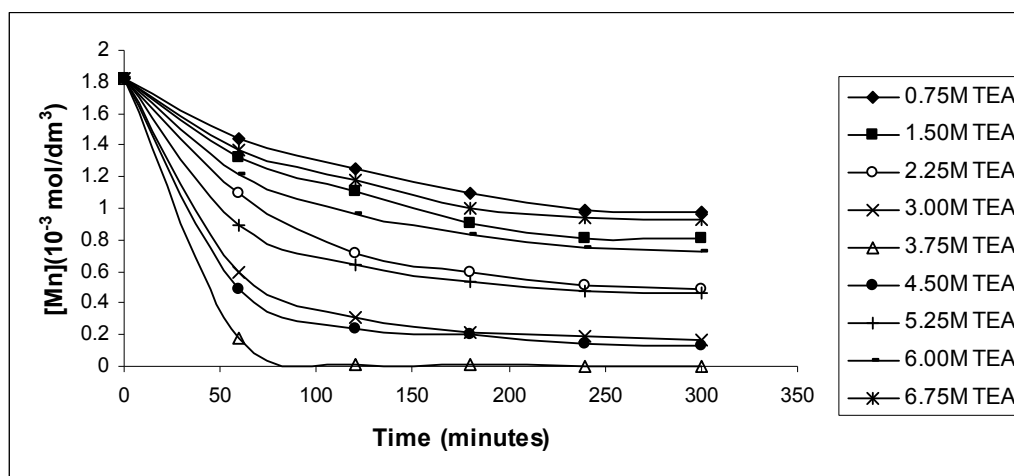


Fig. 4.2 Transport of Mn (II) ion from feed solution with time at various concentrations of TEA (initial Mn ion conc. = $1.82 \times 10^{-3} \text{ mol/dm}^3$ in 1 M H_2SO_4 in feed, FeSO_4 conc. = $9.25 \times 10^{-3} \text{ mol/dm}^3$ in 0.5 M H_2SO_4 in stripping, TEA conc. = 0.75-6.75 M in cyclohexanone, stirring speed = 1500 rpm).

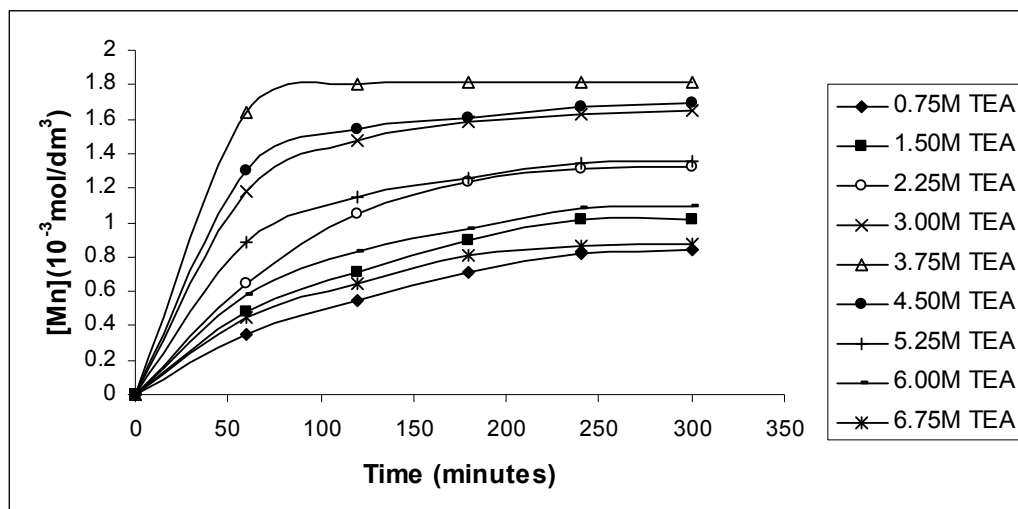


Fig. 4.3 Extraction of Mn (II) ion into stripping phase with time at various concentrations of TEA (same operating conditions as given in Fig. 4.2).

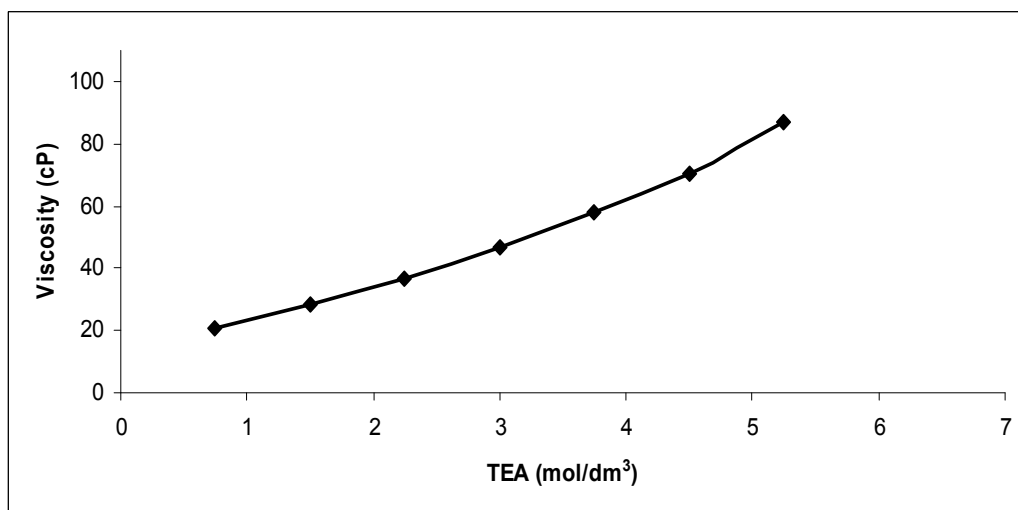


Fig. 4.4 Viscosity of triethanolamine-cyclohexanone solutions.

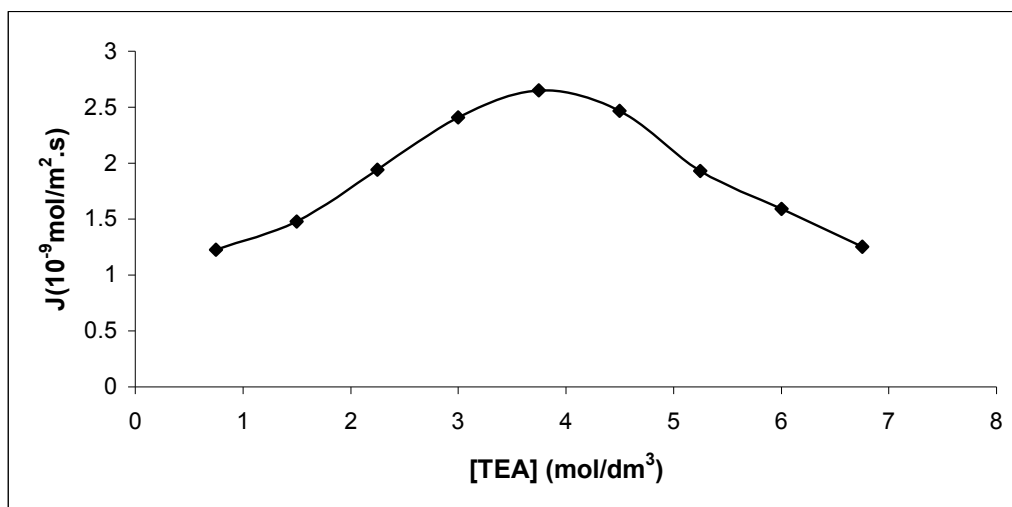


Fig. 4.5 Flux of Mn (II) ion at various concentrations of TEA (same operating conditions as given in Fig. 4.2).

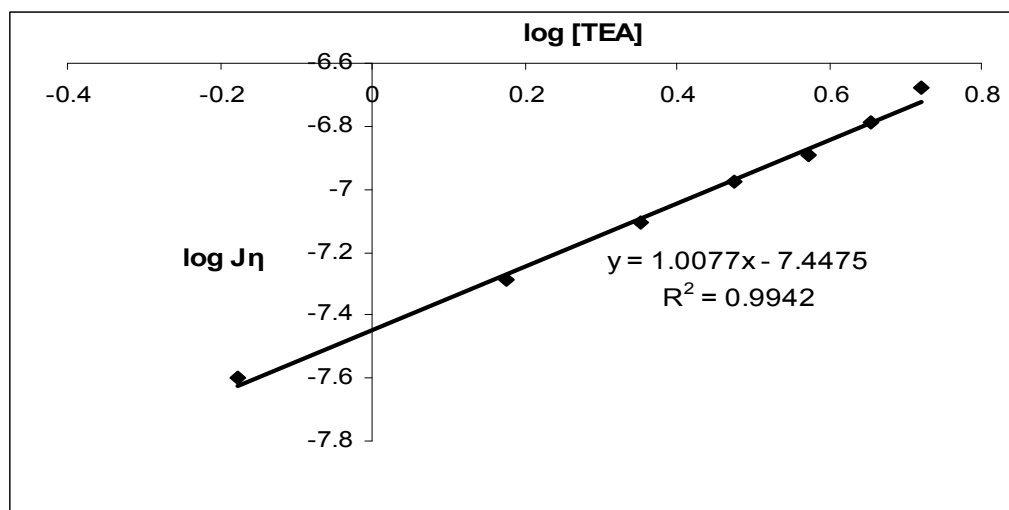


Fig. 4.6 log $J\eta$ versus log [TEA] (same operating conditions as given in Fig. 4.2).

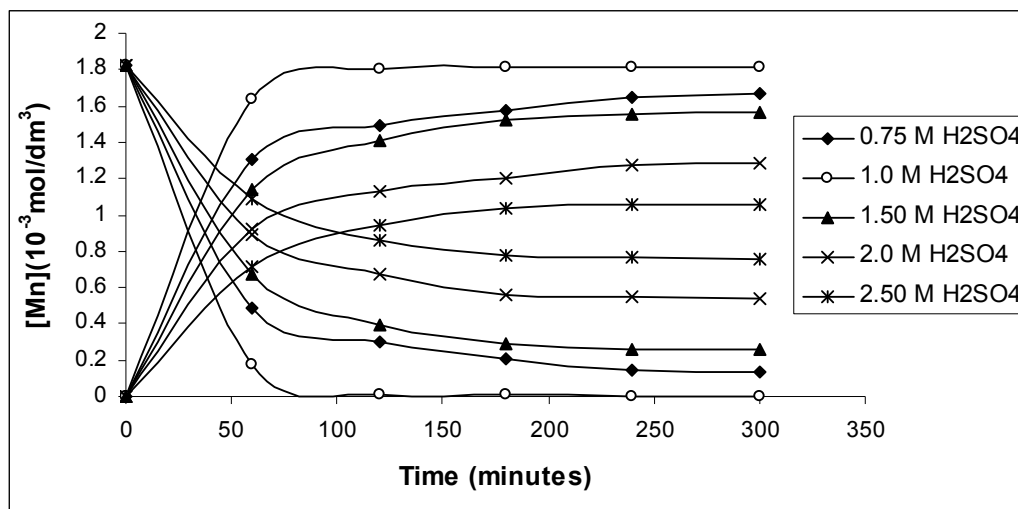


Fig. 4.7 Concentration variation of Mn ions in feed and stripping solution against time, at various H_2SO_4 concentrations in feed (initial Mn ion conc. $= 1.82 \times 10^{-3} \text{ mol/dm}^3$ in feed, H_2SO_4 conc. in feed $= 0.75\text{--}2.50 \text{ M}$, FeSO_4 conc. $= 9.25 \times 10^{-3} \text{ mol/dm}^3$ in $0.5 \text{ M H}_2\text{SO}_4$ in stripping, TEA conc. $= 3.75 \text{ M}$ in cyclohexanone, stirring speed $= 1500 \text{ rpm}$).

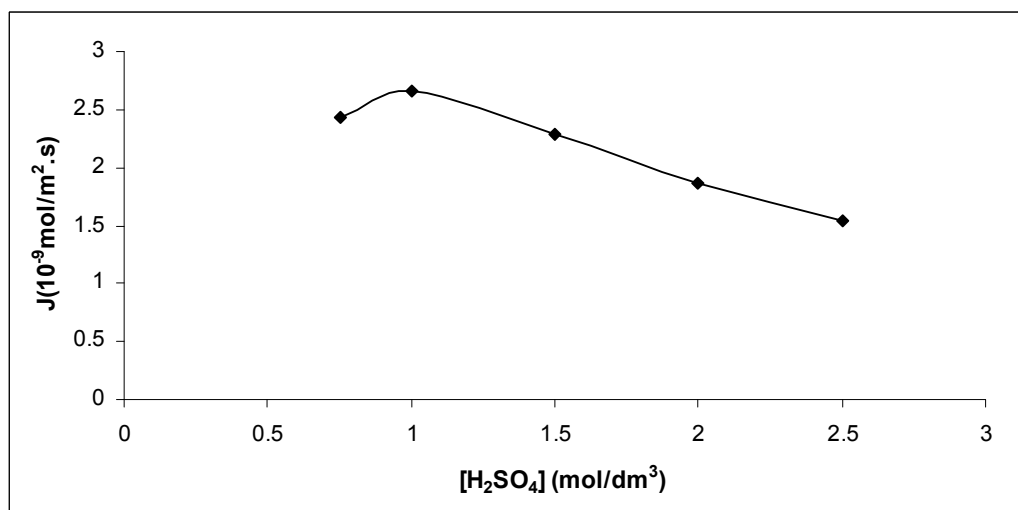


Fig. 4.8 Influence of concentrations of H_2SO_4 in feed on flux of Mn (same operating conditions of Fig. 4.7).

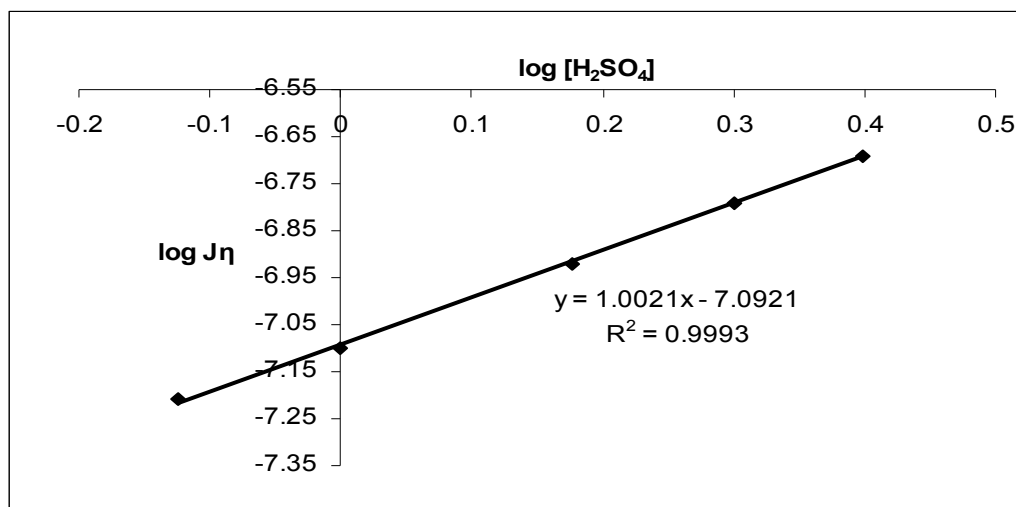


Fig. 4.9 log $J\eta$ versus log $[H_2SO_4]$ (same operating conditions of Fig. 4.7).

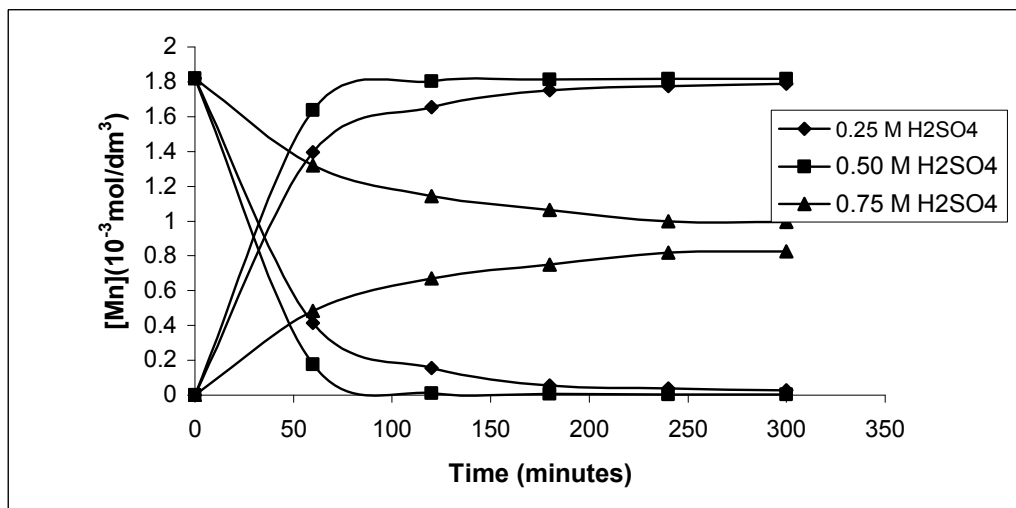


Fig. 4.10 Concentration variation of Mn ions in feed and stripping phase against time at different concentrations of H_2SO_4 in stripping (initial Mn ion conc. = 1.82×10^{-3} mol/dm³ in 1 M H_2SO_4 in feed, $FeSO_4$ conc. = 9.25×10^{-3} mol/dm³, H_2SO_4 conc. in stripping = 0.25-0.75 M, TEA conc. = 3.75 M in cyclohexanone, stirring speed = 1500 rpm).

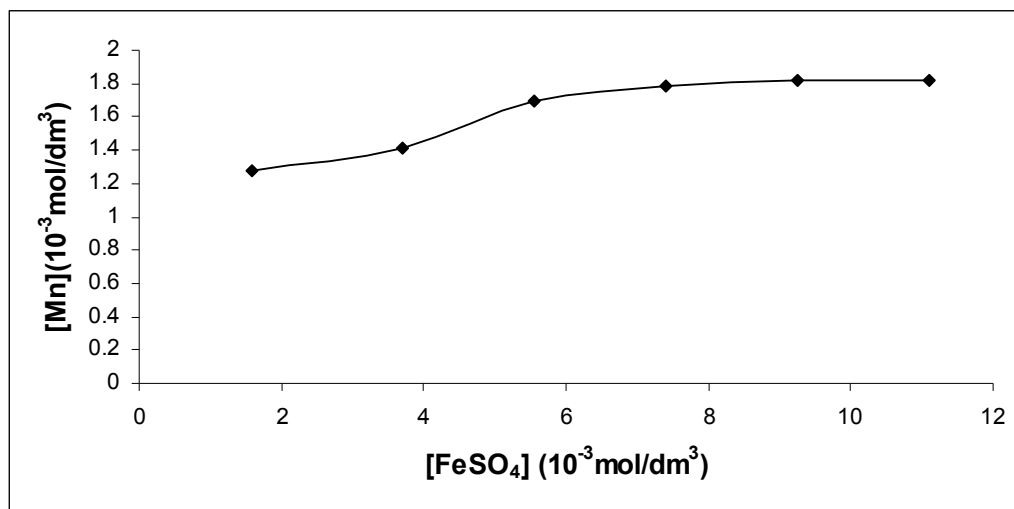


Fig. 4.11 Extraction of Mn (II) ion in stripping versus different concentrations of FeSO₄ (initial Mn ion conc. = 1.82×10^{-3} mol/dm³ in 1M H₂SO₄ in feed, FeSO₄ conc. in stripping = $1.58 - 11.1 \times 10^{-3}$ mol/dm³, H₂SO₄ conc. in stripping = 0.5 M, TEA conc. = 3.75 M in cyclohexanone, stirring speed = 1500 rpm).

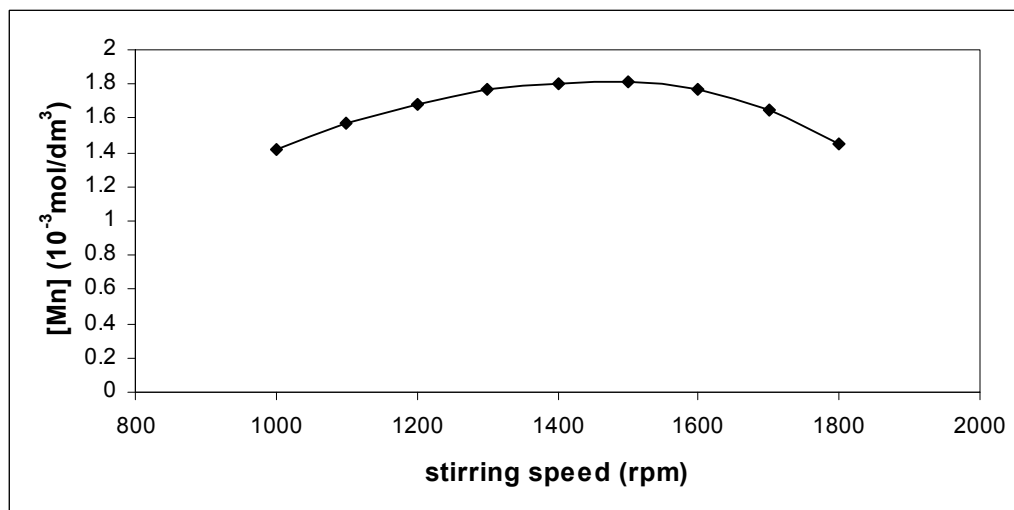


Fig. 4.12 Extraction of Mn (II) ions in stripping versus stirring speed in feed and stripping solution (initial Mn ion conc. = 1.82×10^{-3} mol/dm³ in 1 M H₂SO₄ in feed, FeSO₄ conc. = 9.25×10^{-3} mol/dm³ in 0.5 M H₂SO₄ in stripping, TEA conc. = 3.75 M in cyclohexanone, stirring speed = 1000-1800 rpm).

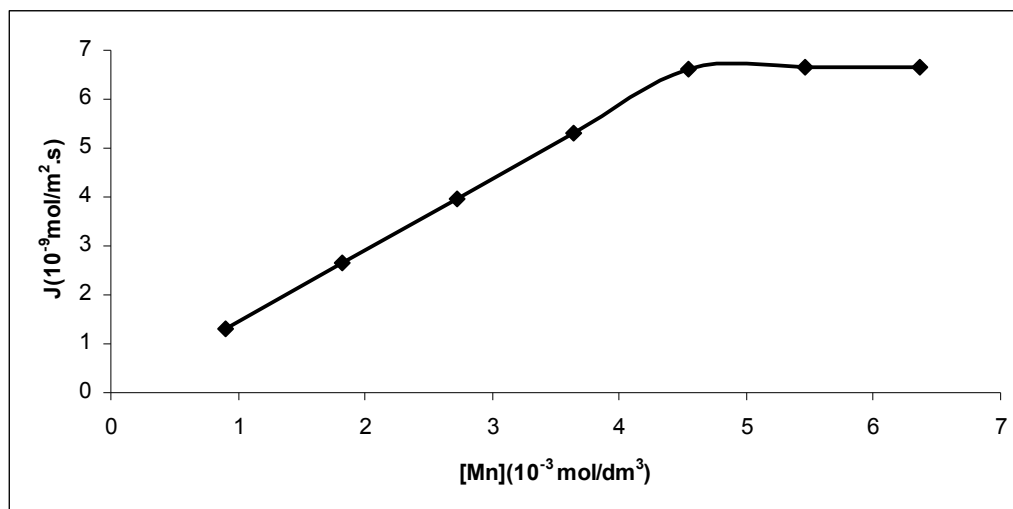


Fig. 4.13 Influence of metal ion concentration in feed on Mn ions flux (initial Mn ion conc. = 0.91×10^{-3} mol/dm³ to 6.37×10^{-3} mol/dm³ in 1 M H₂SO₄ in feed, FeSO₄ conc. = 9.25×10^{-3} mol/dm³ in 0.5 M H₂SO₄ in stripping, TEA conc. = 3.75 M in cyclohexanone, stirring speed = 1500 rpm).

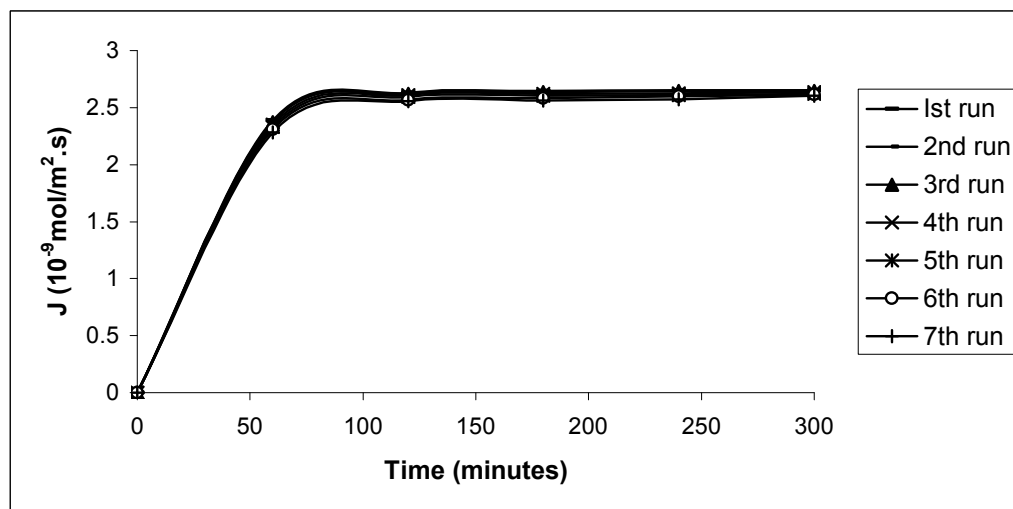


Fig. 4.14a Stability of SLM: flux versus time (initial Mn ion conc. = 1.82×10^{-3} mol/dm³ in 1 M H₂SO₄ in feed, FeSO₄ conc. = 9.25×10^{-3} mol/dm³ in 0.5 M H₂SO₄ in stripping, TEA conc. = 3.75 M in cyclohexanone, stirring speed = 1500 rpm).

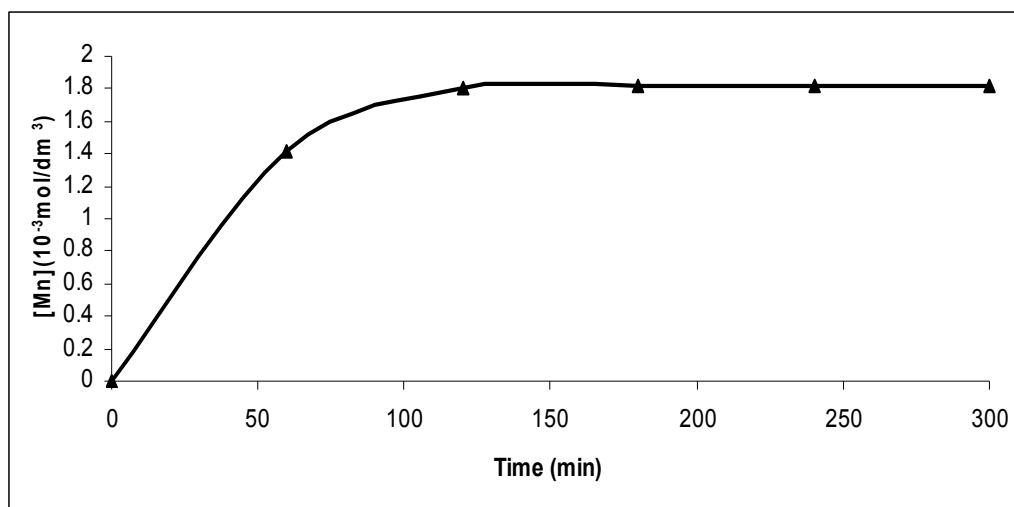


Fig. 4.14b Durability of polypropylene support after treatment for 30 days in 3.75 M TEA – cyclohexanone (same operating conditions of Fig. 4.14a).

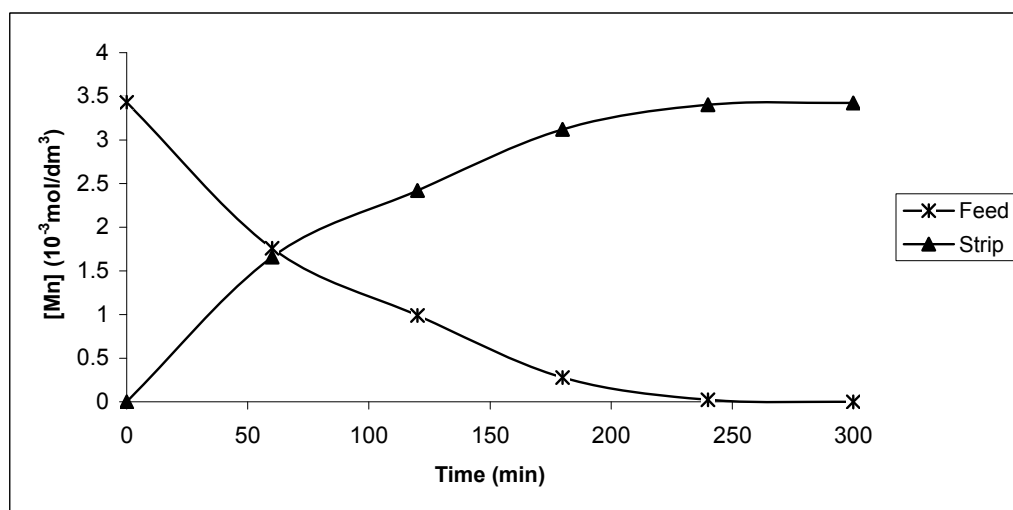


Fig. 4.15 Variation in Mn ions concentration in feed and stripping solution vs. time (discharged zinc carbon battery solution in feed). Initial Mn ion conc. in feed = $3.43 \times 10^{-3} \text{ mol/dm}^3$ in 1.0 M H_2SO_4 , FeSO_4 conc. = $9.25 \times 10^{-3} \text{ mol/dm}^3$ in 0.5 M H_2SO_4 in stripping, TEA conc. = 3.75 M in cyclohexanone, stirring speed = 1500 rpm.

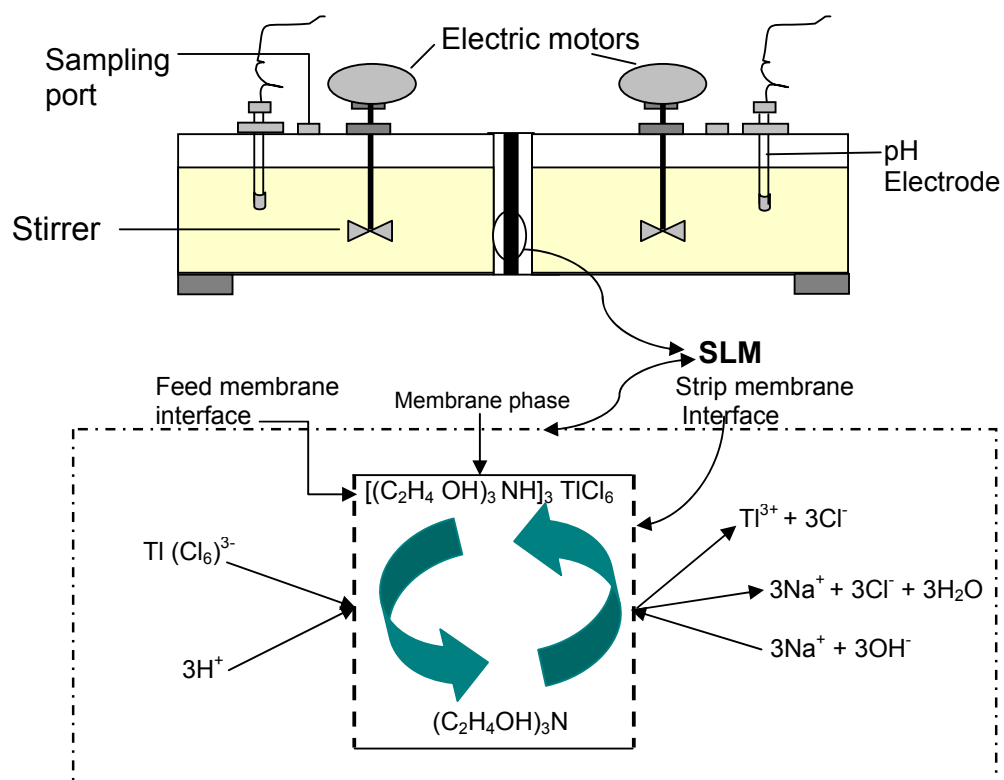


Fig. 4.16 Schematic diagram of membrane cell with the transport mechanism of Tl (III).

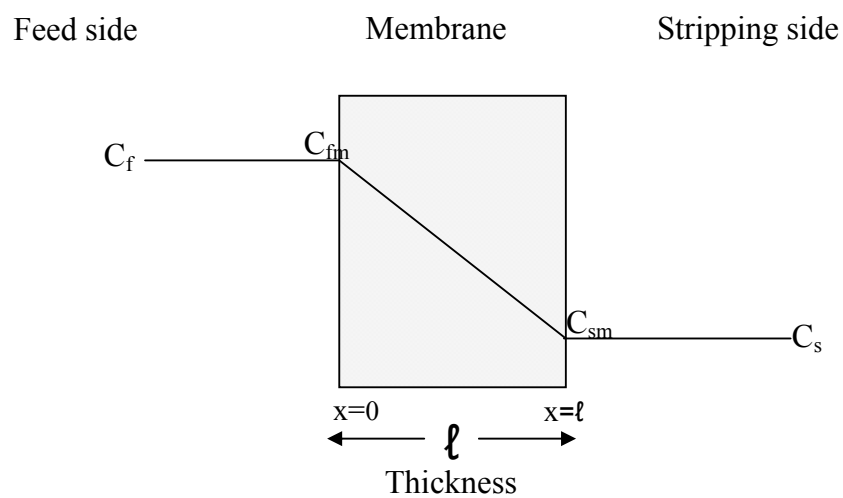


Fig. 4.17 Concentration gradient of Tl (III) ion inside the membrane.

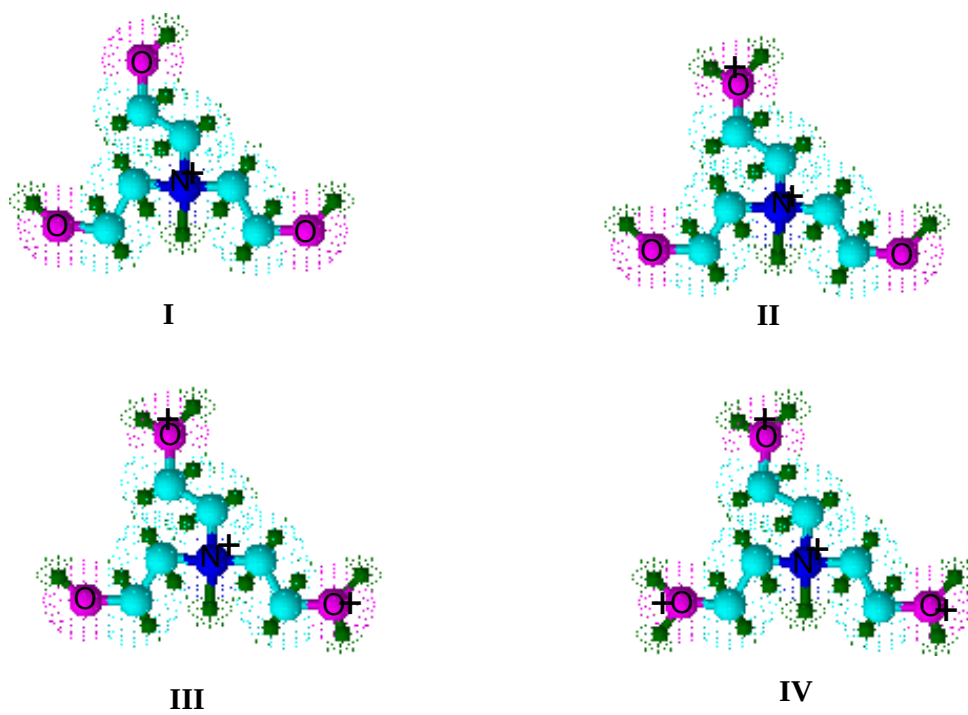


Fig. 4.18 Positively-charged species of TEA.

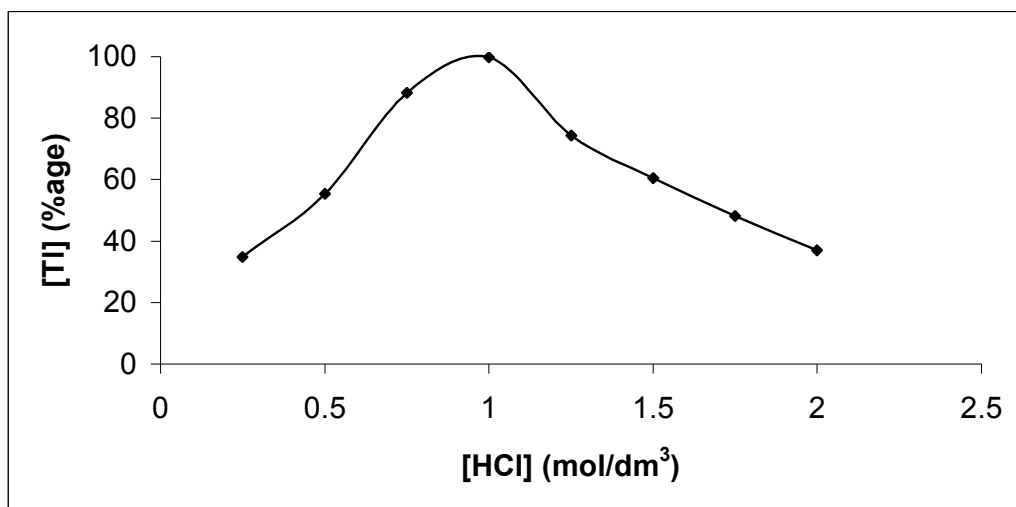


Fig. 4.19 Influence of concentration of HCl on recovery of Tl (III) in stripping phase (Feed solution = 1.95×10^{-4} mol/dm³ of Tl (III) in 0.25 to 2.0 mol/dm³ of HCl, stripping solution = 1.0 mol/dm³ of NaOH, membrane phase = 5.26 mol/dm³ of TEA, experimental time = 4 hours).

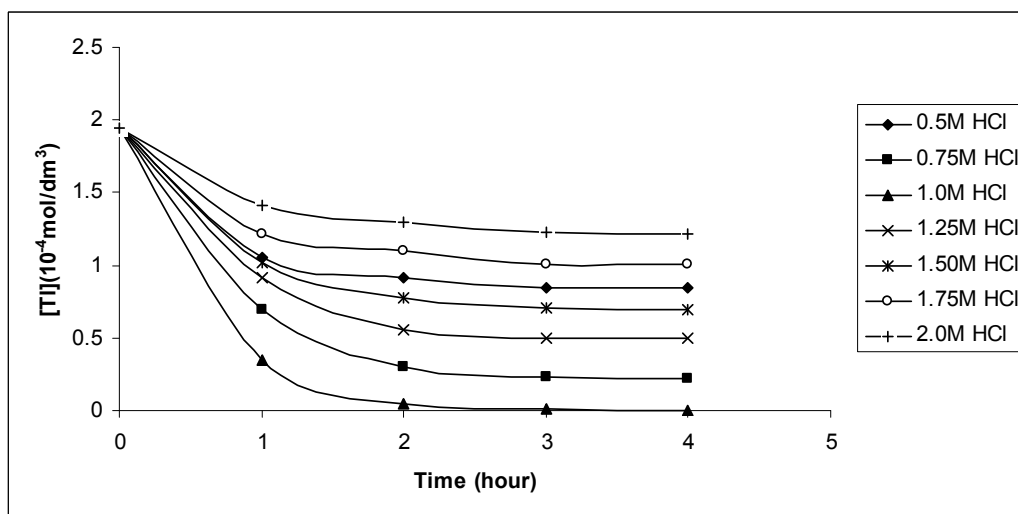


Fig. 4.20 Tl (III) concentration variation (decrease) in feed solution with time using various HCl concentrations (same operating conditions as given in Fig. 4.19).

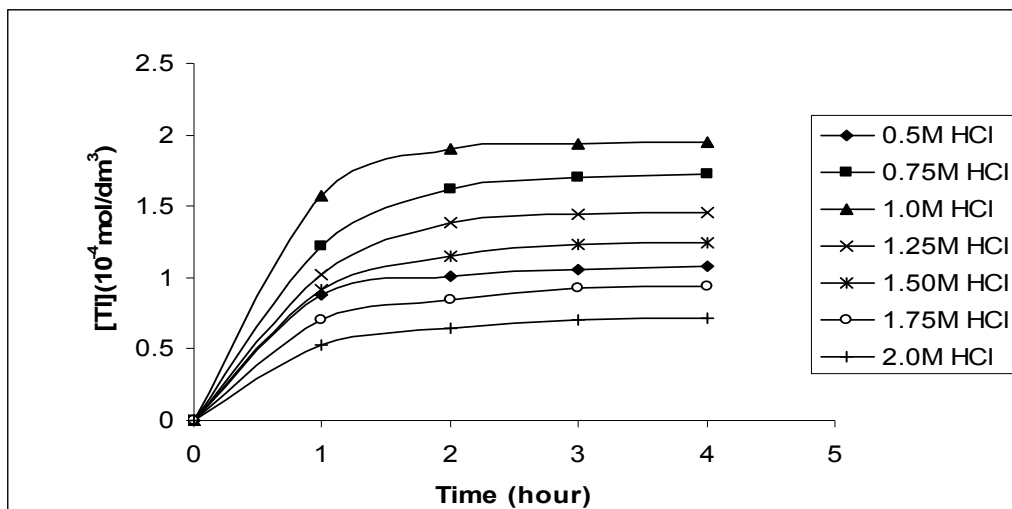


Fig. 4.21 Tl (III) concentration variation (increase) in stripping solution with time using various concentrations of HCl (same operating conditions as given in Fig. 4.19).

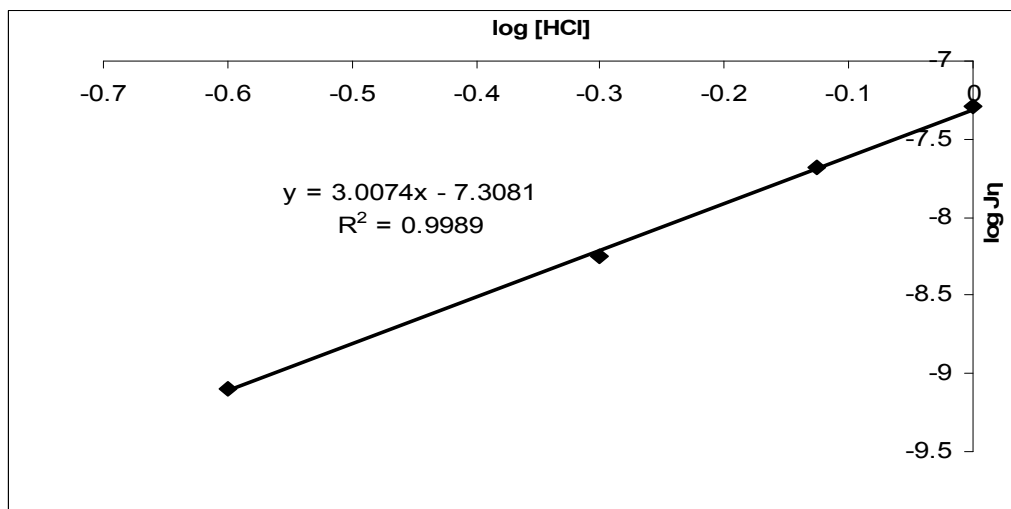


Fig. 4.22 Plot of $\log J\eta$ against $\log [\text{HCl}]$ (same operating conditions as given in Fig. 4.19).

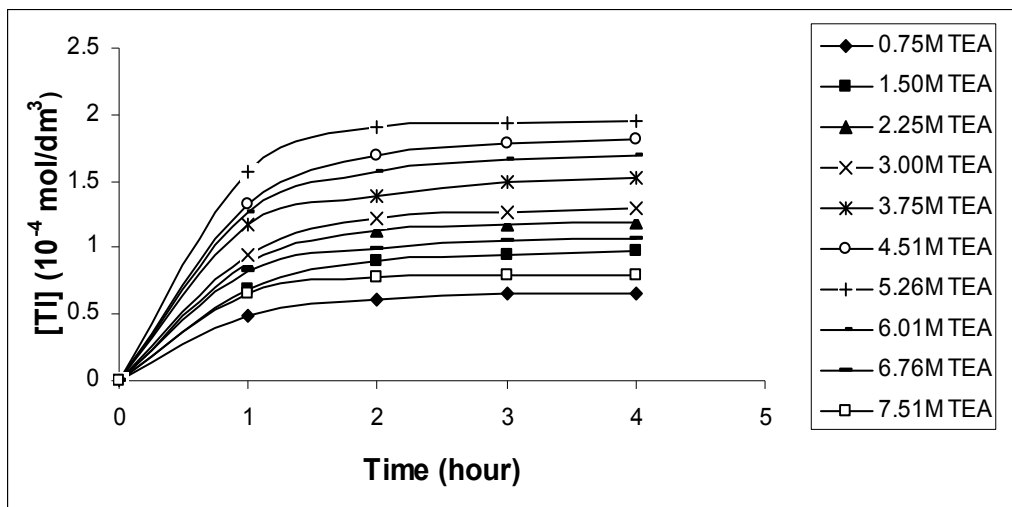


Fig. 4.23 Influence of TEA concentration on extraction of Tl (III) in stripping phase with time (Feed solution = 1.95×10^{-4} mol/dm³ of Tl (III) in 1.0 mol/dm³ of HCl, stripping solution = 1.0 mol/dm³ of NaOH, membrane phase = 0.75-7.51 mol/dm³ of TEA).

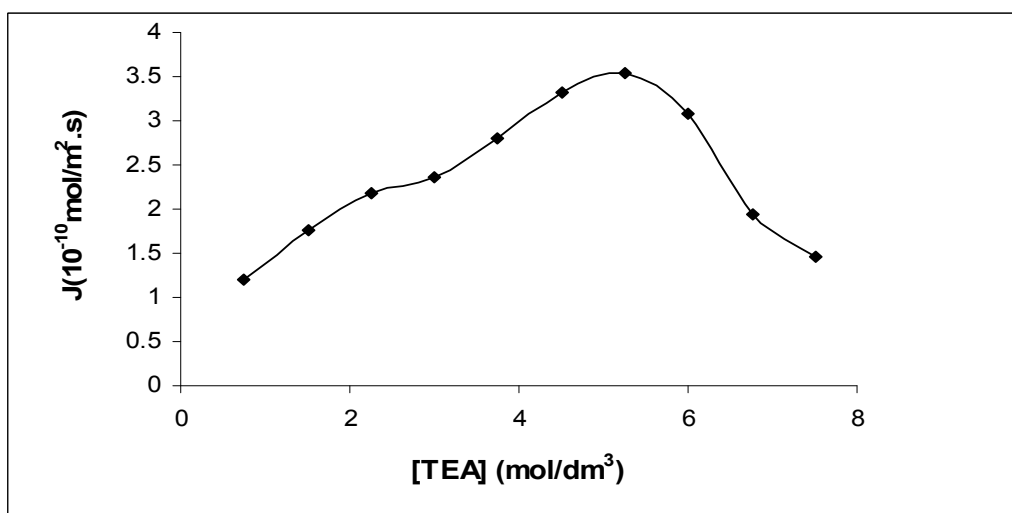


Fig. 4.24 Influence of TEA concentration on Tl (III) flux (same operating conditions as given in Fig. 4.23).

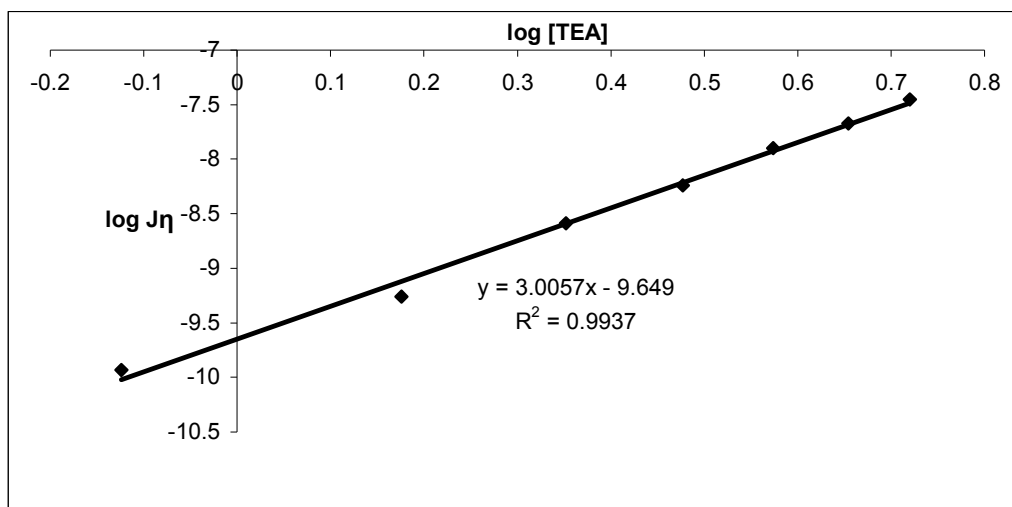


Fig. 4.25 $\log J\eta$ versus $\log [\text{TEA}]$ (same operating conditions of Fig. 4.23).

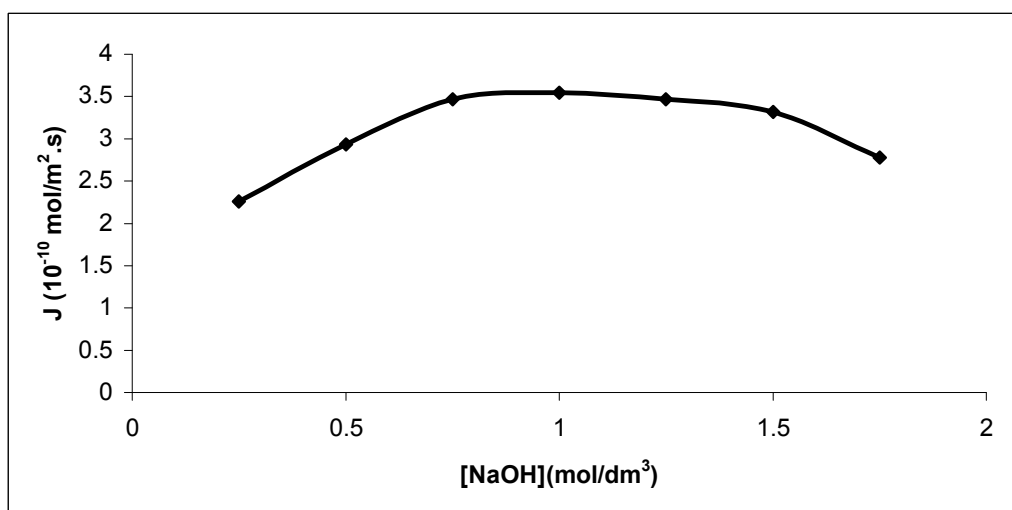


Fig. 4.26 Effect of NaOH concentration on Tl (III) flux (Feed solution = 1.95×10^{-4} mol/dm³ of Tl (III) in 1.0 mol/dm³ of HCl, stripping solution = 0.25-1.75 mol/dm³ of NaOH, membrane phase = 5.26 mol/dm³ of TEA).

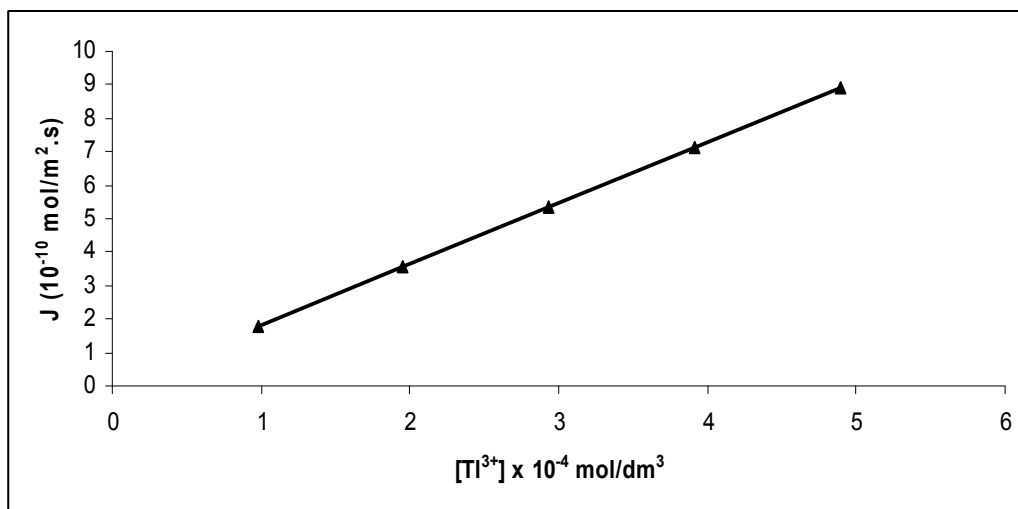


Fig. 4.27 Influence of Tl (III) concentration in feed on its flux (Feed solution = $0.978 \times 10^{-4} \text{ mol/dm}^3$ to $4.893 \times 10^{-4} \text{ mol/dm}^3$ of Tl (III) in 1.0 mol/dm^3 of HCl, stripping solution = 1.0 mol/dm^3 of NaOH, membrane phase = 5.26 mol/dm^3 of TEA).

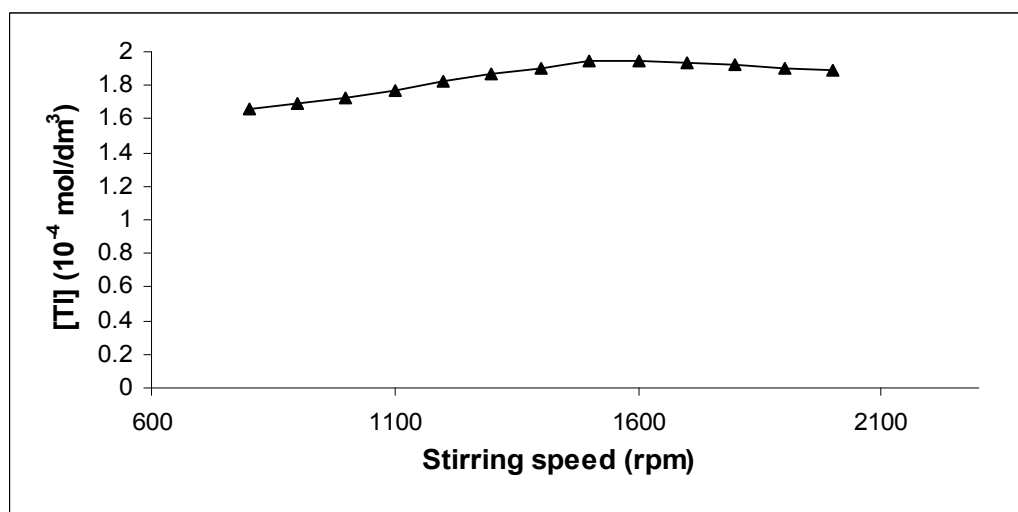


Fig. 4.28 Extraction of Tl (III) in stripping solution versus stirring speed in feed and stripping solution (Feed solution = $1.95 \times 10^{-4} \text{ mol/dm}^3$ of Tl (III) in 1.0 mol/dm^3 of HCl, stripping solution = 1.0 mol/dm^3 of NaOH, membrane phase = 5.26 mol/dm^3 of TEA, stirring speed = 800 rpm to 2000 rpm).

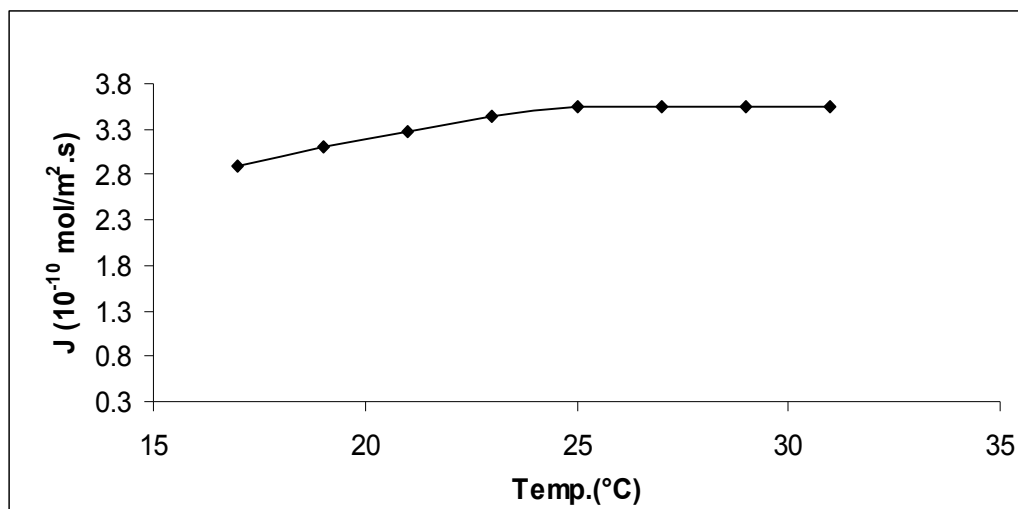


Fig. 4.29 Effect of temperature on flux of Tl (III) (Feed solution = 1.95×10^{-4} mol/dm³ of Tl (III) in 1.0 mol/dm³ of HCl, stripping solution = 1.0 mol/dm³ of NaOH, membrane phase = 5.26 mol/dm³ of TEA).

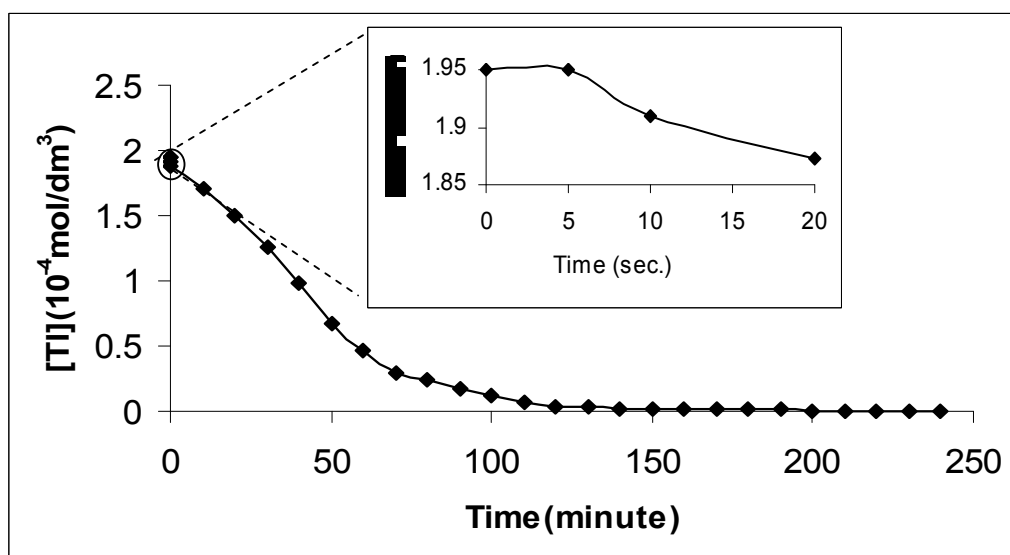


Fig. 4.30 Residence time of Tl(III) (same operating conditions as given in Fig. 4.29).

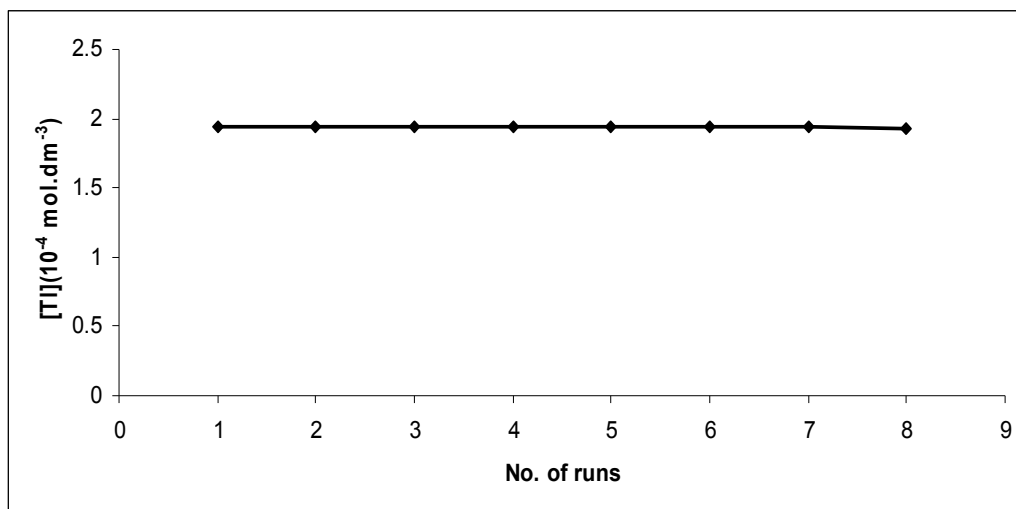


Fig. 4.31 Stability of SLM, Tl(III) concentration in stripping phase versus number of runs (same operating conditions as given in Fig. 4.29).

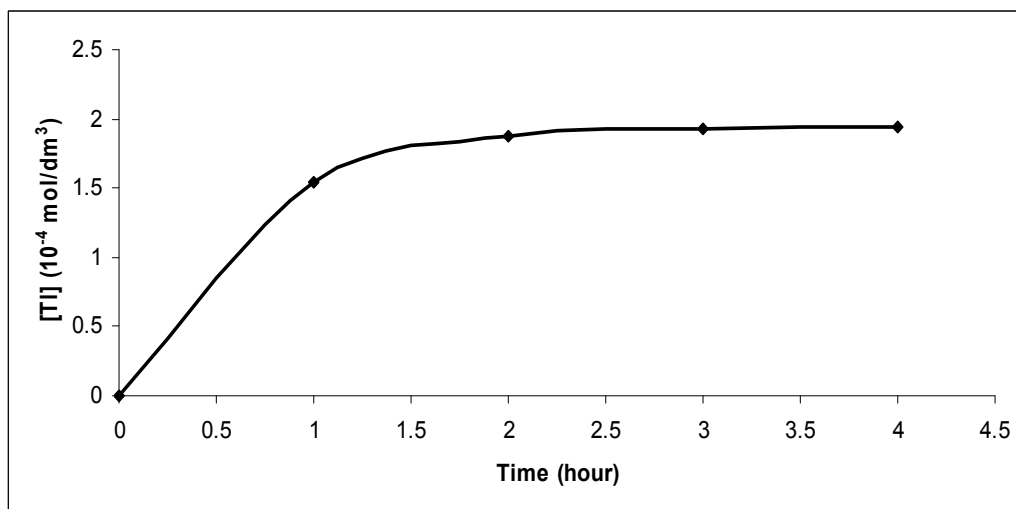


Fig. 4.32 Durability of polypropylene support after treatment for 60 days with 5.26 mol/dm^3 TEA-xylene solution (same operating conditions as given in Fig. 4.29).

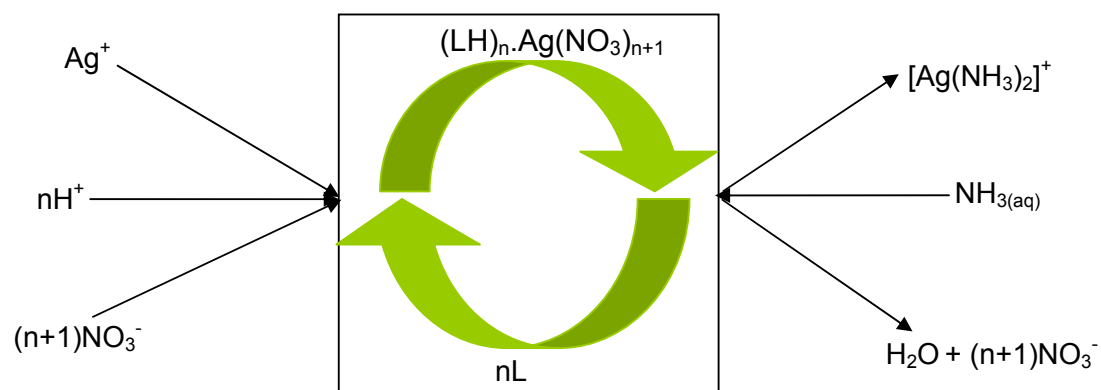


Fig. 4.33 Schematic diagram showing Ag (I) transport.

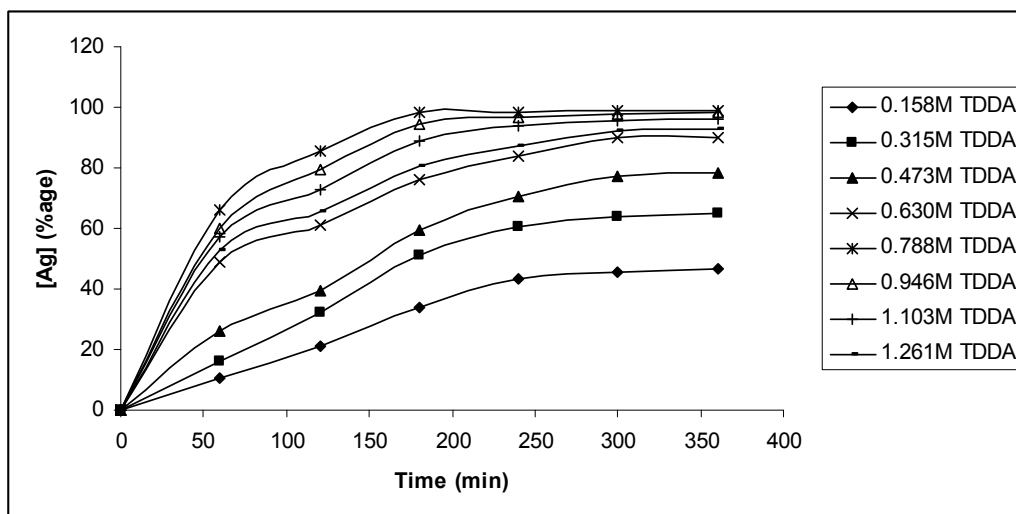


Fig. 4.34 Influence of concentration of TDDA on extraction of Ag (I) in stripping phase with time (Feed solution = 0.75 mol/dm^3 of HNO_3 , membrane phase = 0.158 M to 1.261 M of TDDA, stripping solution = 1.0 mol/dm^3 of $\text{NH}_{3(\text{aq})}$).

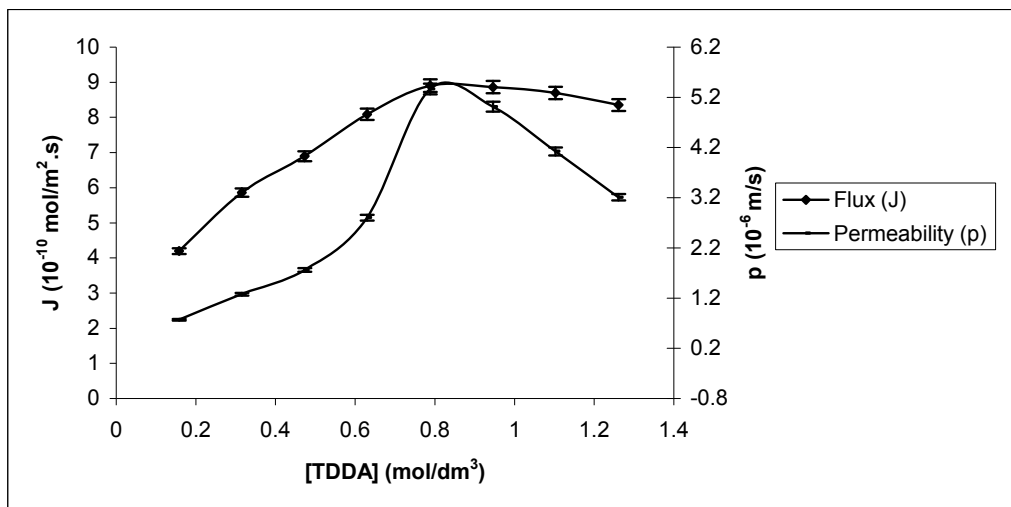


Fig. 4.35 Flux (J) and permeability (p) variation at various concentrations of TDDA in membrane phase (same operating conditions as given in Fig. 4.34).

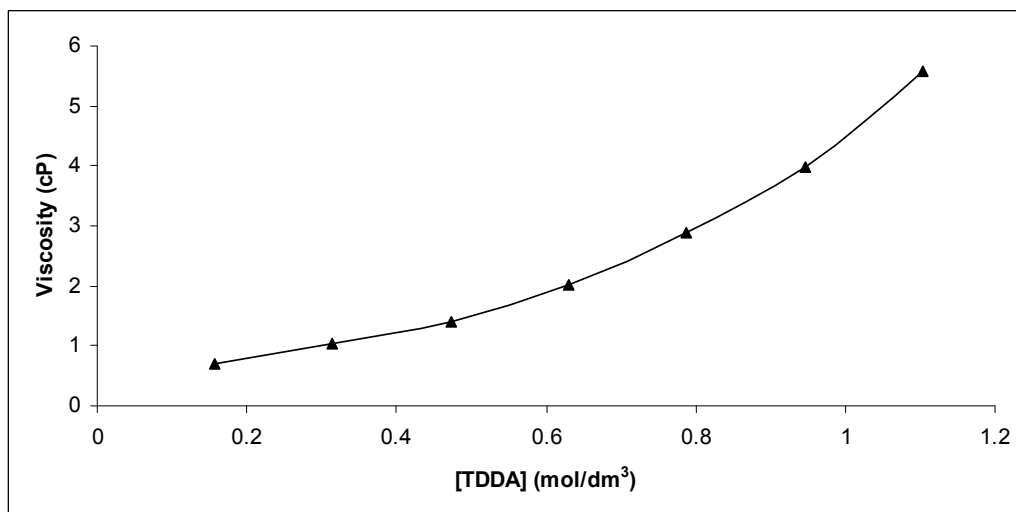


Fig. 4.36 Viscosity of TDDA-cyclohexane solutions.

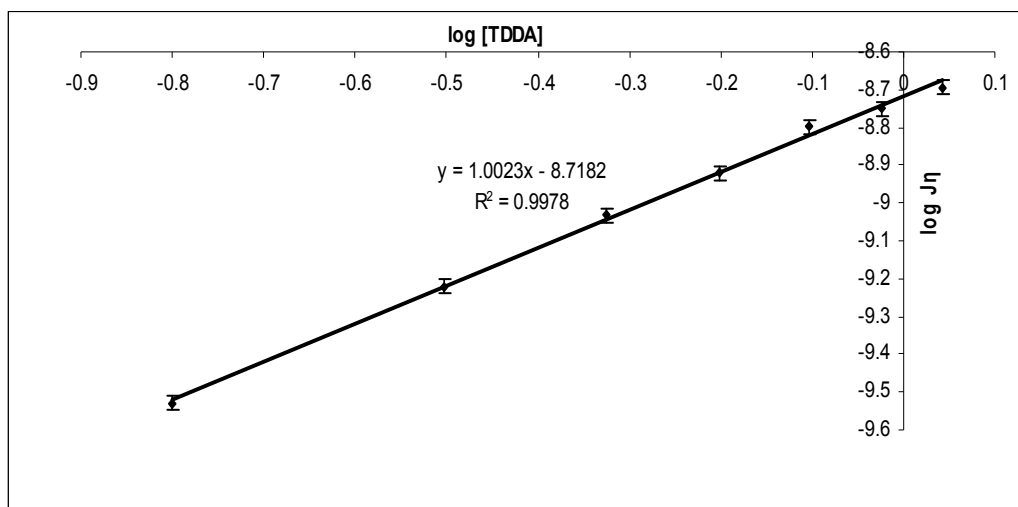


Fig. 4.37 Plot of $\log J\eta$ against $\log [\text{TDDA}]$ (same operating conditions as given in Fig. 4.34).

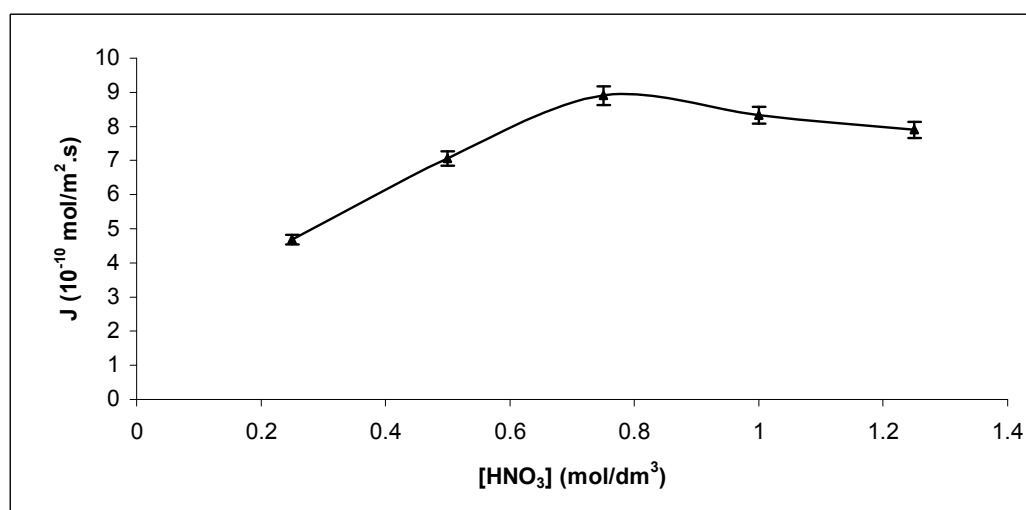


Fig. 4.38 Influence of HNO_3 concentration in feed solution on flux (J) of Ag(I) (Feed solution = 0.25 mol/dm^3 to 1.25 mol/dm^3 of HNO_3 , membrane phase = 0.788 M of TDDA, stripping solution = 1.0 mol/dm^3 of $\text{NH}_{3(\text{aq})}$, time = 4.0 hours).

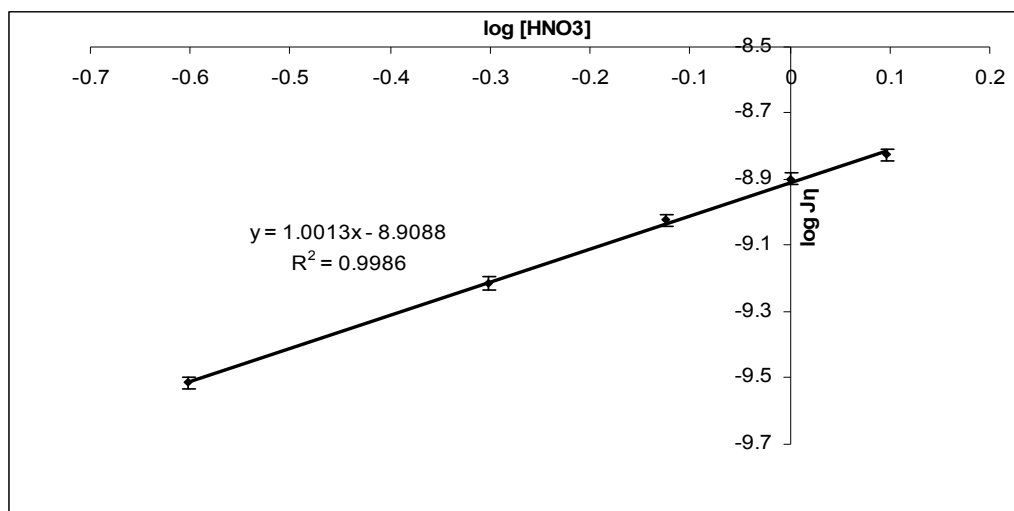


Fig. 4.39 Plot of $\log J\eta$ against $\log [\text{HNO}_3]$ (same operating conditions as given in Fig. 4.38).

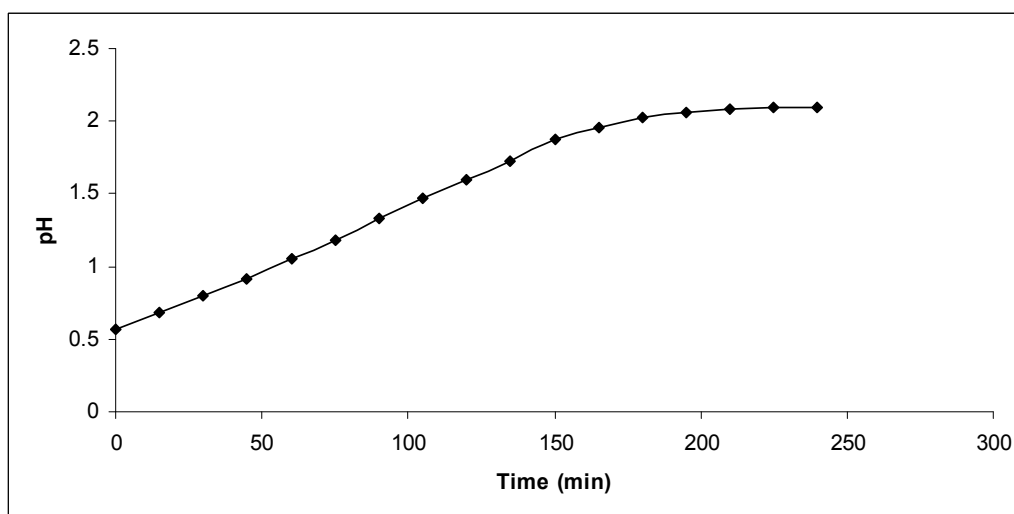


Fig. 4.40 pH variation in the feed solution (Feed solution = 0.75 mol/dm^3 of HNO_3 , membrane phase = 0.788 M of TDDA, stripping solution = 1.0 mol/dm^3 of $\text{NH}_{3(\text{aq})}$).

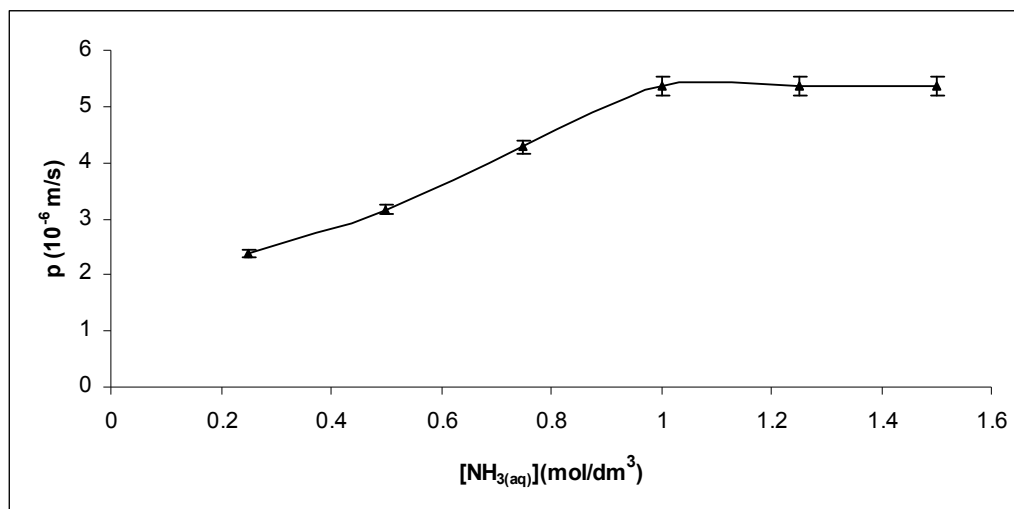


Fig. 4.41 Effect of $\text{NH}_{3(\text{aq})}$ concentration on permeability of Ag (I) (Feed solution = 0.75 mol/dm^3 of HNO_3 , membrane phase = 0.788 M of TDDA, stripping solution = 0.25 mol/dm^3 to 1.5 mol/dm^3 of $\text{NH}_{3(\text{aq})}$, time = 4.0 hours).

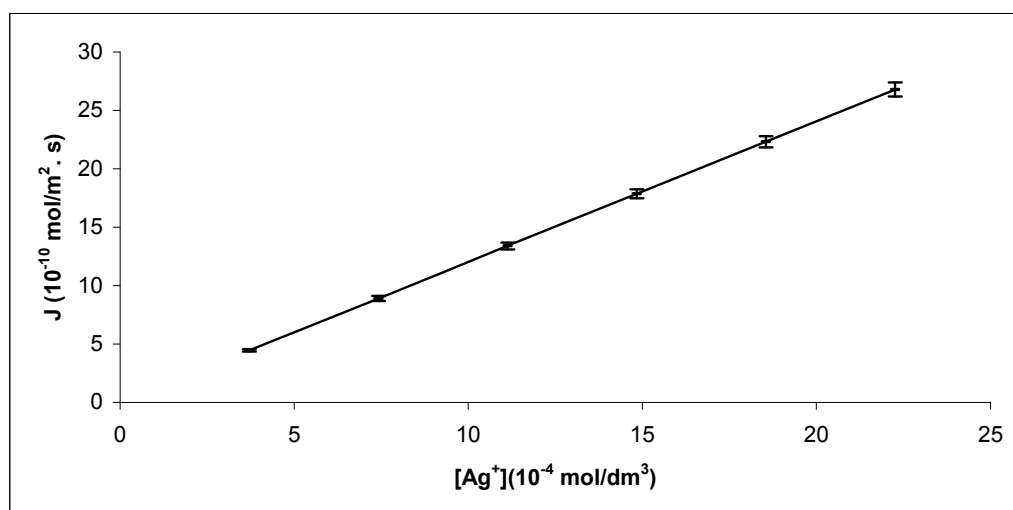


Fig. 4.42 Effect of Ag (I) concentration in feed solution on its flux (Feed solution = $3.71 \times 10^{-4} \text{ mol/dm}^3$ to $22.26 \times 10^{-4} \text{ mol/dm}^3$ of Ag (I) in 0.75 mol/dm^3 of HNO_3 , membrane phase = 0.788 M of TDDA, stripping solution = 1.0 mol/dm^3 of $\text{NH}_{3(\text{aq})}$, time = 4.0 hours).

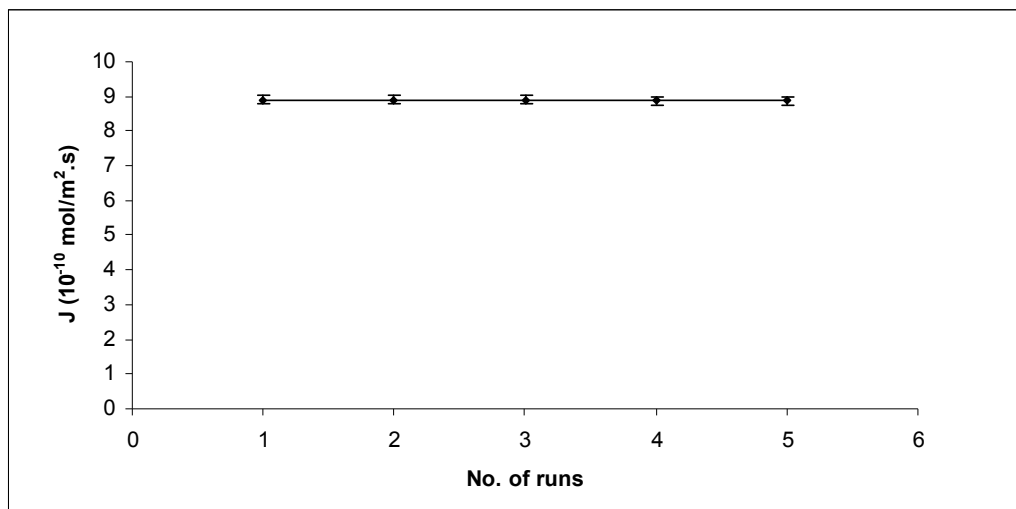


Fig. 4.43 Stability of SLM; permeability versus number of runs (Feed solution = 0.75 mol/dm³ of HNO₃, membrane phase = 0.788 M of TDDA, stripping solution = 1.0 mol/dm³ of NH_{3(aq)}).

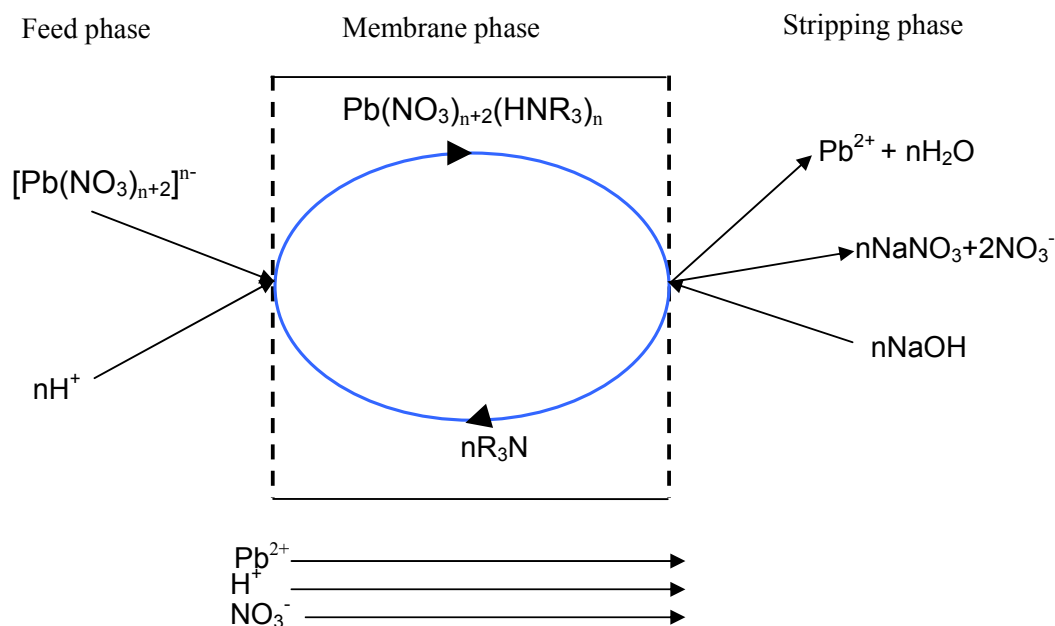


Fig. 4.44 Schematic representation of Pb (II) transport.

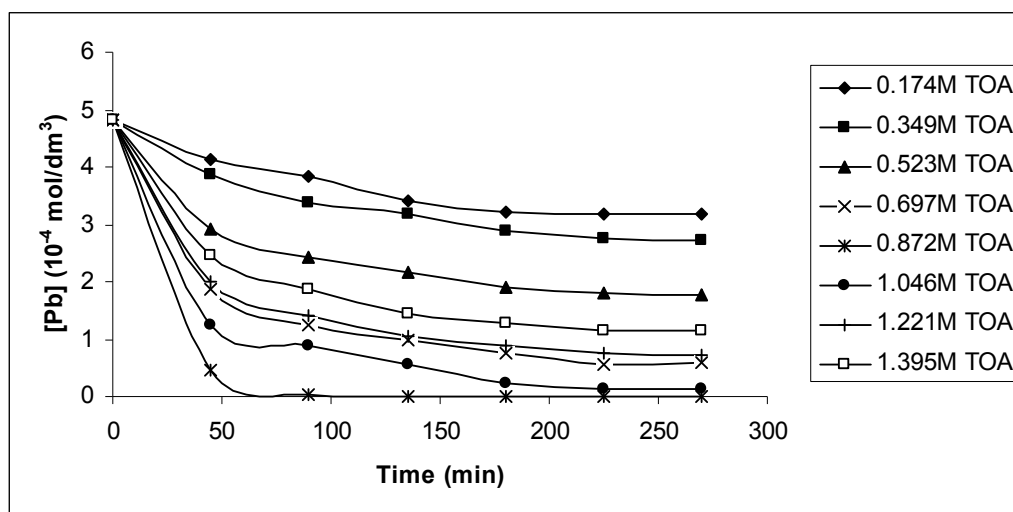


Fig. 4.45 Effect of TOA concentration on extraction of Pb (II) in feed solution with time (Feed solution = 4.826×10^{-4} mol/dm³ of Pb (II) in 0.2 mol/dm³ HNO₃, stripping solution = 0.2 mol/dm³ of NaOH, membrane phase = 0.174-1.395 M of TOA in xylene).

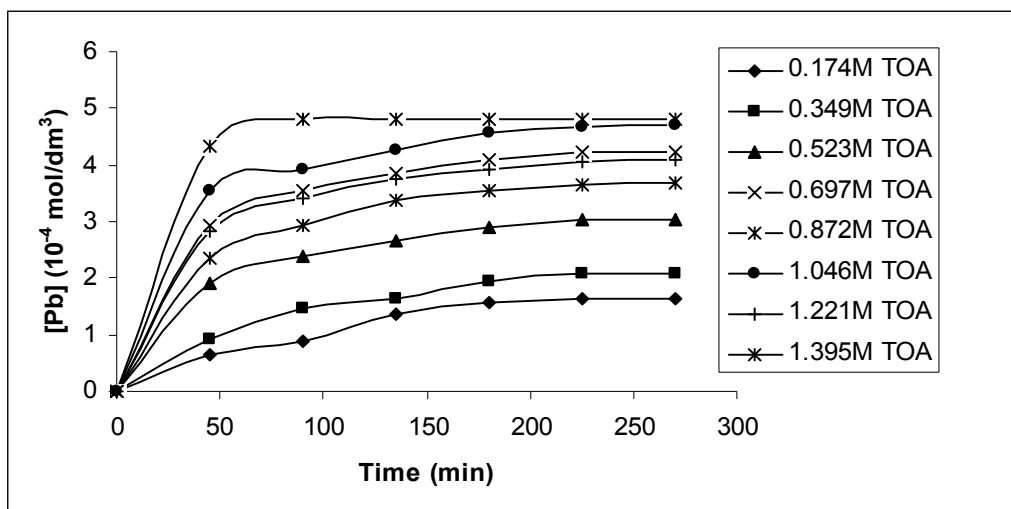


Fig. 4.46 Effect of TOA concentration on extraction of Pb (II) in stripping phase with time (same operating conditions as given in Fig. 4.45).

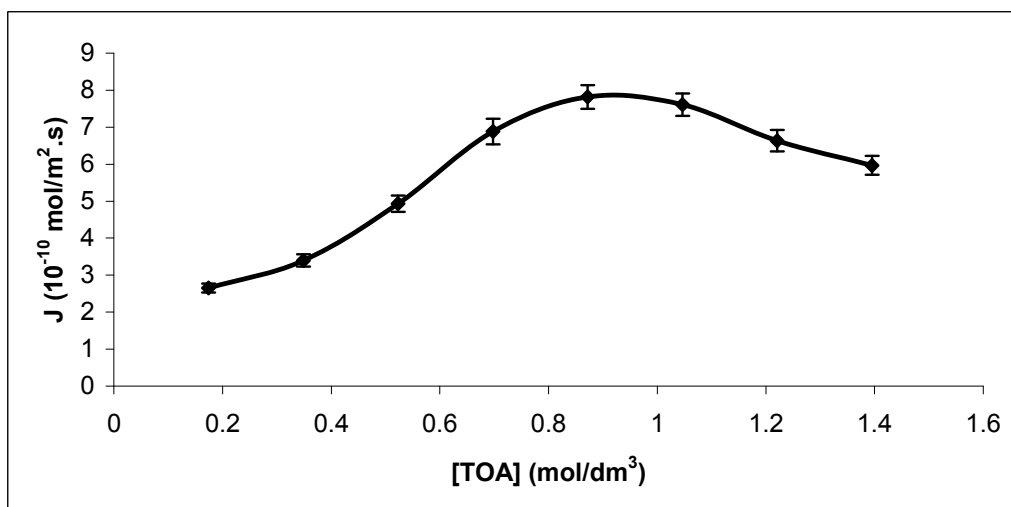


Fig. 4.47 Effect of TOA concentration on flux of Pb (II) (same operating conditions as given in Fig. 4.45).

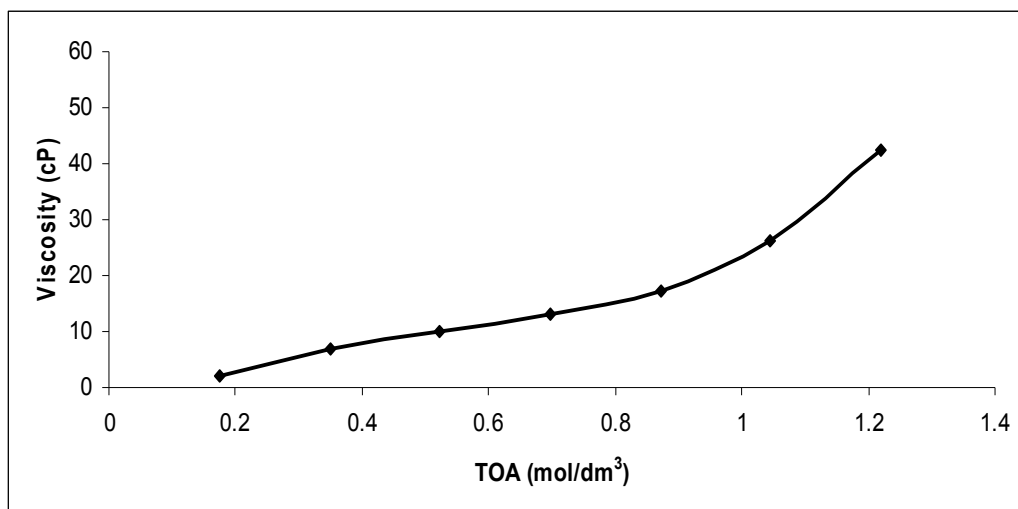


Fig. 4.48 Viscosity of TOA-Xylene solutions.

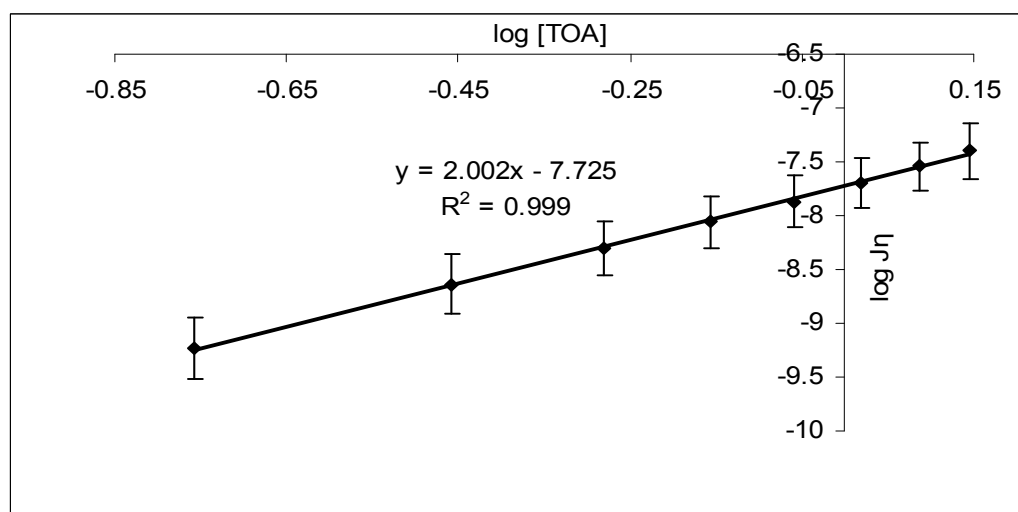


Fig. 4.49 Plot of $\log J\eta$ versus $\log [\text{TOA}]$ (same operating conditions as given in Fig. 4.45).

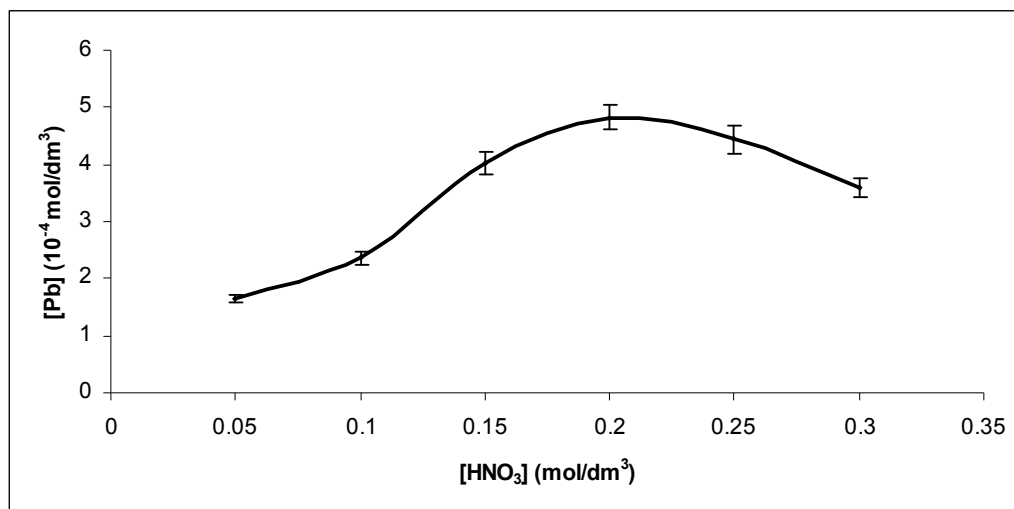


Fig. 4.50 Extraction of Pb (II) in stripping solution vs. various concentrations of HNO₃ in feed solution (Feed solution = 4.826×10^{-4} mol/dm³ of Pb (II) in 0.05 to 0.30 mol/dm³ HNO₃, stripping solution = 0.2 mol/dm³ of NaOH, membrane phase = 0.872 M of TOA in xylene).

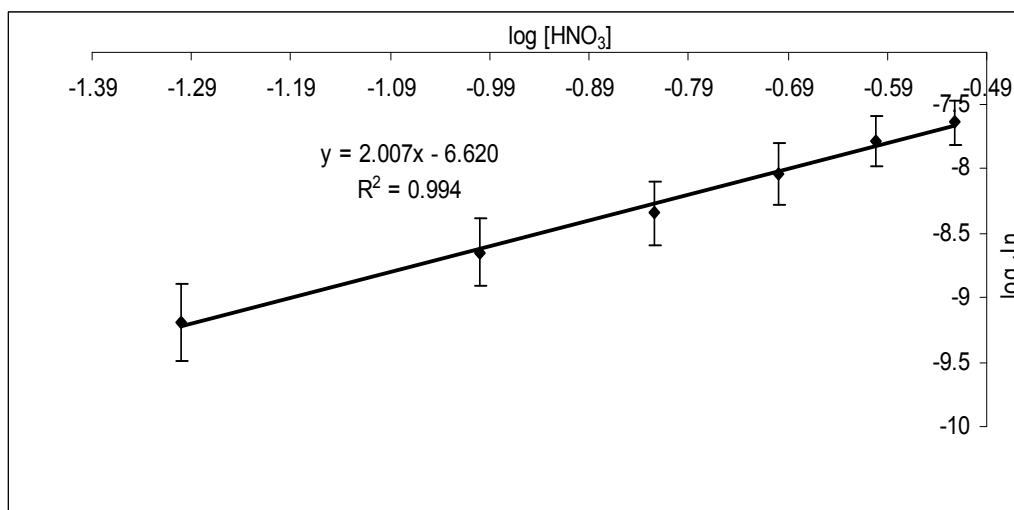


Fig. 4.51 Plot of log Jη versus log [HNO₃] (same operating conditions as given in Fig. 4.50).

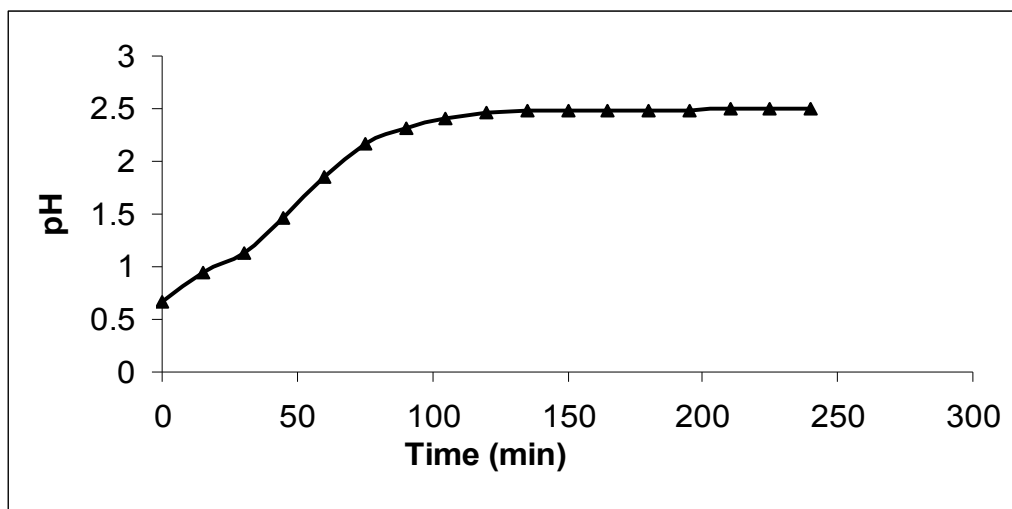


Fig. 4.52 pH variation in the feed solution (Feed solution = 4.826×10^{-4} mol/dm³ of Pb (II) in 0.2 mol/dm³ HNO₃, stripping solution = 0.2 mol/dm³ of NaOH, membrane phase = 0.872 M of TOA in xylene).

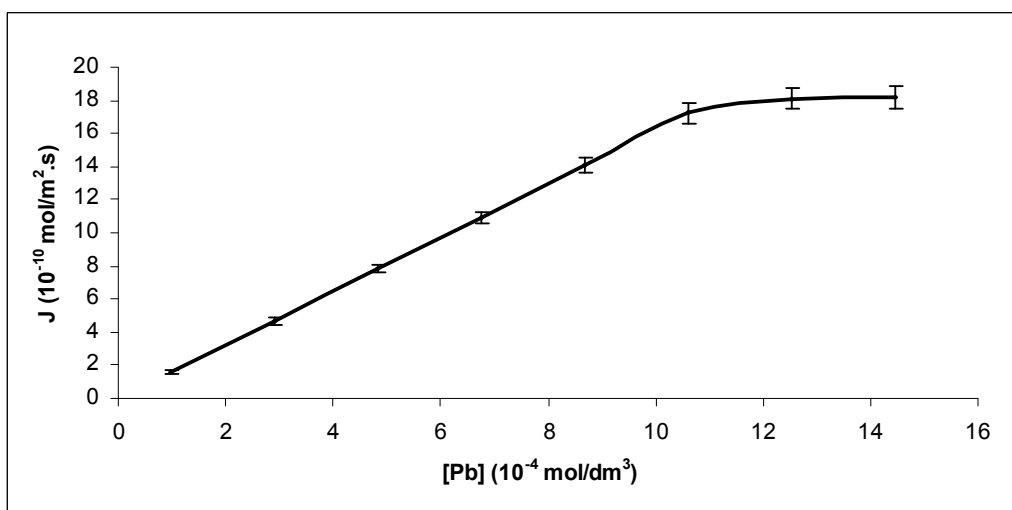


Fig. 4.53 Effect of Pb (II) concentration in feed solution on its flux (Feed solution = 0.963×10^{-4} mol/dm³ to 14.47×10^{-4} mol/dm³ of Pb (II) in 0.2 mol/dm³ HNO₃, stripping solution = 0.2 mol/dm³ of NaOH, membrane phase = 0.872 M of TOA in xylene).

Table 4.1**Analysis of Discharged Zinc Carbon Dry Battery Cell Solution**

Sr.No.	Metal ion	Concentration (mol/dm ³)
01	Manganese	3.43×10^{-3}
02	Nickel	Nil
03	Zinc	0.77×10^{-3}
04	Copper	Nil

Table 4.2**Recovery of Tl(III) from Coal Ash**

Metal ions	Metal ion concentration (10 ⁻⁴ mol/dm ³)		
	Initial feed	Final feed*	Final strip*
Thallium	0.821	0.0011	0.8196
Copper	Nil	Nil	Nil
Nickel	4.25	0.0128	4.237
Chromium	6.15	0.0319	6.118
Zinc	1.51	0.001	1.502

* after 110 mins.

Conditions: Feed solution = 1.0 mol/dm³ of HCl, stripping solution = 1.0 mol/dm³ of NaOH, membrane phase = 5.26 mol/dm³ of TEA.

Table 4.3**Effect of Membrane Thickness on Flux of Ag(I)**

Membranes	Flux of Ag (I) (10^{-10} mol/m ² .s)
Celgard 2500	8.901
Celgard 2502	8.053
Celgard 4400	7.231

Conditions: Feed solution = 0.75 mol/dm³ of HNO₃, membrane phase = 0.788 M of TDDA, stripping solution = 1.0 mol/dm³ of NH_{3(aq)}, time = 4 hours.

Table 4.4**Composition of Silver Plating and Photographic Waste Solutions**

Sample	Metal ions	[M] in feed solution (10^{-4} mol/dm ³)	[M] in stripping solution (10^{-4} mol/dm ³)
Silver plating solution	Ag	4.339	4.335
	Cr	Nil	Nil
	Zn	Nil	Nil
	Cu	Nil	Nil
Photographic waste solution	Ag	2.887	2.885
	K	23.75	Nil
	Mg	1.22	Nil
	Na	21.65	Nil
	Fe	3.345	Nil

Conditions: Feed solution = 0.75 mol/dm³ of HNO₃, membrane phase = 0.788 M of TDDA, stripping solution = 1.0 mol/dm³ of NH_{3(aq)}, time = 4 hours.

Table 4.5

Effect of Strippant Composition on the Transport of Pb (II) in Stripping Phase

Strippants	CH ₃ COONH ₄	Na ₂ SO ₄	NaOH
Concentration (mol/dm ³)	[Pb ²⁺] 10 ⁻⁴ mol/dm ³	[Pb ²⁺] 10 ⁻⁴ mol/dm ³	[Pb ²⁺] 10 ⁻⁴ mol/dm ³
0.1	0.347	0.165	1.77
0.15	0.351	0.172	3.91
0.2	0.352	0.176	4.812
0.25	0.353	0.177	4.812
0.30	0.353	0.175	4.812

Conditions: Feed solution = 4.826×10^{-4} mol/dm³ of Pb (II) in 0.2 mol/dm³ HNO₃, membrane phase = 0.872 M of TOA in xylene, time = 4.5 hours.

Table 4.6

Recovery of Pb (II) from Paint and Industrial Stream Water

Sample	Metal ion	Metal ion concentration (10 ⁻⁴ mol/dm ³)		
		Initial feed	final feed [*]	final stripping [*]
Paint	Pb ²⁺	4.45	0.002	4.444
	Cr ³⁺	2.52	0.001	2.515
	Zn ²⁺	1.35	0.005	1.342
Industrial stream water	Pb ²⁺	0.17	Nil	0.169
	Zn ²⁺	0.34	0.001	0.337
	Cr ³⁺	0.55	Nil	0.548
	Cu ²⁺	0.77	0.001	0.767

^{*} after 4.5 hours

Conditions: Feed solution = 0.2 mol/dm³ of HNO₃, stripping solution = 0.2 mol/dm³ of NaOH, membrane phase = 0.872 M of TOA in xylene.

CONCLUSIONS

The Mn (II) and Tl (III) have been transported through TEA-cyclohexanone and TEA-xylene SLMs, respectively whereas the TDDA-cyclohexane and TOA-xylene SLMs were used for Ag (I) and Pb (II) transport, respectively, against their concentrations gradient.

In the case of the transport of Mn (II), it was concluded that in the complex formation, one mole of TEA and one mole of proton interact with one mole of Mn (VII) ions to form a complex $(C_2H_4OH)_3NH.MnO_4$, which is responsible for extraction of Mn (II) ions. The optimum conditions found for extraction of Mn (II) ions were: 1.0 M of H_2SO_4 in feed solution, 9.25×10^{-3} mol/dm³ of $FeSO_4$ in 0.5 M of H_2SO_4 in stripping phase, 3.75 M of TEA in membrane phase and stirring speed of 1500 rpm. The durability and stability of SLM were investigated and it was concluded that it is quite stable for 168 hours. Application of this SLM to discharged zinc carbon dry battery cell solution reveals that almost all Mn (II) ions were extracted which confirms the practical utility of this technique.

The optimum conditions studied for transport of Tl (III) were: 1.0 mol/dm³ of HCl in feed solution, 5.26 mol/dm³ of TEA in xylene in membrane phase and 1.0 mol/dm³ of NaOH in stripping phase. It was also concluded that transport of Tl (III) follows the coupled co-ion transport mechanism. 3 moles of TEA and 3 moles of proton associate with one mole of Tl (III) forming a complex, $[(C_2H_4OH)_3NH]_3.TlCl_6$, which is responsible for transport of Tl (III) across the membrane. It was validated that this SLM is quite stable at least for 192 hours. It was also concluded that by increasing temperature from 17 °C to 31 °C, the flux of Tl (III) also increases. It was suggested that addition of H^+ takes place at N atom of TEA rather than on oxygen atoms of hydroxyl groups. Furthermore, it was also suggested that, if somehow, the hydroxyl groups could also be protonated, the liquid membrane would have been more efficient to extract more than one ion of Tl (III) by associating with TEA molecule visualized as $[(H_2O^+C_2H_4)_3.NH]_3[TlCl_6]_4$. By applying this SLM to coal ash acid leach liquors, it was revealed that almost all Tl (III) along with nickel, chromium and zinc ions have been recovered which shows a successful practical application of this technique.

The transport of Ag (I) through tri-n-dodecylamine flat sheet supported liquid membrane was found to be co-ions coupling transport mechanism, as H^+ , NO_3^- and Ag^+ move in same direction. One mole of TDDA and one mole of H^+ associate with one mole of Ag (I) forming a complex, $(LH).Ag(NO_3)_2$, which is responsible for transport of Ag (I). The optimum conditions found for this SLM system were: 0.75 mol/dm^3 of HNO_3 in feed solution, 0.788 M of TDDA in membrane phase and 1.0 mol/dm^3 of $NH_{3(aq)}$ in stripping phase. Moreover, it was also concluded that with the increasing membrane thickness, the flux of Ag (I) decreases. The stability of this SLM system was established for 120 hours. Almost all Ag (I) have been removed when this SLM system was applied to silver plating and photographic waste solutions, suggesting that this technique can be used for recovery of Ag (I) from industrial wastes effluents.

The Pb (II) can be transported by TOA-xylene-polypropylene SLM from acidic (HNO_3) to alkaline (NaOH) solution. The protons and nitrates were found to be the coupling ions and the mechanism of transport is by co-ions coupling of these ions. Two moles of protons and two moles of TOA associate with one mole of Pb (II), forming a complex of $Pb(NO_3)_4(HNR_3)_2$ responsible for transport of Pb (II). The optimum conditions recorded for extraction of Pb (II) were: 0.2 mol/dm^3 of HNO_3 in feed solution, 0.872 M of TOA in xylene in membrane phase and 0.2 mol/dm^3 of NaOH in stripping phase. It was also concluded that NaOH is a better and more suitable stripping agent than CH_3COONH_4 and Na_2SO_4 . The stability of this SLM configuration was investigated for 240 hours and it is found that flux of each run was almost the same and extraction of each run was more than 99% with a relative standard deviation of $\pm 1.5\%$. Approximately 100% of Pb (II) have been recovered when the optimized SLM was applied for the removal of Pb (II) from paint solution and industrial water contaminated with lead.

REFERENCES

1. Scott, K.; Hughes, R. Industrial membrane separation technology. First Ed., Chapman & Hall UK, **1996**.
2. Gyves, J. D.; De San Miguel, E. R. Metal ion separations by supported liquid membranes. *Ind. Eng. Chem. Res.* **1999**, 38, 2182- 2202.
3. Kislik, S. V. Liquid membranes: principles and applications in chemical separations and wastewater treatment. First Ed., Elsevier, UK, **2010**.
4. Baker, R.W. Membrane technology and applications. 2nd Ed., John Wiley & Sons California, **2004**.
5. Ravanchi, M. T.; Kaghazchi, T.; Kargari, A. Application of membrane separation processes in petrochemical industry: a review. *Desalination*, **2009**, 235, 199-244.
6. Bringas, E.; San Roman, M. F.; Irabien, J. A.; Ortiz, I. An overview of the mathematical modeling of liquid membrane separation processes in hollow fiber contractors. *J. Chem. Technol. Biotechnol.* **2009**, 84, 1583-1614.
7. Agreda, D.; Diaz, I. G.; Lopez F. A.; Alguacil, F. J. Supported liquid membranes technologies in metals removal from liquid effluents. *Rev. Metal. Madrid.* **2011**, 47(2), 146-168.
8. Kocherginsky, N. M.; Yang, Q.; Seelam, L. Recent advances in supported liquid membrane technology. *Sep. & Purif. Technol.* **2007**, 53, 171-177.
9. Rehman, S.; Akhtar, G.; Chaudry, M. A.; Bukhari, N.; Najeebullah.; Ali, N. Mn (VII) ions transport by triethanolamine cyclohexanone based supported liquid membrane and recovery of Mn (II) ions from discharged zinc carbon dry battery cell. *J. Membr. Sci.* **2011**, 366, 125-131.
10. Ansari, S. A.; Mohapatra, P. K.; Manchanda, V. K. Recovery of actinides and lanthanides from high level waste using hollow- fiber supported liquid membrane with TODGA as the carrier. *Ind. Eng. Chem. Res.* **2009**, 48, 8605-8612.

11. Hodgson, E. A text book of modern toxicology. 4th Ed., John Wiley & Sons, **2010**.
12. Duruibe, J. O.; Ogwuegbu, M. O. C.; Egwurugwu, J. N. Heavy metal pollution and human biotoxic effects. International Journal of Physical Sciences, **2007**, 2, 112-118.
13. Flora, S. J. S. Metal poisoning: threat and management. Al Ameen J Med Sci. **2009**, 2, 4-26.
14. Sriram, S.; Mohapatra, P. K.; Pandey, A. K.; Manchanda, V. K.; Badheka, L. P. Facilitated transport of americium (III) from nitric acid media using dimethyldibutyltetradecyl-3-malonamide. J. Membr. Sci. **2000**, 177, 163-175.
15. Guell, R.; Antico, E.; Salvado, V.; Fontas, C. Efficient hollow fiber supported liquid membrane system for the removal and preconcentration of Cr (VI) at trace levels. Sep. & Purif. Technol. **2008**, 62, 389-393.
16. Pei, L.; Yao, B.; Zhang, C. Transport of Tm (III) through dispersion supported liquid membrane containing PC-88A in kerosene as the carrier. Sep. & Purif. Technol. **2009**, 65, 220-227.
17. Msagati, T.; Chimuka, L.; Cukrowska, E. Sample preparation using liquid membrane extraction techniques. Water SA. **2008**, 34(3), 421-427.
18. Parthasarathy, N.; Pelletier, M.; Buffle, J. Hollow fiber based supported liquid membrane: a novel analytical system for trace metal analysis. Anal. Chim. Acta. **1997**, 350, 183-195.
19. Martak, J.; Schlosser, S.; Vickova, S. Pertraction of lactic acid through supported liquid membranes containing phosphonium ionic liquid. J. Membr. Sci. **2008**, 318, 298-310.
20. Parsad, R.; Sirkar, K. K. Hollow fiber solvent extraction of pharmaceutical products. J. Membr. Sci. **1989**, 47, 235-249.
21. Hossain, M, M. Reactive extraction of amino acids and dipeptides using an extra-flow hollow fiber module. Sep. & Purif. Technol. **2005**, 42, 227-236.

22. Djane, N-Kotey.; Ndungu, K.; Malcus, F. Supported liquid membrane enrichment using an organophosphorus extractant for analytical trace metal determination in river waters. *Fresenius J. Anal. Chem.* **1997**, 358, 822-827.
23. Naim, M. M.; Monir, A. A. Desalination using supported liquid membranes. *Desalination*, **2002**, 153, 361-369.
24. Luis, P.; Neves, L. A.; Afonso, C. A. M.; Coelho, I. M.; Crespo, J. G.; Garea, A.; Irabien, A. Facilitated transport of CO₂ and SO₂ through supported ionic liquid membranes (SILMs), *Desalination*, **2009**, 245, 485-493.
25. Neves, L. A.; Nemestothy, N.; Alves, V. D.; Cserjesi, P.; Belafi-Bako, K.; Coelho, I. M. Separation of biohydrogen by supported ionic liquid membrane. *Desalination*, **2009**, 240, 311-315.
26. Emsley.; John. Manganese Nature's Building Blocks, An A-Z Guide to the Elements. Oxford UK, Oxford University Press, **2001**, 249-253.
27. Zhang.; Wensheng.; Yong, C. C. Manganese metallurgy review, Part I, Leaching of ores/secondary materials and recovery of electrolytic/chemical manganese dioxide. *Hydrometallurgy*, **2007**, 89, 137-159.
28. Kaufman.; Gilbert, J. Applications for aluminium alloys and tempers; Introduction to aluminum alloys and tempers. ASM International, **2000**, 9, 3-94.
29. Dell, R. M. Batteries fifty years of materials development, *Solid State Ionics*, **2000**, 134, 139-158.
30. Yadav, A. A.; Khopkar, S. M. Solvent extraction separation of manganese (II) with tributyl phosphate. *Sep. Sci. Technol.* **1969**, 4, 349-355.
31. Rane, A. T. Synergic extraction of manganese (II) with thiocyanate and pyridine. *J. Radioanal. Nucl. Chem.* **1971**, 8, 117-122.
32. Nakamura, S.; Imura, H.; Suzuki, N. Synergistic extraction of manganese (II) with theonyltrifluoroacetone and neutral unidentate and bidentate ligands. *J. Radioanal. Nucl. Chem.* **1984**, 82, 33-44.

33. Arvind, T. R.; Deepawati, R. N. A comparative solvent extraction study of manganese (II) with 8-Mercaptoquinoline, 8-quinolinol and its analogues. *Microchimica Acta*. **1986**, 90, 27-42.
34. Malkhede, D. D.; Purushottam, M. D.; Shripad, M. K. Solvent extraction separation of manganese(II) with calixarene substituted with an acetyl group at the lower rim. *Analytical Sciences*, **1999**, 15, 781-784.
35. Cheng, C. Y.; Hughes, C. A.; Barnard, K. R.; Larcombe, K. Manganese in copper solvent extraction and electrowinning. *Hydrometallurgy*, **2000**, 28, 135-150.
36. Watanabe, K.; Shiba, M.; Itagaki, M. Removal of manganese (II) impurity in 2-hydroxyl-1-(2hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid by a simultaneous forward and back-extraction method. *Bunseki Kagaku*, **2000**, 49, 599-604.
37. Kawai, T.; Fujiyoshi, R.; Sawamura, S. Solvent extraction of zinc (II) and manganese (II) with 5, 10, 15, 20-tetraphenyl-21H, 23H-porphine (TPP) through the metal exchange reaction of lead (II)- TPP. *J. Solvent Extr. Res. Development, Jpn.* **2000**, 7, 36-43.
38. El-Sherbini, S. K. A. Simultaneous extraction of manganese from low grade manganese dioxide ore and beneficiation of sulphur slag. *Sep. & Purif. Technol.* **2002**, 27, 67-75.
39. Kostova, D.; Kamburova, M. Solvent extraction of manganese (VII) with a new analytical reagent. *CHEMIJA*, **2008**, 19 (3-4), 27-32.
40. Lorraine, S.; Chimuka, L.; Cukrowska, E.; Pole, S. Extraction and preconcentration of manganese (II) from biological fluids (water, milk and blood serum) using supported liquid membrane and membrane probe methods. *Analytica. Chimica. Acta*. **2003**, 485, 25-35.
41. Molinari, R.; Poerio, T.; Argurio, P. Selective removal of Cu^{+2} versus Ni^{+2} , Zn^{+2} and Mn^{+2} by using a new carrier in a supported liquid membrane. *J. Membr. Sci.* **2006**, 280, 470-477.

42. Bossche, P. V. D. The current legislative development in the EU waste policy: challenge or opportunities for metal industry, published by cobalt development institute, January 2006, 06/1, 1 http://www.thecdi.com/cdi/images/news_df/cobalt_News.january.2006.pdf.
43. Peter, A. L. J.; Viraraghavan, T. Thallium: A review of public health and environmental concerns. *Environ. Int.* **2005**, 31, 493-501.
44. Cheam, V. Thallium contamination of water in Canada. *Water Qual. Res. J. Can.*, **2001**, 36 (4), 851-877.
45. Leonard, A.; Gerber, G. B. Mutagenicity, carcinogenicity and teratogenicity of thallium compounds. *Mutat. Res.* **1997**, 387, 47-53.
46. World Health Organization (WHO), Environmental health criteria, Thallium, WHO: Geneva, Switzerland, **2002**, 182.
47. Kunihiro, W.; Hisashi, I.; Masayuki, I. Extraction-separation of thallium (I) and thallium (III) under pseudo three phase equilibrium in the presence of heavy metals. *Bunseki Kagaku*, **2000**, 49 (9), 691-697.
48. Zendelovska, D.; Stafilov, T. Extraction, separation and electrothermal atomic absorption spectrometric determination of thallium in some sulfide minerals. *Anal. Sci.* **2001**, 17 (3), 425.
49. Khopkar, S. M.; Malkhede, C. Solvent extraction separation of thallium (III) from associated elements with hexaacetyl calix[6]arene. *Ind. J. Chem.* **2003**, 42A, 2939- 2944.
50. Vanura, P. Extraction of thallium with cesium dicarbollylcobaltate in the presence of 18-crown-6. *J. Radioanal. Nucl. Chem.* **2001**, 250 (1), 169-171.
51. Rajesh, N.; Subramanian, M. S. A study of the extraction behavior of thallium with tribenzylamine as the extractant, *J. Hazard. Matter.* **2006**, 135, 74-77.
52. Talanov, V. S.; Roper, E. D.; Buie, N. M.; Talanova, G. G. A new fluorogenic mono- ionizable calix[4]arene dansylcarboxamide as a selective chemosensor of soft metal ions Tl^+ and Hg^{2+} . *Tetrahedron Lett.* **2007**, 48, 8022-8025.

53. Mahamuni, S. V.; Wadgaonkar, P. P.; Anuse, M. A. Rapid liquid-liquid extraction of thallium (III) from succinate media with 2-octylaminopyridine in chloroform as the extractant. *J. Serb. Chem. Soc.* **2008**, 73 (4), 435-451.
54. Fang, D. W.; Liu, X. Z.; Yang, J-Zhen.; Xiong, Y.; S-Liang Zang, Thermodynamics of solvent extraction of thallium with diethylhexyl phosphoric acid. *Phy. Chem. Liq.*, **2009**, 47 (3), 274-281.
55. Chamsaz, M.; Arab-Zavar, M. H.; Darroudi, A.; Salehi, T. Preconcentration of thallium (I) by single drop microextraction with electrothermal atomic absorption spectroscopy detection using dicyclohexano-18-crown-6 as extractant system. *J. Hazard Matter.* **2009**, 167, 597-601.
56. Trtic, T. M.; Vladislavljevic, G. T.; Comor, J. J. Single-stage and two-stage solvent extraction of Tl (III) in hollow fiber contactors under recirculation mode of operation. *Sep. Sci. Technol.* **2001**, 36 (2), 295-312.
57. Zolgharnein, J.; Shams, H.; Azimi, G. Selective and efficient liquid membrane transport of thallium (III) ion by potassium-dicyclohexyl-18-crown-6 as specific carrier. *Sep. Sci. Technol.* **2007**, 42, 2303-2314.
58. Brown, G. E.; Foster, A. L.; Ostergren, J. D. Mineral surfaces and bioavailability of heavy metals: A molecular-scale perspective. *Proc. Natl. Acad. Sci.* **1999**, 96, 3388-3395.
59. Meyer, P. A.; Brown, M. J.; Falk, H. Global approach to reducing lead exposure and poisoning. *Mutation Research*, **2008**, 659, 166-175.
60. Appel, C.; Dean Rhue, L. Q. Ma. R.; Reve, W. Selectivities of potassium-calcium and potassium-lead exchange in two tropical soils. *Soil Sci. Soc. Am. J.* **2003**, 67, 1707-1714.
61. Hozharbi, S. Lead-based paint is a hazard to young children: Implications for Pakistani children. *J. Pak. Med. Assoc.* **2002**, 52, 224-226.

62. Kadir, M. M.; Janjua, N. Z.; Kristensen, S.; Fatmi, Z.; Sathiakumar, N. Status of children's blood lead levels in Pakistan: Implications for research and policy. *Public Health*. **2008**, 122, 708-715.
63. Hanif, M.; Butt, M. A.; Khattak, M. A. Hazards in Pakistan, Environmental and urban affairs division ministry of housing and works, government of Pakistan. **1987**.
64. Inglezakis, V.; Grigoropoulau, H. Modeling of ion exchange of Pb^{2+} in fixed beds of clinoptilolite. *Micropor. Mesopor. Mater.* **2003**, 61, 3079-3086.
65. Kavallieratos, K.; Rosenberg, J. M.; Chen, W. Z.; Ren, T. Fluorescent sensing and selective Pb (II) extraction by a dansylamide ion exchanger. *J. Am. Chem. Soc.* **2005**, 127, 6514-6515.
66. Menoyo, B.; Elizalde, M. P.; Almela, A. Extraction of lead by cyanex 302 from phosphoric acid media. *Solvent Extr. Ion Exch.* **2001**, 19 (4), 677-698.
67. Shilimkar, T. N.; Anuse, M. A. Rapid extraction of lead (II) from succinate media with n-octylaniline in toluene. *Sep. & Purif. Technol.* **2002**, 26, 185-193.
68. Manzoori, J. L.; Zadeh, H. A. Extraction and preconcentration of lead using cloud point methodology: application to its determination in real samples by flame atomic absorption spectrometry. *Acta Chim. Solv.* **2007**, 54, 378-384.
69. Ghaedi, M.; Shokrollahi, A.; Niknam, K.; Niknam, E.; Najibi, A.; Soylak, M. Cloud point extraction and flame atomic absorption spectrometric determination of cadmium (II), lead (II), palladium (II) and silver (I) in environmental samples. *J. Hazard. Matter.* **2009**, 168, 1022-1027.
70. Ghaedi, M.; Montazerzohori, M.; Soylak, M. Solid phase extraction method for selective determination of Pb (II) in water samples using 4-(4-ethoxybenzylidene) thiophenol. *J. Hazard. Matter.* **2007**, 142, 368-373.
71. Lamb, J. D.; Nazarenko, A. Y. Lead (II) ion sorption and transport using polymer inclusion membrane containing tri-octylphosphine oxide. *J. Membr. Sci.* **1997**, 134, 255-259.

72. Burham, N. Separation and preconcentration system for lead and cadmium determination in natural samples using 2-amino-acetylthiophenol modified polyurethane foam. *Desalination*, **2009**, 249, 1199-1205.
73. Singh, S. K.; Misra, S. K.; Tripathi, S. C.; Singh, D. K. Studies on permeation of uranium (VI) from phosphoric acid medium through supported liquid membrane comprising a binary mixture of PC88A and Cyanex 923 in n-dodecane as carrier. *Desalination*, **2010**, 250, 19-25.
74. Tang, B.; Yu, G.; Fang, J.; Shi, T. Recovery of high purity silver directly from dilute effluents by an emulsion liquid membrane-crystallization process. *J. Hazard. Matter.* **2010**, 177, 377-383.
75. Minhas, F.T.; Solangi, I. B.; Memon, S.; Bhanger, M. I. Kinetic study of an effective Pb (II) transport through a bulk liquid membrane containing calix[6]arene hexaester derivatives as a carrier. *Sep. Sci. Technol.* **2010**, 45, 1448-1455.
76. Kazemi, S. Y.; Shamsipur, M. Selective transport of lead (II) through a bulk liquid membrane using a cooperative carrier composed of benzylaza-12-crown-4 and oleic acid. *Bull. Korean Chem. Soc.* **2005**, 26 (6), 930-934.
77. Sabry, R.; Hafez, A.; Khedr, M.; El-Hassanin, A. Removal of lead by an emulsion liquid membrane part I. *Desalination*, **2007**, 212, 165-175.
78. Ulewicz, M.; Lesinska, U.; Bochenska, M.; Walkowiak, W. Facilitated transport of Zn (II), Cd (II) and Pb (II) ions through polymer inclusion membranes with calix[4]-crown-6 derivatives. *Sep. & Purif. Technol.* **2007**, 54, 299-305.
79. Escobar, A.; Schimmel, K. A.; Gyves, J. D.; De San Miguel, E. R. Hollow fiber dispersion free extraction and stripping of Pb (II) in the presence of Cd (II) using D2EHPA under recirculating operation mode. *J. Chem. Tech. Biotechnol.* **2004**, 79, 961-973.
80. Akhond, M.; Shamsipur, M.; Highly efficient cooperative membrane transport of lead (II) ions by aza-18-crown-6 and palmitic acid. *Sep. Sci. Technol.* **1997**, 32 (7), 1223-1232.

81. Chaudry, M. A.; Bukhari, N.; Mazhar, M. Coupled transport of Ag (I) ions through triethanolamine-cyclohexanone-based supported liquid membranes. *J. Membr. Sci.* **2008**, 320, 93-100.
82. Amiri, A. A.; Safavi, A.; Hasaninejad, A. R.; Shrgghi, H.; Shamsipur, M. Highly selective transport of silver ion through a supported liquid membrane using calix[4] pyrroles as suitable ion carriers. *J. Membr. Sci.* **2008**, 325, 295-300.
83. Shamsipur, M.; Hashemi, O. R.; Lippolis, V. A supported liquid membrane system for simultaneous separation of silver (I) and mercury (II) from dilute feed solutions. *J. Membr. Sci.* **2006**, 282, 322-327.
84. Sole, K. C.; Ferguson, T. L.; Hiskey, J. B. Solvent extraction of silver by cyanex 272, cyanex 302 and cyanex 301. *Solvent Extr. Ion. Exch.* **1994**, 12, 1033.
85. Sevdic, D.; Meider, H.; Parkovic, D. Solvent extraction of silver and mercury by o-dibutyl phenylamino-phenylmethanethio phosphonate from chloride solutions. *Solvent Extr. Ion. Exch.* **1990**, 8, 643.
86. Stankovic, V.; Outarra, L.; Zonnevillje, F.; Comninellis, C. Solvent extraction of silver from nitric acid solutions by calix[4]arene amide derivatives. *Sep. & Purif. Technol.* **2008**, 61 (3), 366-374.
87. El-Ghaffar, M. A.; Mohamed, M. H.; Elwakeel, K. Z. Adsorption of silver (I) on synthetic chelating polymer derived from 3-amino-1,2,4-triazole-5-thiol and glutaraldehyde. *Chem. Eng. J.* **2009**, 151 (1-3), 30-38.
88. Tuzen, M.; Soylak, M. Column solid phase extraction of nickel and silver in environmental samples prior to their flame atomic absorption spectrometric determinations. *J. Hazard. Matter.* **2009**, 164 (2-3), 1428-1432.
89. Lee, S. C.; Mok, Y. S.; Lee, W. K. Application of emulsion liquid membrane technology to the extraction of silver. *J. Ind. & Eng. Chem.* **1996**, 2, 130-136.
90. Othman, N.; Mat, H.; Goto, M. Separation of silver from photographic wastes by emulsion liquid membrane system. *J. Membr. Sci.* **2006**, 282 (1-2), 171-177.

91. Akhond, M.; Tashkhourian, J. Highly selective transport of Ag^+ ion through a liquid membrane containing 2-mercaptobenzothiazole as a carrier. *Bull. Korean Chem. Soc.* **2003**, 24 (4), 489-493.
92. Rounaghi, G. H.; Kazemi, M. S.; Sadeghian, H. Transport of silver ion through bulk liquid membrane using macrocyclic and acyclic ligands as carriers in organic solvents. *J. Incl. Phenom. Macrocycl. Chem.* **2008**, 60, 79-83.
93. Farhadi, K.; Bahar, S.; Maleki, R. Separation study of silver (I) ion through a bulk liquid membrane containing meloxican. *J. Braz. Chem. Soc.* **2007**, 18(3), 595-600.
94. Gherrou, A.; Kerdjoudj, H.; Molinari, R.; Drioli, E. Removal of silver and copper ions from acidic thiourea solutions with a supported liquid membrane containing D2EHPA as carrier. *Sep. & Purif. Technol.* **2002**, 28, 235- 244.
95. Saito, T. Transport of silver (I) ion through a supported liquid membrane using bathocuproine as a carrier. *Sep. Sci. Technol.* **1998**, 33 (6), 855-866.
96. Shamsipur, M.; Kazemi, S. Y.; Azimi, G.; Madaeni, S. S.; Lippolis, V.; Garau, A.; Isaia, F. Selective transport of silver ion through a supported liquid membrane using some mixed aza-thioether crowns containing a 1, 10-phenanthroline sub-unit as specific ion carriers. *J. Membr. Sci.* **2003**, 215, 87-93.
97. Altin, S.; Yildirim, Y.; Altin, A. Transport of silver ions through a flat-sheet supported liquid membrane. *Hydrometallurgy*, **2010**, 103, 144-149.
98. Bhattacharya, A.; Mohapatra, P. K.; Ansari, S. A.; Raut, D. R.; Manchanda, V. K. Separation of trivalent actinides from lanthanides using hollow fiber supported liquid membrane containing cyanex-301 as the carrier. *J. Membr. Sci.* **2008**, 312 (1-2), 1-5.
99. Zaghbani, A.; Tayeb, R.; Bonnamour, I.; Felix, C.; Vocanson, F.; Lamartine, R.; Dhahbi, M.; Seta, P. Affinity membranes for the extraction of Cd^{2+} metal ions by facilitated transport ensured by a new thiocalix[4]arene complexing agent incorporated in supported liquid membranes (SLM). *J. Membr. Sci.* **2005**, 258 (1-2), 5-7.

100. Shuxiang, Gu.; Yuanda, Yu.; Dingsheng, He.; Ming, Ma. Comparison of transport and separation of Cd (II) between strip dispersion hybrid liquid membrane (SDHLM) and supported liquid membrane (SLM) using tri-n-octylamine as carrier. *Sep. & Purif. Technol.* **2006**, 51(3), 277-284.
101. Bukhari, N.; Chaudry, M. A.; Mazhar, M. Cobalt (II) transport through triethanolamine cyclohexanone supported liquid membranes. *J. Membr. Sci.* **2004**, 234, 157-165.
102. Molinari, R.; Argurio, P.; Pirillo, F. Comparison between stagnant sandwich and supported liquid membranes in copper (II) removal from aqueous solutions: flux, stability and model elaboration. *J. Membr. Sci.* **2005**, 256 (1-2), 158-168.
103. Ishikawa, J.; Sakamoto, H.; Otomo, M. Highly silver ion-selective transport through liquid membranes containing cyclic and acyclic polythiamonoazaalkanes bearing an easily ionizable moiety. *Analyst*, **1997**, 122, 1383-1386.
104. Yaftian, M. R.; Burgard, M.; Dieleman, C. B.; Matt, D. Rare-earth metal-ion separation using a supported liquid membrane mediated by a narrow rim phosphorylated calix[4]arene. *J. Membr. Sci.* **1998**, 144 (1-2), 57-64.
105. Alguacil, F. j.; Alonso, M.; Lopez, F. A.; Delgado, A. L. Active transport of cobalt (II) through a supported liquid membrane using the mixture DP8R and Acorga M5640 as extractant. *Desalination*, **2011**, 281, 221-225.
106. Sriram, S.; Mohapatara, P. K.; Pandey, A. K.; Manchanda, V. K.; Badheka, L. P. Facilitated transport of americium (III) from nitric acid media using dimethyldibutyltetradecyl-1,3-malonamide. *J. Membr. Sci.* **2000**, 177, 163-175.
107. Prakorn, R.; Ura, P. Synergistic extraction and separation of mixture of lanthanum and neodymium by hollow fiber supported liquid membrane. *Korean J. Chem. Eng.* **2003**, 20 (4), 724-730.
108. Marchese, J.; Valenzuela, F.; Basualto, C.; Acosta, A. Transport of molybdenum with Alamine 336 using supported liquid membrane. *Hydrometallurgy*, **2004**, 72, 309-317.

109. Alguacil, F. J.; Caravaca, C.; Martin, M. I. Transport of chromium (VI) through a cyanex 921-supported liquid membrane from HCl solution. *J. Chem. Technol. Biotechnol.* **2003**, 78, 1048-1053.
110. Madaeni, S. S.; Zand, H. R. K. Selective transport of bismuth ions through supported liquid membrane. *Chem. Eng. Technol.* **2005**, 28 (8), 892-898.
111. Rosell, A.; Palet, C.; Valiente, M. Selective separation and concentration of vanadium (V) by a chemical pumping hollow-fiber supported liquid membrane. *Anal. Chim. Acta.* **1997**, 349, 171-178.
112. Harnandez, L.; Bolarin, Ana. Ma.; Sanchez, F.; Patino, F.; Rivera, I.; Salinas, E. Studies on ion transport of Eu (III) and Gd (III) through supported liquid membranes containing di-(2-ethylhexyl) phosphate, as a carrier. *J. Mex. Chem. Soc.* **2007**, 51 (2), 113-116.
113. Swain, B.; Jeong, J.; Lee, J-Chun.; Lee, G-Ho. Separation of Co (II) and Li (I) by supported liquid membrane using Cyanex 272 as mobile carrier. *J. Membr. Sci.* **2007**, 297, 253-261.
114. Swain, B.; Jeong, J.; Lee, J-Chun.; Lee, G-Ho. Extraction of Co (II) by supported liquid membrane and solvent extraction using Cyanex 272 as an extractant: A comparison study. *J. Membr. Sci.* **2007**, 288, 139-148.
115. Guell, R.; Antico, E.; Salvado, V.; Fontas, C. Efficient hollow fiber supported liquid membrane system for the removal and preconcentration of Cr (VI) at trace level. *Sep. & Purif. Technol.* **2008**, 62, 389-393.
116. Chakrabarty, K.; Saha, P.; Ghoshal, A. K. Separation of lignosulfonate from its aqueous solution using supported liquid membrane. *J. Membr. Sci.* **2009**, 340, 84-91.
117. Weidong, Z.; Chunhua, C.; Zisu, H. Transport study of Cu (II) through hollow fiber supported liquid membrane. *Chin. J. Chem. Eng.* **2010**, 18 (1), 48-54.
118. Gaikwad, A. G.; Rajput, A. M. Transport of yttrium metal ions through fibers supported liquid membrane solvent extraction. *J. Rare Earth*, **2010**, 28 (1), 1-6.

119. Chakrabarty, K.; Saha, P.; Ghoshal, A. K. Separation of mercury from its aqueous solution through supported liquid membrane using environmentally benign diluent. *J. Membr. Sci.* **2010**, 350, 395-401.
120. Chaudry, M. A.; Malik, M. T.; Ahmad, M. Supported liquid membrane extraction of W (VI) ions using tri-n-octylamine as carrier. *J. Radioanal. Nucl. Chem.* **1991**, 150 (2), 383-396.
121. Danesi, P. R.; Chiarizia, R.; Castagnola, A. Transfer rate and separation of Cd (II) and Zn (II) chloride species by a trilaurylammonium chloride-triethylbenzene supported liquid membrane. *J. Membr. Sci.* **1983**, 14 (2), 161-174.
122. Danesi, P. R.; Cianetti, C. Permeation of metal ions through a series of two complementary supported liquid membranes. *J. Membr. Sci.* **1984**, 20 (2), 201-213.
123. Parthasarathy, N.; Pelletier, M.; Buffle, J. Hollow fiber based supported liquid membrane: a novel analytical system for trace metal analysis. *Anal. Chim. Acta.* **1997**, 350 (1-2), 183-195.
124. Yafthian, M. R.; Burgard, M.; Dieleman, C. B.; Matt, D. Rare-earth metal-ion separation using a supported liquid membrane mediated by a narrow rim phosphorylated calix[4]arene. *J. Membr. Sci.* **1998**, 144 (1-2), 57-64.
125. Campderros, M. E.; Marchese, J. Facilitated transport of niobium (V) and tantalum (V) with supported liquid membrane using TBP as carrier. *J. Membr. Sci.* **2000**, 164, 205-210.
126. Voorde, Van-De.; Pinoy, L.; De Ketelaere, R. F. Recovery of nickel ions by supported liquid membrane (SLM) extraction. *J. Membr. Sci.* **2004**, 234 (1-2), 11-21.
127. Breembroek, G. R. M.; Van Straalen, A.; Witkamp, G. J.; Van Rosmalen, G. M. Extraction of cadmium and copper using hollow fiber supported liquid membranes. *J. Membr. Sci.* **1998**, 146 (2), 185-195.

128. Venkateswaran, P.; Palanivelu, K. Studies on recovery of hexavalent chromium from plating wastewater by supported liquid membrane using tri-n-butyl phosphate as carrier. *Hydrometallurgy*, **2005**, 78 (1-2), 107-115.
129. Ansari, S. A.; Mohapatra, P. K.; Raut, D. R.; Kumar, M.; Rajeswari, B.; Manchanda V. K. Performance of some extractants used for actinide partitioning in a comparative hollow fiber supported liquid membrane transport study using simulated high level nuclear waste. *J. Membr. Sci.* **2009**, 337 (1-2), 304-309.
130. Reyes-Aguilera, J. A.; Gonzalez, M. P.; Navarro, R.; Saucedo, T. I.; Avila-Rodriguez, M. Supported liquid membranes (SLM) for recovery of bismuth from aqueous solutions. *J. Membr. Sci.* **2008**, 310 (1-2), 13-19.
131. Sastre, A. M.; Madi, A.; Alguacil, F. J. Facilitated supported liquid-membrane transport of gold (I) using LIX 79 in cumene. *J. Membr. Sci.* **2000**, 166, 213-219.
132. Junwen, Lv.; Yang, Q.; Jiang, J.; Chung, Tai-Shung. Exploration of heavy metal ions transmembrane flux enhancement across a supported liquid membrane by appropriate carrier selection. *Chem. Eng. Sci.* **2007**, 62, 6032-6039.
133. Gill J. S.; Singh, H.; Gupta, C. K. Studies on supported liquid membrane for simultaneous separation of Fe (III), Cu (II) and Ni (II) from dilute feed. *Hydrometallurgy*, **2000**, 55 (1), 113-116.
134. Fane, A. G.; Yang, X. J. Performance and stability of supported liquid membranes using LIX 984N for copper transport. *J. Membr. Sci.* **1999**, 156, 251-263.
135. Rathore, N. S.; Sonawane, J. V.; Kumar, A.; Venugopalan, A. K.; Singh, R. K.; Bajpai, D. D.; Shukla, J. P. Hollow fiber supported liquid membrane: a novel technique for separation and recovery of plutonium from aqueous acidic waste. *J. Membr. Sci.* **2001**, 189, 119-128.
136. Lothongkum, A. W.; Suren, S.; Chaturabul, S.; Thamphiphit, N.; Pancharoen, U. Simultaneous removal of arsenic and mercury from natural-gas-co-produced water from the gulf of Thailand using synergistic extractant via HFSLM. *J. Membr. Sci.* **2011**, 369, 350-358.

137. Parhi, P. K.; Das, N. N.; Sarangi, K. Extraction of cadmium from dilute solution using supported liquid membrane. *J. Hazard Matter.* **2009**, 172, 773-779.
138. Danesi, P. R.; Horwitz, E. P.; Rickert, P. G. Rate and mechanism of facilitated americium (III) transport through a supported liquid membrane containing a bifunctional organophosphorus mobile carrier. *J. Am. Chem. Soc.* **1983**, 87, 4708-4715.
139. Dreher, T. M.; Stevens, G. W. Instability mechanism of supported liquid membranes. *Sep. Sci. Technol.* **1998**, 33 (6), 835-853.
140. Alpoguz, H. K.; Kaya, A.; Memon, S.; Yilmaz, M. Facilitated supported liquid membrane transport of Hg^{2+} using calix[4]arene derivatives. *J. Macromol. Sci.* **2007**, 44, 17-20.
141. Juang, R-Shin.; Lee, S-Hwa. Analysis of the transport rates of europium (III) across an organophosphinic acid supported liquid membrane. *J. Membr. Sci.* **1996**, 110, 13-23.
142. Claudia, F.; Manuela, H.; Victoria, S.; Enriqueta, A. Selective recovery and preconcentration of mercury with a benzoylthiourea-solid supported liquid membrane system. *Anal. Chim. Acta.* **2005**, 547 (2), 255-261.
143. Kubota, F.; Kakoi, T.; Goto, M.; Furusaki, S.; Nakashio, F.; Hano, T. Permeation behavior of rare earth metals with a calix[4]arene carboxyl derivative in a hollow-fiber membrane. *J. Membr. Sci.* **2000**, 165 (2), 149-158.
144. Adebayo, A. O.; Sarangi, K. Separation of copper from chalcopryrite leach liquor containing copper, iron, zinc and magnesium by supported liquid membrane. *Sep. & Purif. Technol.* **2008**, 63, 392-399.
145. Ren, Z.; Zhang, W.; Liu, Y.; Dai, Y.; Cui, C. New liquid membrane technology for simultaneous extraction and stripping of copper (II) from wastewater. *Chem. Eng. Sci.* **2007**, 62 (22), 6090-6101.
146. Kunungo, S. B.; Mohapatra, R. Coupled transport of Zn (II) through a supported liquid membrane containing bis (2, 4, 4-trimethylpentyl) phosphinic acid in

- kerosene. II. Experimental evaluation of model equations for rate process under different limiting conditions. *J. Membr. Sci.* **1995**, 105 (3), 227-235.
147. User's manual. PE 2400 Series II CHNS/O analyzer, Perkin Elmer USA, **1998**.
 148. Rehman, S. U.; Akhtar, G.; Chaudry, M. A. Coupled transport of Tl^{3+} through triethanolamine-xylene-polypropylene supported liquid membranes. *J. Ind. Eng. Chem.* **2012**, 18, 492-498.
 149. Vogel, I. A text book of quantitative inorganic analysis. third ed, **1971**.
 150. Chaudry, M. A.; Ahmad, S.; Malik, M. T. Supported liquid membrane technique applicability for removal of chromium from tannery wastes, *Waste Management*, **1997**, 17(4) 211-218.
 151. Huidong, Z.; Biyu, W.; Yanxiang, W.; Qilong, R. Instability mechanism of some supported membranes for phenol transport, *Chin. J. Chem. Eng.* **2009**, 17(5), 750-755.
 152. Wang, B.; Lin, J.; Wu, F.; Peng, Y. Stability and selectivity of supported liquid membrane with ionic liquids for the separation of organic liquids by vapor permeation, *Ind. Eng. Chem. Res.* **2008**, 47, 8355-8360.
 153. H-Fernandez, F. J.; De los Rios A. P.; Alonso, F. T.; Palacios, J. M.; Villora, G. Preparation of supported ionic liquid membranes: Influence of the ionic liquid immobilization method on operational stability, *J. Membr. Sci.* **2009**, 341, 172-177.
 154. Dell, R. M. Batteries: fifty years of materials development, *Solid State Ionics* **2000**, 134, 139-158.
 155. Svehla, G. Vogel's qualitative inorganic analysis, seventh ed., Pearson Education Publisher, **2007**.
 156. Goto, H.; Kakita, Y.; Ichinose, N. Studies on the extraction and determination of metal salts with methyl isobutyl ketone, extraction of thallium, *J. Chem. Soc. Jpn.* **1967**, 88, 640.

157. Pawelka, Z.; Huyskens, T. Z. Alkyl substituent effect on the polarity of phenols–tri-n-alkylamine complexes, *Can. J. Chem.* **2003**, 81, 1012–1018.
158. Panja, S.; Ruhela, R.; Misra, S. K.; Sharma, J. N.; Tripathi, S. C. A.; Dakshinamoorthy, Facilitated transport of Am (III) through a flat-sheet supported liquid membrane (FSSLM) containing tetra(2-ethyl hexyl) diglycolamide (TEHDGA) as carrier, *J. Membr. Sci.* **2008**, 325, 158-165.
159. Chaudry, M. A.; Islam, N. U.; Rehman, N. U. Extraction of Pd (II) ions using tri-n-octylamine xylene base supported liquid membranes, *J. Radioanal. Nucl. Chem.* **1997**, 218(1), 53-60.
160. Christan, G. D. Analytical chemistry, sixth ed., John Wiley & Sons, **2004**.
161. Inoue, K.; Baba, Y. Solvent extraction equilibria of lead (II) with acidic organophosphate and phosphonate, *Solvent Extr. Ion. Exch.* **1987**, 5(6), 1031-1044.
162. Q-Yang Lv, J.; Jiang J.; Chung, T. S. Exploration of heavy metal ions transmembrane flux enhancement across a supported liquid membrane by appropriate carrier selection, *Chem. Eng. Sci.* **2007**, 62, 6032-6039.
163. Chaudry, M. A.; Bukhari, N.; Mazhar, M.; Tazeen, F. Vanadium (V) ions transport through tri-n-octylamine cyclohexane supported liquid membranes. *Sep. & Purif. Technol.* **2007**, 54, 227-233.

LIST OF PUBLICATIONS (Published from this work)

Published

1. Rehman, S.; **Akhtar, G.**; Chaudry, M. A.; Bukhari, N.; Ullah, N.; Ali, N. Mn (VII) ions transport by triethanolamine cyclohexanone based supported liquid membrane and recovery of Mn (II) ions from discharged zinc carbon dry battery cell. J. Membr. Sci. **2011**, 366, 125-131.
2. Rehman, S.; **Akhtar, G.**; Chaudry, M. A. Coupled Transport of Tl^{3+} through Triethanolamine-Xylene-Polypropylene Supported Liquid Membranes. J. Ind. Eng. Chem. **2012**, 18, 492-498.
3. Rehman, S.; **Akhtar, G.**; Chaudry, M. A.; Ali, K.; Ullah, N. Transport of Ag^+ through tri-n-dodecylamine supported liquid membranes. J. Membr. Sci. **2012**, 389, 287-293.

Submitted/In process

1. Rehman, S.; **Akhtar, G.**; Chaudry, M. A. Coupled Transport of Pb^{2+} through TOA-Xylene-Polypropylene Supported Liquid Membranes. Can. J. Chem. Eng. In press.