Liquid Membrane Based Technology for Removal of Pollutants from Wastewater

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Liquid Membrane Based Technology for Removal of Pollutants from Wastewater

Thesis

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requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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Dedication

To My Parents and husband

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CERTIFICATE

It is certified that the work contained in the thesis entitled **"Liquid Membrane Based Technology for Removal of Pollutants from Wastewater"** by **Kabita Chakrabarty** has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

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Abstract

Liquid membrane (LM) technology has drawn attention of the research community since the early ‘90s and it has increased manifold in recent years. This thesis aims at exploring the efficacy of LM technology for the separation and pre-concentration of lignosulfonate (LS) and mercury (II) from their aqueous solutions. A suitable LM that can extract the said solutes is identified through equilibrium study. Experimentation with various solvents and carrier agents reveal that the dichloroethane (solvent) and trioctylamine (carrier) are the best combination for separation of the LS and Hg(II). The performance of various LM based processes *viz.* in the area of bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM) in the separation of LS and mercury using the identified LM is then investigated.

Coupled transport of LS and coupled transport of mercury through BLM is carried out to identify the best set of operating conditions and mode of transport that would yield optimum performance of the BLM. The effects of operating conditions, *viz.* pH, temperature, carrier concentration, stirring speed, initial feed and strip phase concentrations on the transport of LS as well as on mercury are investigated and optimized. Co-transport mode of transfer is found to be more efficient in comparison to counter-transport mode so far as recovery is concerned. It is understood that LM based transport is highly dependent on feed phase pH. The optimized values of pH, carrier concentration and stirring speed in BLM are 2, 4% (v/v) and 500 rpm for LS and 2.5, 1.5%(v/v) and 500 rpm for mercury respectively.

The study of LM was continued with a flat sheet supported liquid membrane (FSSLM). The SLM combination “Nylon 6,6-TOA-dichloroethane” was found to be the suitable for both separation of LS and separation of mercury(II). The SLM is found to be stable till 10 hours. It is observed that extraction of LS is increased with increase in concentration of NaOH up to

0.5M NaOH and that for mercury up to 0.1M NaOH. Transport of LS is found to be well described by a permeation model similar to metal ions transport. Separation of mixture of mercury and LS behaves in a similar way as their pure solutions.

Environmentally benign solvent is applied as a diluent in SLM to study its performance on the removal of mercury. The SLM combination "PVDF-TOA-Coconut oil" shows encouraging results and it is stable for a period of 98 hours. The fundamental parameters, such as feed phase pH and concentration, strip phase concentration, carrier concentration, *etc.*, affecting the transfer of mercury through the SLM are studied. The carrier concentration has marginal effect on extraction as about 91% separation of mercury is achieved without any carrier in the SLM. Coconut oil shows better performance in the separation of mercury compared to the other organic solvents such as dichloroethane and heptane.

Since ELM based separation of mercury has been successfully studied by many researchers and since no such attempt for LS is available till date, separation efficiency of the ELM based process for LS is studied. The ELM contains TOA as carrier, dichloroethane as solvent and polyethylene glycol (PEG) as surfactant. The fundamental parameters (*viz*. surfactant concentration, phase ratio, strip phase concentration, carrier concentration, treat ratio) affecting the separation of LS through the ELM are investigated to select the suitable combinations of the process parameters. The maximum separation of LS (about 91%) is achieved at a PEG concentration of 5% (w/v), strip phase concentration of 0.4M NaOH and a phase ratio of 1:1. With increase of strip phase concentration the extraction increases up to a limiting value. However extraction increases with increase of carrier concentration. The LS concentration in the feed has no considerable effect on the extraction process up to 378 mgl^{-1}.

Finally, the efficiency of the identified SLM and ELM combinations are applied for the extraction of LS from industrial black liquor. The SLM combination "Nylon 6, 6-TOA-

dichloroethane" is found to extract about 73% of LS and that by the ELM combination "dichloroethane-TOA-PEG" is 85-86%.

Keywords: Bulk liquid membrane (BLM), Emulsion liquid membrane (ELM), Lignosulfonate (LS), Liquid membrane (LM), Mercury (II), Supported liquid membrane (SLM), Trioctylamine (TOA).

Summary

This research work aims at exploring liquid membrane based processes for the separation and preconcentration of pollutants namely lignosulfonate and mercury (II) from wastewater. It covers the following major topics.

- Selection of a suitable liquid membrane for the separation of the target pollutants.
- Performance study of various liquid membrane based processes such as bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM) in the extraction and recovery of the pollutants.
- Applicability of an environmentally benign liquid membrane process in the extraction of mercury.

The thesis is organized in the following seven chapters:

Chapter I: Introduction and literature review.

Chapter II: Materials and Methods.

Chapter III: Separation of pollutants using bulk liquid membrane (BLM).

Chapter IV: Separation of pollutants using supported liquid membrane (SLM).

Chapter V: Liquid membrane separation with environmentally benign diluent.

Chapter VI: Separation using emulsion liquid membrane (ELM).

Chapter VII: Conclusion and scope of further research.

A brief description of each of the chapters is furnished below:

Chapter-I: Introduction and Literature review

This chapter introduces the purpose of the research. It elaborates on the sources of lignosulfonate (LS) and mercury (II) in wastewater and their impact on environment. Various standard methods of removal of pollutants, available in the literature are discussed along with

their merits and demerits. Liquid membrane (LM) technique has been advocated as the need of the hour along with a brief outline on its principle, feature, classification, and applications. A thorough literature review on each of the above aspects along with their scope of application for separation of LS and mercury are incorporated. Finally, the importance and objective of the thesis are highlighted.

Chapter-II: Materials and Methods

This chapter primarily discusses about three types of LM set-ups (BLM, SLM and ELM) which were indigenously fabricated in the laboratory to carry out the experimental work. The detailed descriptions of each of these set-ups along with their schematic as well as pictorial representations are included in the thesis. The experimental procedures followed in each LM set-up have been described thoroughly. Two phase equilibrium study and three phase BLM study, necessary for selecting best liquid membrane and/or organic-carrier combination, are described in this chapter. This chapter also gives information on the chemicals and reagents used in various experiments along with their sources. The selection of support material for SLM and selection of surfactant for ELM are major challenges because stability issues are critical in both these cases. The chapter describes method of preparation of LM which ensures a stable SLM/ELM. UV-visible spectrophotometer and Atomic Absorption Spectrometer were used for measurement of LS and mercury respectively. A brief description of these instruments along with specifications of various other analytical instruments such as viscometer, tensiometer, optical microscope, *etc.* used during this research work is also presented in this chapter.

Chapter-III: Separation of pollutants using bulk liquid membrane

This chapter presents the results and discussion on the separation of LS and mercury from their aqueous solutions. It is aptly divided into two major parts, (1) Separation of LS and (2) Separation of mercury

The experimentation starts with a two phase equilibrium study between aqueous solution of the target pollutant (LS or mercury) and various organic phases (combinations of organic liquids and carrier agents). The distribution coefficient is defined as the ratio of the amounts of target pollutant present in the organic phase and the aqueous phase after equilibrium is reached. A high distribution coefficient indicates the best possible membrane-carrier combination that would give the best possible separation for pollutant (LS or mercury). Two phase study also helps one to understand the effects of process parameters such as pH, temperature and carrier concentration on the equilibrium distribution of LS/mercury. The best possible combination of the above parameters can thereby be detected in order to set the optimum operating conditions. The LM containing dichloroethane as diluent and trioctylamine (TOA) as carrier has the highest distribution coefficient (21.5) for LS. The optimum operating conditions, as detected by this study, has a pH of 2, carrier concentration of 2% (v/v) and temperature of 40 ºC. The above procedure was repeated for aqueous solution of mercury and same solvent-carrier combination (dichloroethane-TOA) yielded the best performance in this case too. The optimum operating conditions that yield maximum distribution of mercury are, feed phase pH of 2.5 and carrier concentration of 1.5 %(v/v) at room temperature.

This LM (dichloroethane-TOA) has further been used for three phase separation study. The separation performance was evaluated against various parameters such as stirring speed, solute concentration in aqueous phase, carrier concentration and temperature. Both co-and counter transport mode of LS transport were studied. It was observed that transport of LS can be enhanced by increasing the temperature and stirring speed of feed phase. Stirring of strip phase had no appreciable effects on the transport of LS. Recovery of LS is much higher in co-transport mode (about 70%) in comparison to counter transport mode (5-10%). As co-transport mode showed encouraging results for LS, in case of mercury only co-transport

mode was studied. Extraction and recovery of mercury is also found to have optimum operating conditions, which are discussed in this chapter with appropriate reasoning.

Chapter-IV: Separation of pollutant using supported liquid membrane

This chapter presents the results and discussion of the experimental works carried out on separation of LS, mercury and their mixture from their respective aqueous solutions using SLM. The LM, i.e., the solvent-carrier combination, which had shown the best performance for the BLM based separation, has been retained for SLM based study as well. The entire chapter is divided into three major parts (1) Separation of LS (2) Separation of mercury and (3) Simultaneous separation of mixture of LS and mercury.

The experiments were carried out with various support materials (*viz*. polytetrafluoroethylene, polyvinyldinefloride and Nylon 6, 6) and operating conditions (*viz*. carrier concentration, strip phase concentration, salt concentration, *etc*.). The results were analyzed to identify a suitable combination of support and operating conditions that would yield best performance of the SLM in terms of fast and efficient transport of LS. Based on the results of BLM study (Chapter III), co-transport mode of transfer was studied using aqueous NaOH as the strip phase. The maximum separation (about 90%) as well as recovery (about 43%) of LS is obtained with SLM combination of "Nylon 6, 6-TOA-dichloroethane" at 4% (v/v) TOA, feed phase pH of 2 and a strip phase concentration of 0.5M NaOH. The SLM is found to be stable upto 10 hours. However life time of the membrane is 48 hours.

The LM comprising of TOA and dichloroethane has also shown great potential for the separation of mercury using BLM. Thus, an experimental investigation on facilitated transport of mercury through a flat sheet SLM having same support-carrier-solvent combination as LS was carried out. Various operating parameters affecting the transport of mercury were investigated and optimized. It was observed that extraction and recovery of mercury increases with increase in concentration of strip phase and feed pH up to a certain

limit. A feed phase pH of 2.5 and strip phase concentration of 0.1M NaOH provide the maximum extraction (about 81%) as well as recovery (about 70%) of mercury. Extraction of mercury also increases with increase in carrier concentration, however, recovery of mercury decreases after 4% (v/v) TOA. Initial feed concentration does not affect the extraction process appreciably, nevertheless the SLM was found to be equally effective at high as well as at low feed concentration.

It has been observed that the same SLM is suitable for the separation of both LS and mercury. Therefore the performance of the above SLM for simultaneous separation of mixture of mercury and LS is also discussed in this chapter. Experiments were performed at various process parameters such as strip concentration, feed phase pH, carrier concentration and feed composition. Extraction of LS was found to be independent of mercury concentration in the mixture. The mixture of mercury and LS behaves exactly in a similar way as their pure solution. However the extraction is low in comparison to their pure solution. Separation of mercury and LS from their mixture is about 52.6 % and 50.2 %, respectively at 4% (v/v) TOA and 0.2M NaOH (strip phase).

The transport process through LM is a combination of three unique mechanisms *viz.*, diffusion through a feed/strip aqueous layer, a fast interfacial chemical reaction, and diffusion of carrier- complex through the organic membrane. This chapter also describes a theoretical development of solute transport mechanism whereby a permeation model (similar to metal ion transport) for LS transport across the SLM is developed. The diffusional resistances of organic membrane ($\Delta org.$) and aqueous solution ($\Delta aq.$), calculated from the permeation model, are found to be 609.9 and 176.6 s cm^{-1}, respectively.

Chapter-V: Liquid membrane separation with environmentally benign diluent.

The instability problem of SLM is primarily due to the loss of organic liquid from its pores which eventually causes environmental problems. This chapter focuses on the possibility of

using environment friendly diluent, *viz.* coconut oil, for the separation of mercury through SLM. The solubility of LS and its compounds in coconut oil was found to be very poor and hence, only the separation of mercury through such SLM was investigated in this work. The results and discussion of various experiments are presented in this chapter. Various polymeric supports were tested in order to select the best SLM configuration. The SLM configuration "PVDF-TOA-Coconut oil" was found to be the best and it was stable for a period of 98 hours. The fundamental parameters affecting the transfer of mercury through the SLM were studied. It has been observed that with increase of NaOH concentration from 0.05 to 0.1M in the strip phase the extraction of mercury increases sharply. Beyond 0.1M NaOH, extraction of mercury increases marginally with further increase in concentration of NaOH in the strip phase. The extraction process depends on feed phase pH and maximum extraction was achieved at a pH of 1. The carrier concentration has marginal effect on extraction as about 91% separation of mercury was achieved without any carrier in the SLM. The performance of organic solvents (*viz*. dichloroethane and heptane), and that of coconut oil is also compared in this chapter. The efficiency of coconut oil in the separation of mercury is found to be marginally better than that of organic solvents.

Chapter-VI: Separation using emulsion liquid membrane

This chapter focuses on the separation of LS using ELM. Initially water in oil (W/O) type emulsion was prepared by proper selection of surfactant and the phase ratio (the ratio of organic phase to aqueous phase). PEG (polyethylene glycol) was chosen as the right surfactant for this purpose. The effects of the fundamental parameters such as surfactant (PEG) concentration, phase ratio, strip phase concentration and carrier concentration on the transport of LS through the ELM were investigated and optimized. Extraction of LS increased with increase in concentration of PEG upto 4%. About 91% extraction of LS is achieved at optimum conditions *viz.* 0.4M NaOH, 4% (v/v) TOA, treat ratio 50 and phase

ratio 1.5. The ELM module was also applied to actual industrial black liquor (obtained from the effluent from paper mill) in order to study its efficiency in extraction of LS. The ELM module is able to extract 80-86% of LS from the diluted black liquor.

Chapter-VII: Conclusion and scope of further research

This chapter summarizes the inferences drawn from the present research work and provides recommendations towards future direction. Some of the major inferences are as follows:

- All the three types of LM modules studied in this work are found to be equally efficient in the extraction of LS. However each of these modules suffers from their own merits and demerits.
- The SLM module is found to be suitable in the separation of both LS and mercury.
- Both SLM and ELM module can be efficiently applied to extract LS from industrial black liquor.
- SLM module using coconut oil as the diluent shows promising results in the separation of mercury from aqueous solution.

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CHAPTER-I

Introduction and Literature Review

This chapter presents an introduction of the aim of the research along with elaborate literature review on the relevant issues. Principle of liquid membrane, its applications, features and classifications are elaborated in this chapter. It is intended in this thesis to explore the possibility of using liquid membrane for separation of industrial pollutants viz. lignosulfonate and mercury, from wastewater. Hence the sources of the said pollutants and their impact on environment are addressed in this chapter. A thorough literature review on the earlier works related to this research are incorporated. Finally, the importance and objective of the present research works are highlighted.

1. Introduction

The growing environmental concern all over the world obligates the chemical industries to minimize the discharge of their effluent (wastewater) that may contain various pollutants. Several methods for separation of pollutants are available in the literature such as adsorption, precipitation and coagulation, ion exchange, solvent extraction, *etc*. Each of these methods is associated with its inherent merits and demerits. For example, adsorption is an effective, economical (provided the adsorbent has low cost) and simple method used for the removal of pollutants from effluent. Adsorption has been reported as a superior technique for treatment of wastewater in terms of initial cost, flexibility and simplicity of design, ease of operation and the quality of treated effluent [1]. However, it suffers the

drawbacks such as production of secondary pollutants, loss of adsorbents, expensive regeneration process and the disposal of the used adsorbents. Though coagulation and precipitation techniques are simple, they are often expensive, create sludge disposal problem and give rise to secondary pollution problem due to excessive use of chemicals. High electrical energy requirement and consumption of large amount of chemicals are common problems encountered in such methods [1]. Ion exchange is another efficient method applied for the removal of pollutants from wastewater. However, because of expensive resins, this method is commercially unattractive. Solvent or liquid-liquid extraction is a widely used and energy saving process. The major disadvantages of such processes are the loss of solvent and the problems encountered during recovery of the solvent.

In recent times, membrane based technology has emerged as an efficient process for separation of pollutants from wastewater because of its low energy consumption, capability of integration with other processes and adjustable characteristics of the membrane. Membrane separation processes, in general, differ based on size (*viz.* microfiltration, ultrafiltration, nanofiltration), affinity (*viz.* reverse osmosis, pervaporation, gas separation), charge (*viz*. dialysis, electrodialysis) and chemical nature (*viz.*carrier mediated separation) of the separated particles [2-3]. It also differs based on the membrane materials such as solid membrane and liquid membrane [2]. As the name implies, the membrane in one case is in solid form (*viz*. organic or polymeric and inorganic) and in the other case is a liquid such as organic solvents. Though the separations based on solid membrane such as ultrafiltration, reverse osmosis, electrodialysis, *etc.* are more stable, they face the problems of low flux rate, membrane fouling, low selectivity and need of equipments of large size.

Separations based on liquid membrane have the advantages of simultaneous extraction and stripping in a single step, high separation factor and selectivity. The attractiveness of liquid membrane separation lies in the fact that diffusivities of solute in liquids are several orders (10^{-6} to$10^{-5}$$cm^2s^{-1}$) of magnitude higher than that of solid membranes (above 10^{-8} cm^2s^{-1}) [4]. Liquid membrane technique is therefore gaining increased importance in the recent times for the abatement of pollutants from wastewater. The principle and salient features of the liquid membrane are elaborated in the subsequent sections.

1.1 Liquid membrane (LM)

The concept of LM was developed long back in 1902 when Nernst and Riesenfeld studied the properties of systems consisting of an oil layer separating electrolyte solutions [5]. LM is a homogeneous, thin film of liquid (membrane phase) interposed between two other liquid phases, namely feed (or source) phase and receiving (or strip) phase. The membrane liquid must be chosen in such a way that the phase is immiscible with the feed/receiving phase. Feed phase typically contains solute that need to be transported across the thin film LM to the receiving phase. The transport of solute across the LM occurs due to the difference in solubility and diffusivity in the liquid film as well as the concentration gradients in the phases. Depending on the type of application, the source/membrane/strip phase combination can have either aqueous/organic/aqueous configuration or organic/aqueous/organic configuration. From the perspective of wastewater treatment, which is the central theme of this thesis, aqueous/organic/aqueous configuration is followed.

1.1.1 Mechanism in LM separation

The transport mechanism in LM based separation can be categorized into two major types *viz*. passive transport and active transport. The passive transport basically follows solution diffusion mechanism. It involves the transport of selective species from one phase to the other due to gradient in chemical or electrical potential. However, the basic transport mechanism can be altered by adding specific carrier agent or by providing external electric or photo impulses. In active transport, driving force provided by the chemical reactions such as oxidation and reduction are used to transport the solute from feed to receiving phase. It involves the concurrent coupled flow of several species in the system. Keden has proposed a more general definition. According to him, active transport is accomplished only by the cross-coupling of the flux of species, *i* with that of other species or the chemical reaction and the driving force is supplied by the free energy change of the coupled processes [6]. The transport mechanism in LM highly depends on the viscosity of the membrane phase as diffusivity according to Stokes Einstein equation, is inversely proportional to viscosity *i.e*.[2]

$$D = \frac{kT}{6\pi\eta r} \tag{1.1}$$

Where, D is the diffusivity, k is the Boltzmann constant, η is the viscosity of the organic phase, T absolute temperature and r is the molecular radius. Hence, the viscosity of the membrane phase should be low for higher transport. Various transport mechanisms, involved in LM processes are briefly discussed below.

1.1.1.1 Ordinary or free diffusive transport

This is the simplest solution diffusion mechanism. Solution diffusion transport mechanism is usually followed during permeation of solute through dense membrane and also through liquid membrane [7]. The solute diffuses through the dense film due to concentration gradient and hence the solute transport occurs through the membrane. Transport of component, *A* from feed phase to membrane phase occurs by higher solubility or diffusivity of solute, *A* in the membrane phase as shown in Fig. 1.1. The rate of mass transfer in this case is low and depends on the solubility of solute in the organic as well as receiving/strip phase.

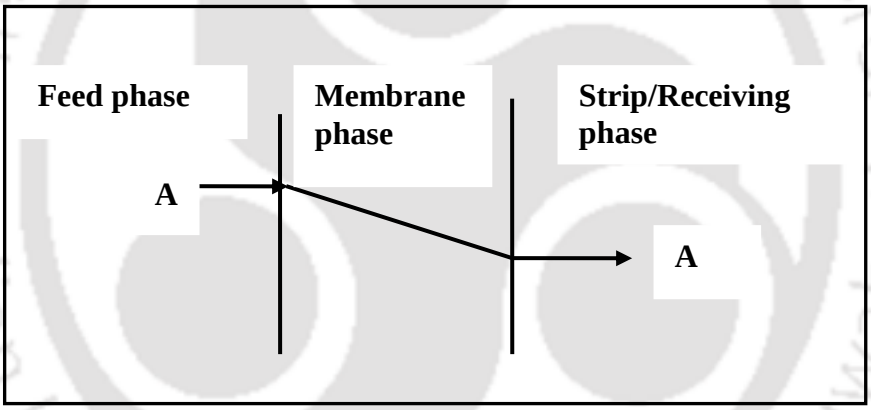


Figure 1.1 Ordinary diffusive transport of component, *A* through LM

1.1.1.2 Carrier mediated or facilitated transport

To increase the rate of mass transfer or efficiency of the LM separation, a carrier agent is added to the membrane phase. The carrier should be soluble only in membrane phase and should have the ability to form complex reversibly with a specific solute. The mechanism is represented schematically through Fig. 1.2(a). Here the transport of component *A* is enhanced by the presence of the carrier molecule, *C*. The carrier, *C* forms a complex, *AC* at the feed/membrane interface. Complex, *AC* then diffuses through the membrane due to

concentration gradient across the membrane and releases the solute, *A* at the membrane / strip interface. The free carrier, *C* then diffuses back to feed/membrane interface due to concentration gradient and the cycle continues. In this case two processes occur simultaneously. Part of component, *A* is transported by free diffusion (*i.e.* solution diffusion mechanism) whilst another part is transported due to the formation of solute-carrier complex that enhanced the solubility of the solute, *A* in the membrane phase. Hence the transport rate is increased. Thus, the mechanism of facilitated or carrier mediated transport can be described by the following steps [2, 8]:

(i) Diffusion of solute from the bulk of the feed phase to the feed-membrane interface.

(ii) Dissolution of solute in the LM.

(iii) Complexation between the carrier, *C* and the solute, *A* at the feed/membrane interface.

(iv) Diffusion of carrier-solute complex across the membrane.

(v) De-complexation at the membrane/ strip (receiving) phase interface.

(vi) Release of solute from the membrane phase to the strip (receiving) phase.

(vii) Diffusion of free carrier back to the feed/membrane interface.

(viii) Diffusion of solute from membrane/strip interface to the bulk of the strip phase.

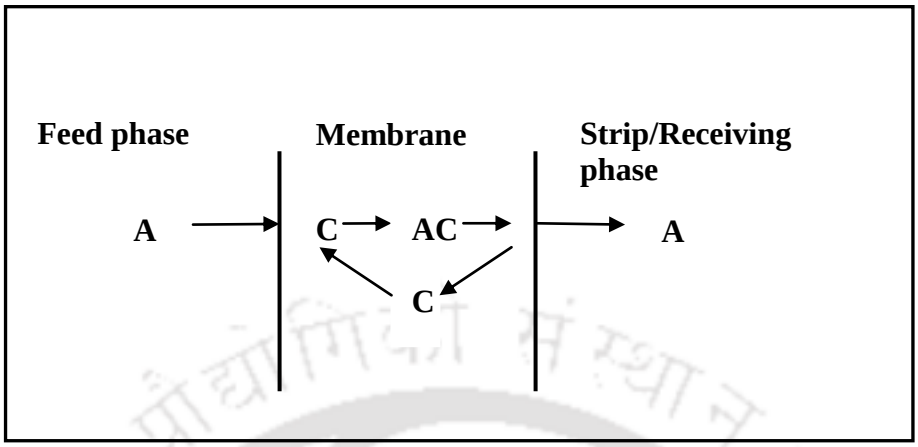


Figure 1.2(a) Mechanism of carrier mediated or facilitated transport in LM with mobile carrier

One basic feature of carrier mediated transport is that the complexation reaction must be reversible. Otherwise solute transport would stop when all the carrier molecules would have formed complex with the solute. Secondly, the affinity between the carrier and solute should not be very strong or very weak. A strong complex *i.e.* one exhibiting high affinity between the carrier and solute may result in slow release at the membrane/strip interface while a weak complex *i.e.* one exhibiting low affinity between the carrier and solute would yield limited facilitation. Therefore, there should be optimum bond energies of this reversible complex. This bond energy is recommended to be in the range of 10 to 50 kJ/mol [2]. Another feature of facilitated transport is the occurrence of two different processes *i.e.* chemical reaction and mass transfer at the same time.

There are two types of carrier mediated transport *viz.* non-coupled transport and coupled transport. Non-coupled transport involves the transport of a single component (*viz.* transport of oxygen from a mixture of oxygen and nitrogen through a water film in presence of cobalt as a carrier) whereas the coupled transport involves the transport of more than one component such as transport of metal ions from aqueous solution. This

research work basically deals with coupled transport and hence the coupled transport is described briefly in the next section.

Two components are often involved in carrier mediated transport and this type of transport is called coupled transport. It is of two types: co-transport and counter transport. If transport of the two species occurs in the same direction, it is called co-transport, while if it occurs in opposite directions it is called counter transport. In co-transport, as shown in Fig. 1.2(b), both the components, *A* and *B* are transported in the same direction that is from feed to receiving phase through the membrane. While in counter transport as represented by Fig. 1.2 (c), solutes *A* and *B* are transported in opposite direction.

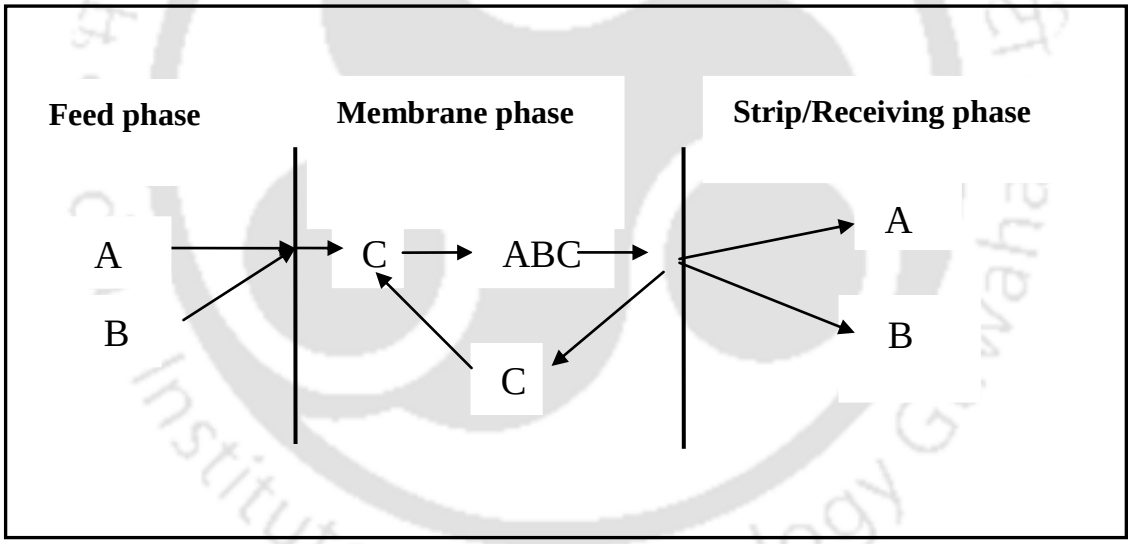


Figure 1.2(b) Mechanism of coupled co-transport in LM

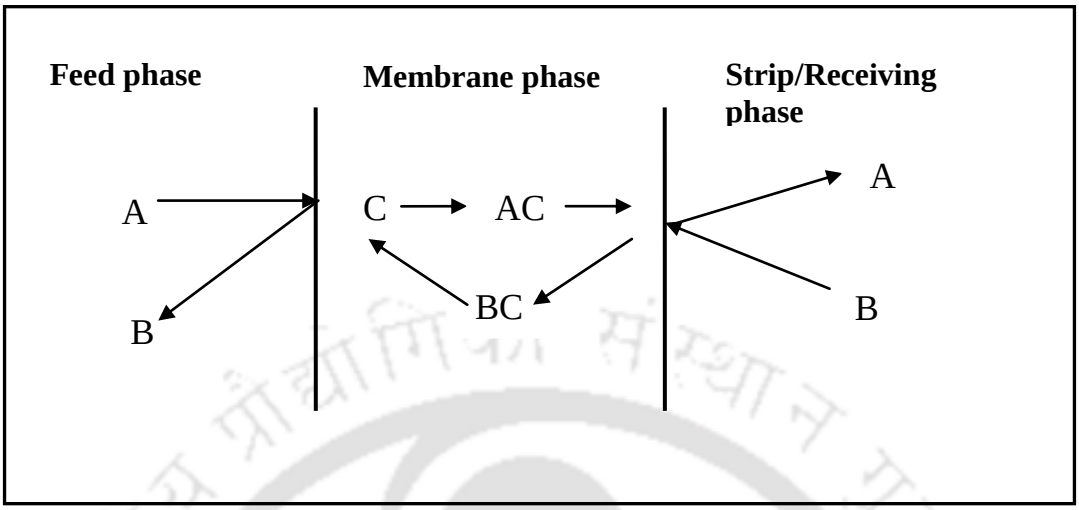


Figure 1.2(c) Mechanism of coupled counter transport in LM

As discussed above, the performance of LM can be enhanced by making it carrier mediated whereby a complexing agent (carrier) selective towards the target element (solute) is dissolved into the membrane phase. The selection of a right carrier is a key factor in all types of carrier mediated LM. The carrier should be very specific and should have high selectivity towards the solute to be removed. In fact every specific solute needs its own specific carrier. The carrier may be mobile or fixed. If it is dissolved in the liquid, it is called mobile carrier. On the other hand the carrier can be bound chemically or physically to a solid polymer which is termed as polymer inclusion membrane. In mobile carrier system, the carrier solute complex diffuses across the membrane whereas in fixed carrier system the solute jumps from one site to the other. The diffusivity in mobile carrier is much higher than the fixed carrier system.

1.1.2 Carrier

Carriers are reagents that play an important catalytic role in the LM system. Carriers attribute to selective separation and concentration of specific solutes with high flux of transport. Small amount of carrier is sufficient for the above purpose because of the small solvent inventory associated with the membrane and also because of their non-volatile nature. Carriers are characterized by [5]

- Ability of quick binding and release of particular solute(s)
- Ability to selective and reversible binding of a component in the solution
- Non-binding with a solvent
- Lack of ability to coalesce and
- Non-toxicity.

Carriers are categorized into three major types *viz*. acidic, basic and neutral carrier, primarily on the basis of their functional groups. The acidic carriers are the most effective for extracting cations as the carriers do form complex salt with cations with the exchange of protons. The acidic carriers do have COOH, P(OH), SO_3H or chelating groups. A typical example of acidic carrier mediated transport is presented in Eq. (1.2) [9]

$$Cu^{2+} + 2C_{16}H_{34}O_3P(OH) \rightarrow C_{16}H_{34}O_3P(OCu) + 2H^+ \qquad (1.2)$$

Where, copper is extracted from its aqueous solution with di(2-ethylhexyl) phosphoric acid. The basic carriers are used for the extraction of the anionic metal complexes. Amines are ideal examples of alkaline/basic carriers. Typical example of basic carrier mediated transport is presented in Eq. (1.3) [10]

$$CdCl_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} + 2R_3N_{(org)} \rightarrow (R_3NH_2)CdCl_{4(org)} \qquad (1.3)$$

Where, Cd (II) is transported in the form of $CdCl_4^{-2}$ from the aqueous acidic solution by the carrier trioctylamine (TOA). TOA (R_3N) accepts a proton to form a positively charged species and cadmium ion is extracted as $(R_3NH_2)CdCl_4$ [10].

Neutral carriers are generally used as cation carriers in liquid membranes for the selective transport of different metal ions. They carry the metal ions by encapsulating them within their cavity. The extraction efficiency of such neutral carriers depends on the size of their cavity and the size of the inserted ions. When such carriers are used as metal ion carriers in the membrane phase, the concurrent transport of an anion with the cation occurs across the liquid membrane. Organic phosphoryl compounds and macrocyclic molecules are the most widely used neutral carriers in LM processes. Typical example of such type of carrier mediated transport is given in Eq. (1.4) [11]

$$Ag^{+}_{(aq)} + NO_3^{-}{}_{(aq)} + DC18C6 \rightarrow Ag[DC18C6]NO_{3_{(org)}} \qquad (1.4)$$

Where, silver ion is co-transported along with the nitrate anion from the aqueous solution by the neutral carrier di-cyclohexanone-18-crown-6. The most frequently used carriers include phospho-organic compounds, crown ethers, hydro-oximes and amines [5]. Typical carriers used in various LM processes are listed in Table 1.1.

Table 1.1 Various carriers used in various LM processes

Acidic carrier	Application in the extraction of	Ref	Basic carrier	Application in the extraction of	Ref.	Neutral carrier	Application in the extraction of	Ref.
Acetylacetone	Cr(III)	12	Primene JMT $[(C_8H_{17})NH_2]$	Mo(VI)	17	Di-benzo -18-crown-6	Na^+, Ur(VI)	22-23
Benzoylacetone	Ur(VI)	13	Trioctylamine $[(C_8H_{17})_3N]$	Cr(VI)	18	Di-cyclohexyle-18-crown-6	Hg (II)	24
β-Hydroxime	Cu(II)	14	Trinonylamine $[(C_9H_{19})_3N]$	Lignosulfonate	19	Cryptana (2,2,1) $[N_2O_5]$	Ag(I), Cu(II) and Zn(II)	25
D2EHPA[di(2-ethylhaxyl) phosphoric acid]	Ag (I), Cu(II)	9	Trilaurylamine	Lignosulfonate	19	Cryptand(2,2,2) $[N_2O_6]$	Ag(I), Cu(II) and Zn(II)	25
Cyanox 272 (R_2POH)	Co(II)	15	Alamine 336 $[R_3N(R:C_8\text{-}C_{10})]$	Citric acid	20			
Trioctylphosphinoxide	As (V)	16	Aliquat 336 $[CH_3(C_8C_{17})_3N]$	Cd (II)	21			

Various combination of LM systems employed in the extraction of different materials in anionic form are presented in Table 1.2.

Table 1.2 LM system employed in the extraction of anions

Materials extracted	Carrier used	Diluent	Stripping agent	Reference
$HgCl_4^{2-}$	Trioctylamine (TOA)	Toluene	NaOH	26
$Hg(pic)^-$	Tetrathia-12-crown-4	Chlorofom	EDTA	27
$Hg(pic)^-$	Bis-calixarene-nitrile derivative	Chlorofom	H_2O	28
$Cr_2O_7^{2-}$	Cyanex 923	Xylene	NaCl	29
$Cr_2O_7^{2-}$	Tri *n*-butylphosphate	Hexane	NaOH	30
Lignosulfonate	TOA	Decanol	NaOH	19
Lignosulfonate	Trilaurylamine	Decanol	NaOH	19
NO_3^-	TOA	Kerosene	NaOH	31

*** (pic) stands for picrate**

LM technology has acquired worldwide importance for its use in separation and concentration of various metals, chemical species and organic substances, especially when they are present in trace amount. It holds an important position in the field of membrane separation due to low consumption of extractant, energy and low installation cost over other conventional separation processes. Various types of LM are described in the next section.

1.1.3 Types of LM

LMs, based on the configurations, are broadly classified into three types: bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM). According to the geometry SLM is again of three types, flat sheet, hollow fibre and spiral wound. Besides these one more LM is included in the LM family (Fig. 1.3) *i.e.* electrostatic pseudo LM.

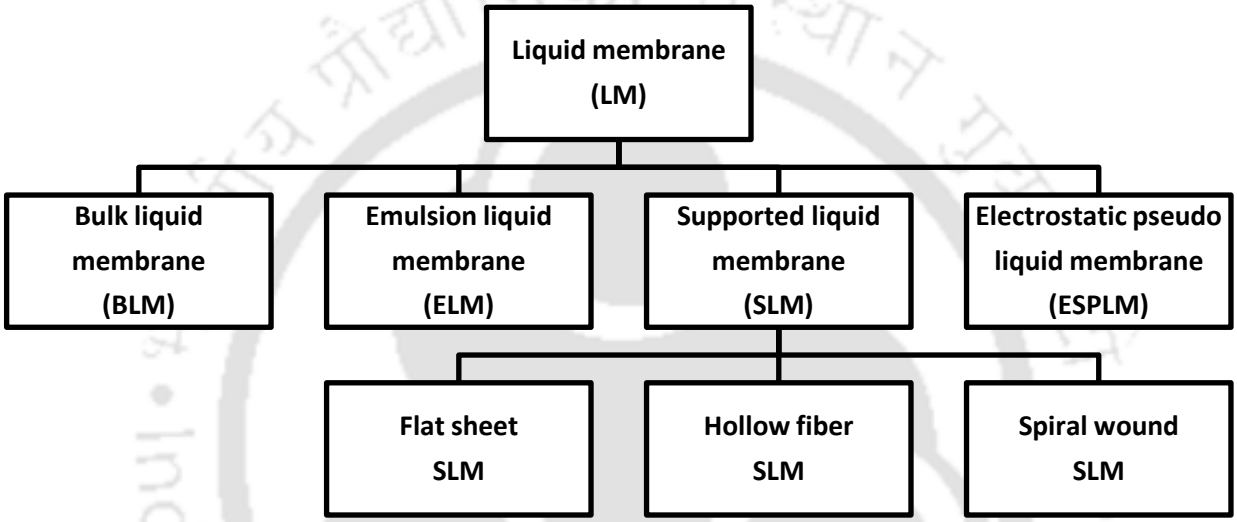


Figure 1.3 Family of liquid membranes

1.1.3.1 Bulk liquid membrane (BLM)

BLM is the simplest of all LMs. In a BLM setup, all three phases of the LM unit are placed in a tank with bulk quantities. Two aqueous phases are separated with a solid barrier (*e.g.* a glass wall) and the membrane phase shares an interface with both these aqueous phases as shown in the schematic representations (Fig. 1.4). The Fig. 1.4(a) shows the case when membrane phase is heavier than the feed and strip phases whereas Fig. 1.4(b) indicates otherwise. BLM is basically used in lab scale studies. BLM separation study is very important and relevant because,

experimentation using BLM helps understanding the separation feasibility of a liquid membrane for any system of concern. Various important equilibrium and kinetic parameters useful for mass transfer studies also can be estimated through simple experimental set-up like BLM. However, up-gradation of the lab scale BLM to a pilot/commercial scale happens to be practically ineffective mainly due to much lower value of surface area to volume ratio.

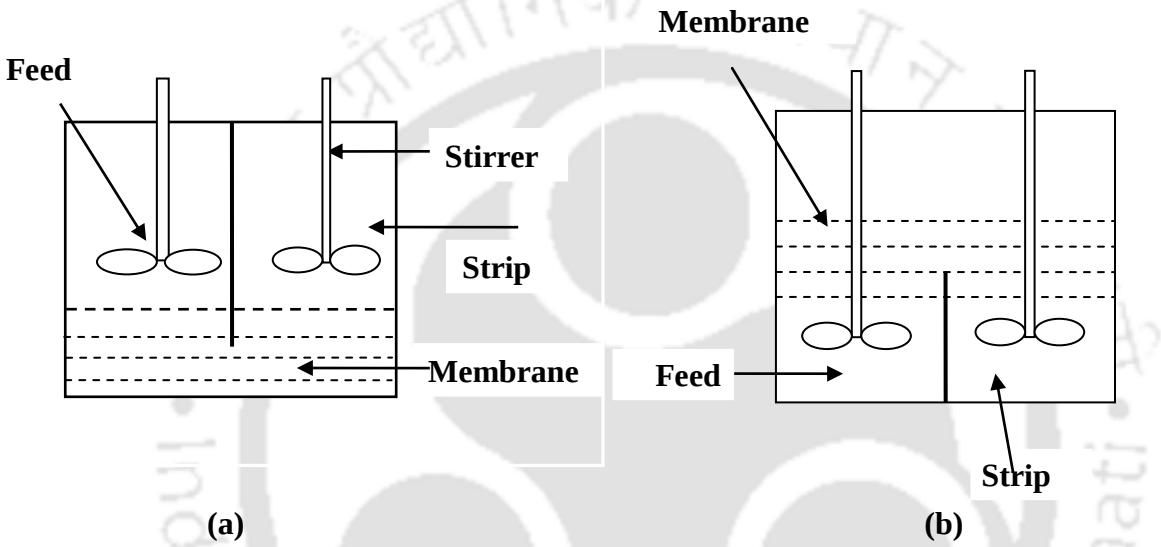


Figure 1.4 Schematic of BLM configuration (a) For heavier membrane liquid (b) For lighter membrane liquid

1.1.3.2 Emulsion liquid membrane (ELM)

ELM (also known as liquid surfactant membrane) is prepared by forming an emulsion between two immiscible phases and dispersing the emulsion into a third continuous phase by agitation. Therefore ELM is also referred to as double emulsion. The membrane in ELM is the liquid phase that separates the encapsulated internal droplets in emulsion from the continuous phase. The encapsulated internal phase and the continuous phase are miscible with each other, but the membrane phase must be immiscible with either of them. The spherical globules of emulsion are typically 10 μm to 1 mm diameter in size. The encapsulated internal droplets of receiving phases

have the typical diameter of 1 to 10 μm. ELM was invented by Norman N. Li in 1968 and this process has already reached to industrial scale [32]. It is of two types: water in oil in water (W/O/W) type or oil in water in oil (O/W/O) type. In W/O/W type, oil acts as the membrane phase and in O/W/O type water acts as the membrane phase. To maintain the stability of the emulsion during extraction process, the membrane phase is augmented with some surfactants and additives as stabilizer and solvent as diluents. To form a stable emulsion, the surfactant should be chosen carefully. The ionized surfactants have relatively high water solubility and thus generally make oil in water emulsions. The non-ionic surfactants, however, can be used to make either type of emulsion. The selection of an appropriate surfactant depends on the hydrophylic-lipophylic balance (HLB) value. The HLB is a parameter which is the percentage of hydrophilic functional groups in the surfactant molecule divided by five. Surfactants with a low HLB are more lipid loving and thus tend to make a water in oil emulsion while those with a high HLB are more hydrophilic and tend to make an oil in water emulsion. A blend of two or more non-ionic surfactants is better than a single surfactant molecule to form a stable emulsion. To provide good emulsion stability, the size of the internal droplets in emulsion should be in the range of 1-3 μm in diameter [33]. Kopp suggested the following set of guidelines for the formation of stable water in oil emulsions [34].

- Organic phase soluble surfactant concentration should be 0.1 to 5 wt. %
- Organic phase viscosity should be 30 to 1000 mPa.s
- Volume ratio of the internal phase to membrane phase should be 0.2 to 2
- Volume ratio of internal phase to continuous external phase should be 0.2 to 0.05
- Volume ratio of continuous phase to emulsion phase should be 1 to 40 and
- Surfactant HLB value should be 6 to 8.

ELM process provides large mass transfer area as large numbers of emulsion globules can be dispersed in a small volume of continuous phase. Therefore, in ELM process a rapid mass transfer occurs from external continuous phase to internal phase. The other advantages of ELMs are [35]

- High diffusive flux and low energy consumption
- Simple configuration/equipment
- Zero disposal
- Recycling of material
- Operational simplicity and
- High efficiency.

A simplified diagram of ELM is shown below through Fig. 1.5.

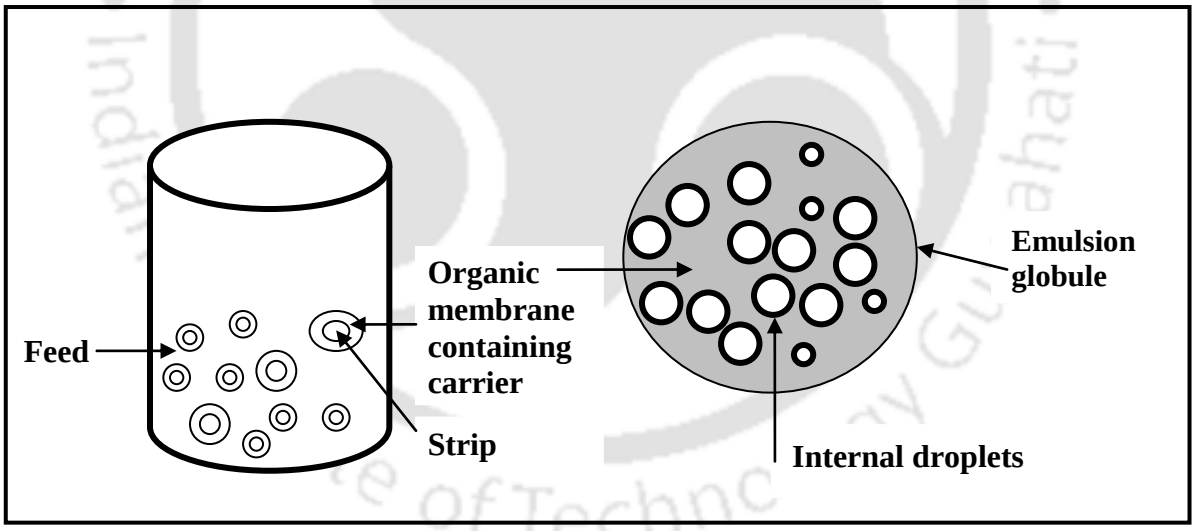


Figure 1.5 Schematic of ELM

Though the ELM process offers high mass transfer efficiency, it has some limitations also. In ELM process, surfactant is employed to maintain membrane integrity. Once the surfactant is dissolved in the solution it is difficult to remove from the solution. This makes the process complicated. In order to recover the receiving phase and in order to replenish the carrier, the

emulsion has to be demulsified. This is a difficult task and consumes a good amount of energy. Emulsion swelling is another troublesome aspect in ELM system which dilutes the internal phase and makes it difficult to recycle [32].

1.1.3.3 Supported liquid membrane (SLM)

SLM or commonly known as immobilized LM is a LM setup in which the membrane liquid (organic or aqueous) is immobilized within the pores of porous solid membrane. Thus, a SLM consists of three main parts (i) support material (ii) membrane liquid (solvent) and (iii) carrier. The membrane phase is prepared by dissolving the carrier agent into the solvent. The porous support material serves as a framework or supporting layer for the membrane phase. The porous support can be inorganic or organic (polymer) with suitable chemical properties and mechanical stability. In the present case, since the application is related to treatment of wastewater, organic solvents were used as membrane liquid and hydrophobic polymeric membranes were used as support materials. The surface porosity and overall porosity of such support materials should be high in order to obtain a high permeation rate or an optimal flux. Besides porosity, permeation rate also depends upon the membrane thickness because the flux is inversely proportional to the membrane thickness [2]. Therefore support should be as thin as possible to obtain high flux. The membrane phase in SLM acts as a diluent.

Based on the geometry of the supports, SLM is in general of three types *viz*. flat sheet, hollow fiber and spiral wound. Flat sheet SLM as the name implies uses support material in sheet form. It is simple in structure, having low cost but requiring large space. A schematic of flat sheet SLM is shown in Fig. 1.6.

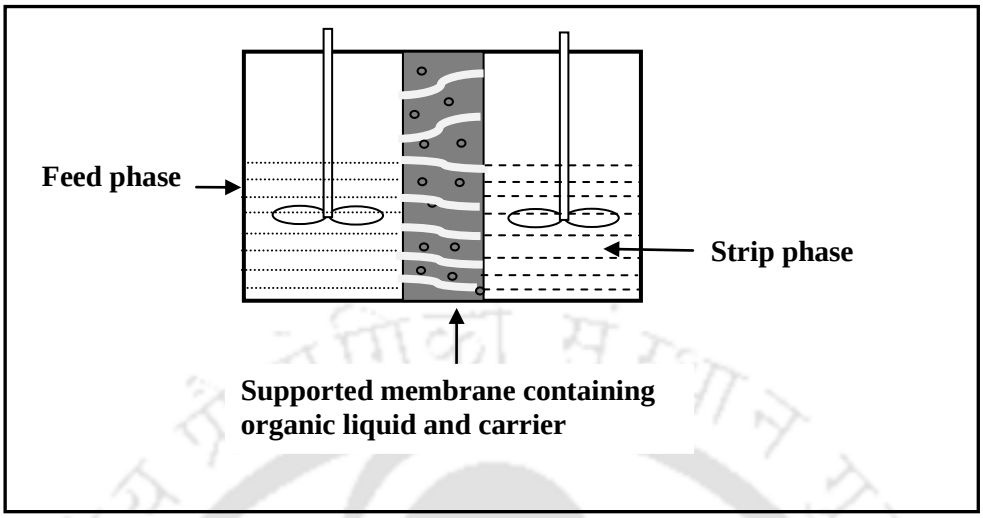


Figure 1.6 Schematic of flat sheet SLM

Hollow fibre SLM (HFSLM) is just like a shell and tube heat exchanger, thus compact with increased mass transfer area per unit volume [32]. It has an outer shell and inside it there are large numbers of thin porous fibers in the shape of tubes (ID: 0.5-1.0 mm) [10] running along the length of the shell, all in nice, neat rows. The pores of the fibers are filled with the membrane phase. The feed phase and strip phase are separately passed through either fiber and shell side or through shell side and fiber respectively, from top to bottom. Carrier in the membrane phase helps faster transport of solute from feed phase to strip phase. A schematic of flat sheet HFSLM is shown in Fig. 1.7.

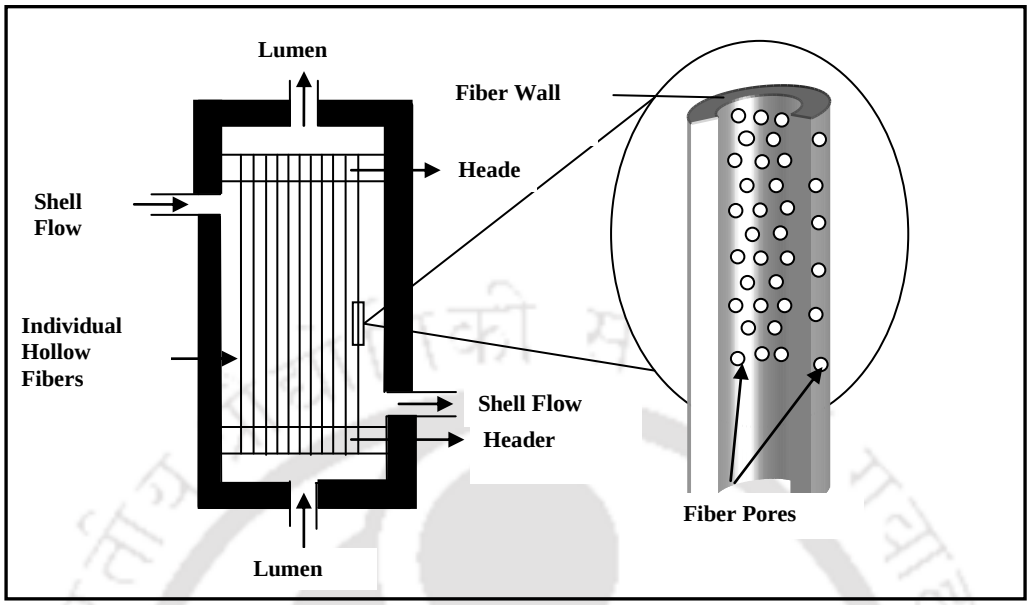


Figure 1.7 Schematic of flat sheet HFSLM

Another type of SLM is hollow-fiber contained liquid membrane (HFCLM). Here two channels of hollow fibers are used for two aqueous phases *i.e.* feed and strip phase with a stationary membrane phase in contact with both. It consists of a cylindrical shell as shown in Fig. 1.8. The shell side is filled with the membrane liquid connected to an external membrane liquid reservoir at a pressure higher than the pressure of both feed and strip solution. In this type of configuration, loss of membrane liquid is automatically replenished from the external membrane liquid reservoir.

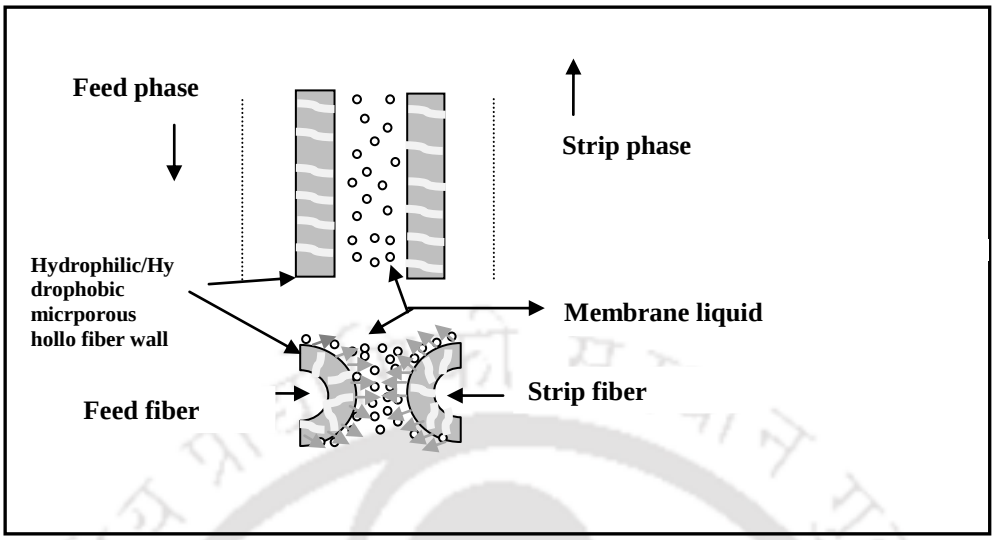


Figure 1.8 Schematic of HFCLM

However, it suffers from the problems like pore fouling, cleaning of fibers between uses, high pressure drop and high cost.

The spiral wound membrane as shown in Fig. 1.9 is infact a plate and frame system wrapped around a central perforated collection pipe in a similar fashion to a sandwich roll [32]. The sandwich is made of four layers: a membrane, a feed channel, another membrane, and a strip channel which forces all the separated materials towards the perforated tube in the centre. The feed flows axially through the cylindrical module parallel along the central pipe whereas the permeate flows radially towards the central pipe. This type of SLM is an intermediate between flat sheet and hollow fiber membrane in terms of stability and surface area per unit volume.

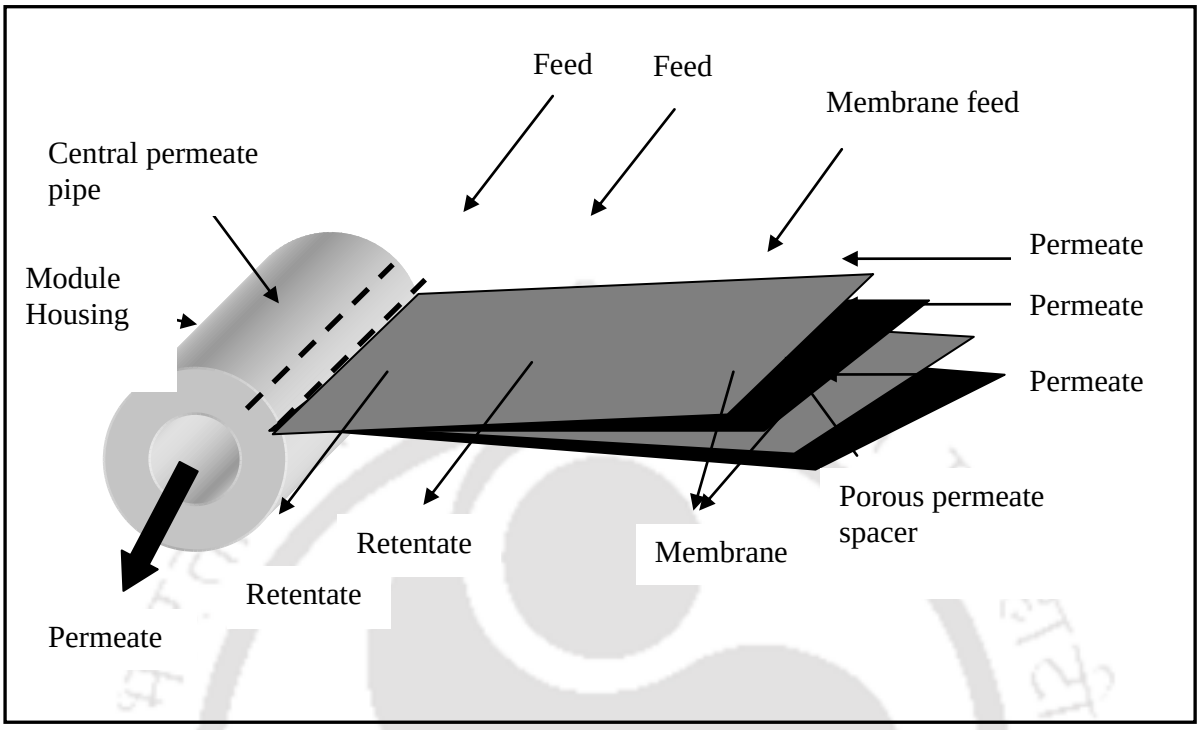


Figure 1.9 Schematic of spiral wound SLM

SLM based separation process has several advantages such as low capital, operating, maintenance and energy cost, high separation factor, low extractant consumption and easy to scale-up. However, the major drawback of SLM is the instability of the liquid film due to the gradual loss of membrane solution by dissolution and spontaneous emulsification during the operation. Thus, identification of a suitable membrane phase to develop a reasonably stable SLM configuration for a particular application is a point of research interest.

1.1.3.4 Electrostatic pseudo liquid membrane (ESPLM)

ESPLM is a combination of an electrostatic technique and the principle of LM, developed by Gu in 1988 [32]. It is a continuous process in which extraction and stripping takes place simultaneously in a specially made reaction tank as shown in Fig. 1.10. Inside the tank, an oil layer exists within the baffle plates that is rather stagnant and acts as the LM. This oil layer

allows the transport of carrier complex from the extraction cell to the stripping cell and regenerated carrier from the stripping cell to the extraction cell while preventing the mixing of the aqueous phases. A high voltage (AC) electrostatic field is applied simultaneously across the extraction and stripping cell. Under the electric field, feed solution added to the extraction cell and stripping solution added to stripping cell are dispersed into large numbers of droplets in the continuous organic phase. In the extraction cell, solute in the aqueous droplets is extracted into the organic phase [36]. The complex formed in the extraction cell, driven by its own concentration gradient, diffuses through the perforated baffle plate into the stripping cell. The extractant is regenerated after the solute is stripped off in the stripping cell and diffuse back to the extraction cell through the perforated baffle plate.

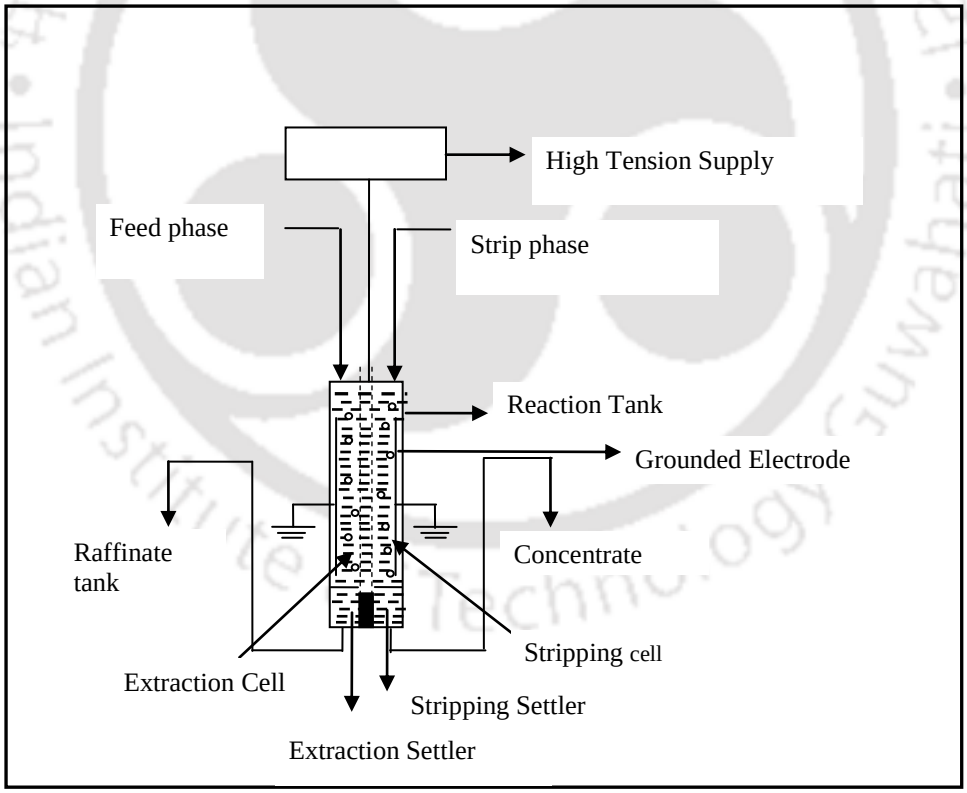


Figure 1.10 Schematic of ESPLM

Though it is a simple process, with easy operation, high flux, negligible leakage and swelling, and low energy consumption, it is only effective when the continuous phase is an organic solution. [32].

1.1.4 Industrial applications of LM

LM technology has gained industrial importance in the last few years as the separation based on solid (polymeric) membrane faced problems of low flux rate, low selectivity, *etc.* as discussed earlier (Section 1). It has been studied extensively in many disciplines such as chemical engineering, inorganic chemistry, biotechnology, and biomedical engineering. It has diversified applications such as gas separation, metal recovery, toxic waste removal, organic removal, enzyme reactors and recovery of fermentation products. Despite having very promising technical performance, only a few processes such as waste treatment (where low concentration solutes must be removed from a large volume of effluent), recovery of trace metals, production of sensing devices and ion selective electrodes have been commercialized till date [34]. Industrial applications of various types of LMs are summarised in this section.

BLMs as such have no industrial applications due to their small contact area and slow process kinetics. However they are used in laboratory based experimentations for evaluating various process parameters that describe the transport through the membranes. SLMs have many laboratory scale and pilot-scale applications. SLMs are successfully applied in metal recovery from wastewater [34] and in gas separation processes such as O_2/CO_2, N_2/CO_2, CO_2/CH_4, SO_2/CO_2- N_2, H_2S/ CO_2 *etc.* [37, 38]. Guha *et al.*[37] presented a large-scale hollow-fiber-contained liquid membrane permeator containing 7008 hydrophobic polypropylene hollow fibers. They used water and an aqueous 20% diethanolamine solution as the LM for separating the gas mixtures CO_2/N_2 and CO_2/CH_4, respectively. This module recovered 87% N_2 and 94%

CH_4 and was reported as efficient for large scale separation of gas mixtures with minimum maintenance. Sengupta *et al.* [38] presented a pilot plant study on the treatment of flue gas containing SO_2, CO_2, O_2, N_2 and moisture. They used polypropylene as the support and water and aqueous solutions of $NaHSO_3$, Na_2SO_3, sulfolene *etc.* as the LM and achieved excellent permeability of SO_2. A pilot plant study of the recovery of uranium and chromium was presented by Babcock [34]. He used a hollow fibre module having polysulfone as support and mixture of kerosene and tertiary amine as LM. Babcock also tried to commercialise an SLM process to produce oxygen enriched air. He used a spiral wound module containing cobalt based carrier. This module produced 80 to 90% oxygen in a single pass and at optimum condition. The SLM had a separation factor (O_2 permeability/N_2 permeability) of 25. Hughes et al. [39] presented a pilot plant study of recovery of ethylene and propylene from a polypropylene reactor off gas stream. They used a hollow fibre module containing 22.3-37.2 m^2 membrane area and achieved a permeate stream with propylene concentrations in excess of 98 mole %.

ELM technology has many pilot scale and few industrial scale applications. Most of the industrial scale ELM process installations are on the recovery of zinc from wastewater of textile industries. Five industrial plants of ELM have been reported in the literature and out of five four related to the recovery of zinc [10]. For example, Glanzstoff in Austria having a capacity of 0.7 m^3h^{-1}, CFK Schwarz in Germany with a capacity of 0.2 m^3h^{-1} and AKZO/Ede in Netherlands with a capacity of 0.2 m^3h^{-1} [5]. Another industrial application of ELM is the treatment of phenolic wastewater from plastic industry in China. This plant treats 0.5 tons of solution containing 1000 mgl^{-1} of phenol per hour and brings down the phenol level to 0.5 mgl^{-1}[5, 10]. There are several pilot plant installations on the recovery of metals from wastewater of

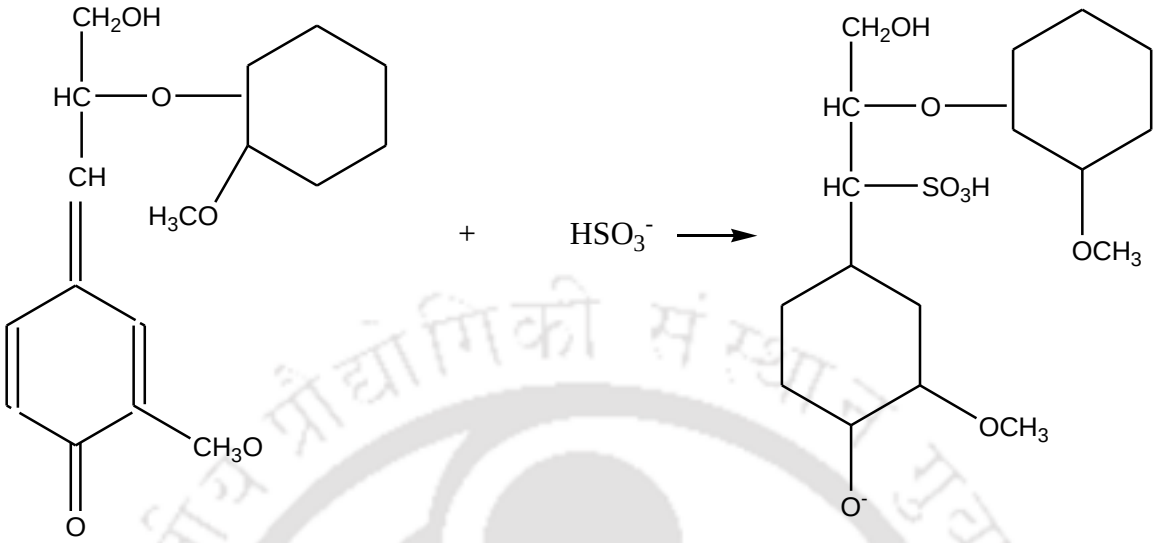
metallurgical plant. These include recovery of cadmium, copper, lead, iron, cobalt, nickel, manganese, magnesium, calcium and sodium.

1.2 Pollutants studied

Transport of solute occurs in LM in the form of salt through diffusion mechanism. As discussed in Section 1, various properties (*viz.* size, affinity, charge and chemical nature) of solute in feed phase influences the transport process through LM. The size of the solute is also an important criterion for mass transfer. In order to assess the competence of the LM, two different pollutants of wide difference in molecular size have been chosen for the present study, *viz*. lignosulfonate (LS, a lignin based polydispersed polyelectrolyte macromolecule) and mercury (small sized carcinogenic heavy metal ion). The sources, properties and impacts of these pollutants on the environment have been discussed in this section.

1.2.1 Lignosulfonate [19, 40-42]

Lignosulfonate (LS) also called lignin sulfonate is a polydispersed polyelectrolyte derived from the sulphite pulping of wood. It is basically found in the spent liquor of sulphite pulping of pulp and paper industries. It is a spherical macromolecule that has two kinds of functional groups (SO_3^{-2} and OH^-). In the sulphite pulping process, lignin is converted to LS. The chemical reaction and model structure of LS is shown in Fig. 1.11. Depending on the type of pulping process, LS of various bases including sodium, calcium, magnesium and ammonium LS can be obtained.



Lignin **Lignosulfonate (LS)**

Figure 1.11 Model structure of LS [40]

LS exhibits complex physical and chemical properties. Some important physical and chemical properties are:

- LS is a polydispersed macromolecule having heterogeneous structure. Its polydispersity is in the range of 6-8. Its molecular weight ranges from 20,000-50,000.
- LS is soluble in water at any pH, however insoluble in most of the common organic solvent. It imparts brownish black colour to water.
- LS exhibits surface activity but have only a slight tendency to reduce interfacial tension between liquids.

- LS contains various functional groups such as phenolic hydroxyl, sulfonate, methoxyl and carboxyl groups. The sulfonate group present in LS is about 17.5% per unit weight of LS.
- LS can be oxidized in alkaline media by oxygen or air and other oxidizing agents such as copper hydroxide, nitrobenzene and ozone.

The usefulness of commercial LS products comes from their dispersing, binding, complexing and emulsifying properties. LS were first used in leather tanning and dye baths in 1880s. Since then LS found numerous applications in various fields. Some of the important applications of LS are [40]:

- Extensive usage of commercial grade LS includes production of vanillin, animal feed pellet binders, dispersant for dyes, pigments, clay and ceramics, pesticides and insecticides and in cement mixture.
- LS finds its application in boiler and cooling tower water treatment where it prevents scale deposition. In such systems, LS sequester hard water salts and thus prevent their deposition on metal surface. Typical use level for such applications ranges from 1-1000 mgl^{-1}.
- LS is used in industrial cleaning applications where it acts as dirt dispersants and suspending agent. Typical use level in such cases ranges from 0.05-2%.
- The other uses of LS include as retarders for oil well drilling cement, as additives, as expanders for lead acid batteries, as sacrificial agent in enhanced oil recovery, as precipitating agent in protein recovery and as wood preservatives. Medicinally it is used as antithrombotic and antiviral agent.

Extensive scientific research and testing has shown that LS are non-toxic, non-irritating and can be safely used in animal and human food contact products. Though LS is nontoxic it imparts colour to the water bodies making the water unsuitable for reuse and also creates problem for the aquatic life [43].

1.2.2 Mercury

Mercury is a heavy metal that exists in several forms. Its zero oxidation state Hg^0 exists as vapor or as liquid metal. Its mercurous state Hg^+ exists as inorganic salts and its mercuric state Hg^{2+} may form either inorganic salts or organomercury compounds. Mercury enters the environment from two major sources: natural and anthropogenic. The natural sources of mercury in surface and underground water are natural erosion of soil and ore deposits. Its concentration varies from 0.08 and 0.4 $mgkg^{-1}$ in rocks, sediment or soil samples [44]. Urban and industrial discharges, agricultural materials, mining and combustion are the major anthropogenic sources of mercury in the environment [45]. Global anthropogenic inputs of mercury into the environment were estimated at about $3.2–30\times10^6$ $kgyr^{-1}$, whereas global natural mercury emissions were considered to be 3×10^6 $kgyr^{-1}$[44]. Combining anthropogenic inputs and natural sources, a total of approximately 806×10^6 kg mercury has been released into the soil, 118×10^6 kg into water and 741×10^6 kg into the atmosphere [44]. The major industries causing mercury pollution are chloro-alkali, oil refining, electrical, rubber processing, battery, paint, fluorescent lamp, fertilizer, pharmaceuticals, plastics and pulp and paper [46-48]. The maximum concentration of mercury in wastewater from various sources is about 10 mgl^{-1}[49].

The toxicity of mercury depends strongly on its redox state [50]. Elemental mercury (Hg^0) is hazardous due to its potential to release mercury vapor. Mercury (II) salts are usually more toxic than their mercury (I) counterparts because of their higher solubility in water and high tendency

for binding to the proteins [51]. Its toxicity also depends on the transport route. For instance in water, inorganic mercury is converted by bacteria to methyl mercury (organic mercury) which is known to bioaccumulate in the fish tissue. This process additionally increases the danger of mercury exposure even at ultra-trace levels of concentration. Similarly the danger of elemental mercury also lies in their transport routes. Mercury vapour is easily inhaled, enters the blood stream in the lungs and is thus distributed throughout the body. Within cells, it is oxidized to reactive Hg^{2+} [7]. Mercury hazards to living organisms such as marine samples are due to the accumulation and biomagnifications character of this toxic element that can influence the entire food chain and humans who consume marine food [52].

The major toxicological effects of mercury poisoning include brain damage, chromosome breakage and dysfunction of liver, kidney and damage of central nervous system, paralysis and blindness. It also induces cellular toxicity by binding to intracellular sulfhydryl groups even at very low concentration [53-55]. Besides these mercury is a persistent and bio-accumulative substance. Considering its severe health hazard, the maximum level of mercury in drinking water and wastewater is restricted to 1 μgl^{-1} and 5 μgl^{-1}, respectively by the European environmental regulations [55]. Hence from the above introduction, it is evident that removal of mercury from water as well as wastewater has special environmental importance.

Hence an effort is made in this research to study a combinatorial approach in the separation and recovery of LS and mercury so that both the pollutants can be separated simultaneously and efficiently through LM technique.

1.3 Literature review

LM based technique has been advocated as the need of the hour. As a result there have been numerous literatures reported on the studies of LM based separation. This section presents a thorough review of these literatures, which is presented under three sub-sections *viz.* LM for general applications, LM for extraction of LS and LM for extraction of mercury.

1.3.1 LM for general applications

Since Li invented LMs as separation technique in 1968, it is considered as an effective tool for a wide variety of separations. Thereafter a number of researchers applied this technology in diverse areas such as separation of gases, wastewater treatment, separation of chemical compounds, *etc*. Richard D Noble and his co-workers have summarized these works in their book named 'LM Technology' [34]. The review of the literature in the past two decades shows that LMs have been used for separation of metals such as Cu, Cd, Fe, Pt, Ag, Au, Ni, Sr, As, Hg, Cr, Co, Pb, Zn *etc*. alkali metals such as sodium, lithium, cesium *etc*., organic and inorganic acids such as acetic acid, nitric acid *etc*., biochemical compounds such as amino acid, antibiotics *etc*., aromatics such as benzene, toluene *etc*., pharmaceutical products such as diclofenac, penicillin, cephalosporin-C *etc*. and for removal of phenols from wastewater.

Separation of metal ions in hydrometallurgical applications has received considerable interest. Lazarova [56] and his co-workers studied the kinetics of copper ion transport through BLM comprising of LIX-860 as carrier, n-paraffin (C_{10}-C_{13}) as diluents and sulphuric acid as stripping agent. The principal parameters such as feed pH, carrier concentration, stirring speed, temperature, *etc*. affecting the transport of copper were studied. The maximum flux was obtained at a feed pH of 2.1 and carrier concentration of 10 vol. %. They achieved about 99% separation of copper; however recovery was 20% in a period of 9 hours and at optimum conditions. The

extraction of copper was reported as temperature independent and diffusion controlled process whereas the stripping of copper-LIX-860 complex in the sulphuric acid solution was controlled by both diffusion and chemical reaction. Castro *et al.* [57] evaluated the feasibility of a BLM to recover copper from natural water using pyridine-2 acetaldehyde benzoylhydrazone as the mobile carrier in toluene. The flux of copper was studied in terms of the process variables such as carrier concentration, volume of organic phase, pH of feed and strip phase, stirring speed and temperature. They reported 100% preconcentration efficiency at optimum conditions. Thus, the LM developed by Castro *et al.*[57] showed better recovery of copper in comparison to that by Lazarova and his co-workers. Castro *et al.* [58] also carried out similar type of works with cadmium and obtained 100 % recovery of cadmium in 7 hours and at optimum conditions. Gherrou *et al.* [9] worked on SLM separation of mixture of silver and copper from acidic thiourea solution using di (2-ethylhexyl) phosphoric acid as carrier in chloroform. The fundamental parameters such as carrier concentration, pH of feed and strip solution, thiourea concentration in the feed, temperature, concentration of silver and copper in feed solution, *etc.* influencing the transport of silver and copper ion were determined and optimized. It was reported that in presence of thiourea (0.1M) the flux of silver was 1.96 times higher than that of copper. Lv *et al.* [21] investigated the efficiency of three types of carrier such as aliquat 336, kelex 100 and LIX 54 in the removal of cadmium by SLM. They used EDTA as the stripping agent and PTFE membrane as support. Highest flux of cadmium at a carrier concentration of 50% (v/v) was obtained with aliquat 336 (1.12×10^{-9} $molcm^{-2}s^{-1}$) followed by kelex 100 (1.5×10^{-10} $molcm^{-2}s^{-1}$). LIX 54 was not suitable for cadmium extraction. It was also reported that cadmium flux is a function of initial cadmium concentration. Sznejer *et al.* [59] worked on the ELM extraction of cadmium using di(2-ethylhexyl) phosphoric acid as carrier, Span 80 as emulsifier

and nitric acid as strip phase. The process parameters affecting the extraction of cadmium were studied and optimised. About 90-95% separation of cadmium was achieved within 3-6 minutes and at optimum conditions. The extraction of cadmium achieved in this process was found to be less in comparison to that reported by Castro *et al*. [58]. However, the extraction time required was very less in this case. They demonstrated experimentally that the principal resistance to mass transfer lie at the outer oil-water interface. Cruz *et al.* [60] studied the separation of nickel ion from sulphate solution using SLM containing di (2-ethylhexyl) phosphoric acid as carrier in kerosene. They found that extraction of nickel is possible in acidic condition (pH<3) only. They also concluded that high nickel concentration and large membrane thickness have detrimental effects on nickel transport through SLM. Alguacil *et al.* [29] presented a carrier facilitated SLM separation of chromium using Cyanex 923 in xylene as carrier and durapore and fluoropore as support materials. They observed that permeation of chromium was influenced by stirring speed and feed phase pH but unaffected by organic diluents and composition of the strip phase. They also concluded that separation of chromium (IV) is more preferable than chromium (III). Rovira and Sastre [61] studied the transport of palladium (II) through SLM containing di(2-ethylhexyl) thiophosphoric acid in kerosene as carrier and polyvinylidene fluoride as support. The fundamental parameters such as carrier concentration, stirring speed, diluents *etc*. affecting the transport of palladium were studied. They also developed a permeation model describing the mechanism of palladium transport through the SLM. The SLM was found to be selective for palladium over iron, platinum, ruthenium and zinc and showed good performance for five consecutive runs. Zhang *et al.* [62] developed an unsteady-state model to describe the permeation of iron (III) through SLM containing di(2-ethylhexyl) phosphoric acid in *n*-decanol as carrier. According to the model the rate controlling step for iron transport from feed phase to

strip phase is a combination of the reactions at the interface and the diffusion of the complex through the membrane. The model was found to fit the experimental data reasonably. Kedari *et al.* [63] investigated the selective transport of plutonium across a SLM containing di(2-ethylhexyl) phosphonic acid in dodecane as carrier. They studied the transport rate of plutonium over various anionic (SO_4^{2-}, NO_3^-, PO_4^{3-} *etc.*) impurities. Transport rate of plutonium in presence of anionic impurities followed the order: $ClO_4^->NO_3^->Cl^->SO_4^{2-}>PO_4^{3-}$. Selective permeability of plutonium was observed in the presence of several cationic impurities *viz.* Al, B, Be, Fe, Ca, *etc.* with good reusability of the membrane support. Perez *et al.* [16] studied the transport of arsenic (V) through SLM containing trioctylphosphineoxide (Cyanex-921) in kerosene as carrier from aqueous acidic solution. They investigated the various process parameters such as nature of stripping solution, extractant concentration and stirring rate. They observed that Na_2SO_4 as stripping solution gives the highest separation (94%) of arsenic and with increase of carrier concentration the rate of extraction also increases. Kocherginsky *et al.* [64] developed a BLM containing di(2-ethylhexyl) phosphoric acid in xylene as carrier for the separation and preconcentration of strontium from highly alkaline solution. They achieved 100 % removal of radioactive strontium using sulphuric acid as a stripping phase.

Goyette *et al.* [22] studied the photofacilited transport of sodium ions through SLM. They used photoactive crown ether as the carrier and investigated the fundamental parameters *viz.* nature of diluents and support materials, illuminating intensity, *etc*. affecting the transport of sodium ions. A porous glass frit as membrane support, 2-fluorotoluene as diluents and photoactive crown ether as carrier produced an optically stable SLM. They concluded that illumination of the feed side of the membrane provided a selective flux enhancement of five to seven times for sodium ions in the presence of an equal concentration of lithium ions. Nakatsuji *et al.* [65] presented a

comparative study between BLM and ELM separation of lithium ions using two types of carriers such as lipophilic quinaldic acid and nitrophenol derivatives. They observed that both the carriers could selectively transport lithium ion from the alkaline medium, concentrate in an acidic medium and the flux of lithium ions in ELM system is greater than that in BLM system. They found that emulsifier play an important role in the success of the ELM system. Mahapatra *et al.* [66] presented separation of cesium (I) by solvent extraction as well as by SLM. The SLM contains di *t*-butyl benzo-18-crown-6 in nitrobenzene as carrier. They investigated the effect of feed acidity, composition of diluents and nature of extracted species on the transport of cesium. About 80% extraction of cesium was achieved in 24 hours with the diluent mixture, 60% nitrobenzene and 40% toluene, 0.1M extractant concentration and at a feed acidity of 2M HNO_3. Lin and Long [31] presented the ELM separation of nitrate ions from water. Various parameters (*viz.* carrier types and its concentration, diluents, stirring speed, internal phase *etc.*) affecting the transport of nitric acid were investigated. About 94% of nitric acid was removed in 10 minutes with trioctylamine in solvent "100 neutral" as carrier and sodium carbonate as internal phase at 360 rpm. Span 80 was used as emulsifier. Yordanov and Boyadzhiev [20] studied extraction of citric acid by ELM containing alamine 336 in chloroform as carrier and sodium hydroxide as strip phase. The principal parameters such as carrier concentration, stirring speed, phase ratio and treat ratio, that have significant effect on the extraction of citric acid were investigated and optimized. They achieved 97% extraction and 15 fold preconcentration of citric acid at optimum conditions. Teramoto *et al.* [67] presented an experimental and theoretical study on the ELM separation of amino acids such as tryptophan (Trp) and phenylalanine (Phe) using di(2-ethylhexyl) phosphoric acid as carrier. They proposed a permeation model considering diffusional process at the external as well as at the organic phase and extraction equilibrium at

aqueous-organic interface. They found that the effects of various process parameters on the transport of amino acid could be satisfactorily explained by the proposed model.

Matsumoto *et al.* [68] presented a SLM separation method for the selective separation of aromatic hydrocarbons (*viz.* benzene, toluene and xylene) using room temperature ionic liquid (Imidazolium based) as the membrane phase. They observed that benzene, toluene and *p*-xylene were successfully transported through SLM. The selectivity of aromatic hydrocarbons was greatly improved. However, the permeation rate was less than those of water.

Sahoo *et al.* [69] studied the extraction of cephalosporine C (CPC), an antibiotic from fermentation broth using BLM as well as ELM containing aliquat-336 in heptanes and kerosene as carrier. Span 80 was used as emulsifier and 1M NaCl with citrate buffer as strip phase. The process parameters such as carrier concentration, stirring speed, pH of aqueous phases were investigated and optimized. They found that with increase of carrier concentration and stirring speed both the extraction and stripping of CPC increases. They achieved an identical extraction rates in fermentation broth as well as in synthetic solution in both BLM and ELM systems.

Lee [70] reported an ELM separation of penicillin G using dilute polymeric solution in kerosene as the membrane phase, Amberlite LA-2 (N-lauryl-N-trialkylmethylamine) as a carrier and sodium carbonate as strip phase. They investigated the effects of polymer composition and surfactant on the extraction efficiency of penicillin G. They found that the ELM systems with 8 vol.% of surfactant concentration, emulsion stability increased with an increase in polymer concentration, but degree of extraction sharply decreased at the polymer concentration higher than 2.0 wt.%, independent of the W/O ratio. They achieved a high degree of extraction and enrichment ratio of penicillin G concentration at the polymer concentration range between 0.5 and 2.0 wt. %.

Parka *et al.* [71] developed ELM process to treat the model industrial wastewaters containing phenols and selected substituted phenols (hydroquinone, three chlorophenols and two nitrophenols) at relatively high concentrations of about 1000 mgl^{-1}. They used Span 80 as emulsifier, polyisobutylene solution as stabilizer and sodium hydroxide as the strip phase. They observed that under optimized operating conditions, all the compounds except hydroquinone were extracted with the maximum extraction efficiency of over 96% and within a time period of 2-30 minutes.

Strict environmental regulations have now a days shifted the research activities towards the development of efficient LM based on environment friendly diluents. The conventionally used solvents in LM are toxic, flammable and volatile in nature [10]. The solubility of these solvents in water leads to health hazards. Venkateswaran *et al.* [72] reported SLM separation of copper using vegetable oil such as coconut oil as diluent. They reported coconut oil as a novel and stable diluent for the separation of Cu^{2+} from copper plating wastewater and achieved about 60-70% removal of copper. The extraction achieved here is less than that reported by Lazarova *et al.* [56] (99%) and Castro *et al.* (100%) [57]. Muthuraman and Palanivelu [73] studied the transport of textile dyes through vegetable oil based SLM. They investigated the efficiency of palm oil, sunflower oil and coconut oil as diluents in the separation of dyes. They reported coconut oil as novel diluent for this separation.

From the review of the above literatures it has been observed that the researchers have applied LM based techniques in diverse fields. Various combinations of membrane liquid, pollutants, carriers, stripping agents were used in different types of LMs with various process conditions. Performances of the LMs in most of the cases were found to be either excellent or satisfactory.

1.3.2 Extraction of LS

Various methods have been developed for the separation and recovery of LS from spent liquor. The oldest and the most widely used industrial process is the Howard process where LS is precipitated from spent liquor by addition of excess lime [40]. The precipitation processes have the advantage of low cost for high volume treatment. However it suffers from the drawbacks such as treatment and disposal of sludge. Again LS can not be recovered in its pure form by precipitation. In recent times, membrane technology has emerged as an efficient process for concentration and purification of macromolecular species in aqueous solutions [75]. Although its application in paper industries is yet to be successful, many researchers are putting their consistent effort to develop an efficient membrane separation process for the treatment of paper mill effluent [74, 19, 75-76].

A number of researchers applied membrane technology, *viz.* reverse osmosis and UF, to pulp and paper industries in order to recover valuable chemicals and to produce reusable water. Neytzell and Wilde [77] developed a series of UF membranes with different molecular masses to treat spent liquor. They showed that LS can be recovered from spent liquor and the ratio of sugar and acetic acid to total dissolved solid (TDS) in the starting feed could be increased significantly in the permeate. Concentration of over 300 gl^{-1} TDS was achieved at a flux of 8.3-67 $lm^{-2}h^{-1}$. Sridhar and Bhattacharya [75] used a cellulose acetate complex membrane to treat the spent liquor of concentration up to 5% and achieved a permeate flux of 37.8 $lm^{-2}h^{-1}$ at 550 kPa. Liu *et al.* [74] used inorganic membrane of microfiltration (MF) and UF range to treat spent liquor and they showed that 80% of lignin can be removed by MF membranes and 90% by UF membranes. Chakravorty and Srivastava [76] applied UF membrane and reverse osmosis to integrated pulp and paper mill wastewater and achieved 90% rejection of lignin. Bansal and Wiley [78]

extensively used reverse osmosis process to treat pulp and paper mill wastewater. The reverse osmosis process can treat large volume of wastewater and rejection of LS is also high. However this process is not selective, all contaminant ions and most dissolved non-ions are also removed. Most of these membrane processes have the drawback of fouling and require a high level of pretreatment. The merits and demerits of various LS separation processes are summarized in Table 1.3. Chakravorty *et al.* [79-80] synthesized ion exchange membrane for electrodialytic treatment of bleaching plant effluent. They synthesized ion-exchange membranes based on chemical grafting of styrene on poly-ethylene film with benzoyl peroxide as initiator under optimum processing conditions obtained during experimental work. Electro-chemical properties of the membrane were evaluated and utilized in designing a multi-compartment electrodialysis (ED) cell for electrodialytic treatment of bleach plant effluent from the pulp and paper industry. Electrodialytic studies under optimum conditions of 20 $mAcm^{-2}$ current density indicated the technical feasibility of developing a process for abatement of pollution along with recycling of water from multi-stage bleaching effluent.

Very few literatures are available on the solvent extraction and LM separation of LS. Kontturi *et al.* [19] studied liquid-liquid extraction of LS from sulfite spent liquor using various solvents *viz.* alcohols, ketons and cyclohexane and found that the process was not suitable for large scale application due to difficulties in separating the components and loss of solvent. Kontturi *et al.* [81] also developed a SLM comprising of decanol-trilaurylamine and polytetrafluoroethylene and explained their experimental results with a simple mass transfer model. They observed that the membrane was stable for about 48 hours however the flux of LS was too low for practical purpose. Thus, there exists a scope of research for finding more efficient method of separation for LS from aqueous solution.

Table 1.3 Merits and demerits of LS separation processes

Methods of LS recovery	Performance
Howard process or chemical precipitation [40]	Separation of LS is about 95-98%. However, it consumed large quantity of chemicals and disposal of the precipitate is a problem.
UF using series of polymeric membranes [77]	LS can be recovered efficiently with a permeate flux of 8.3-67 $lm^{-2}\,h^{-1}$.
UF using cellulose acetate complex membrane [75]	Spent liquor of concentration up to 5% can be treated with a permeate flux of 37.8 $lm^{-2}h^{-1}$.
MF and UF using inorganic membrane [74]	80% removal of lignin from spent liquor was achieved with membrane of microfiltration range and 90% with ultrafiltration range. However, the membranes are prone to fouling.
Reverse osmosis [76]	90% removal of lignin from integrated pulp and paper mill was achieved. However, the membranes are prone to fouling and can not withstand the severe condition of paper mill wastewater.
SLM having the composition decanol-trilaurylamine-PTFE [81]	The flux of LS was very low (about 150×10^{-6} $mgcm^{-2}s^{-1}$at optimum conditions).

1.3.3 Extraction of mercury

Conventional methods of mercury treatment are precipitation, coagulation, electrodialysis, reverse osmosis, adsorption, solvent extraction, chemical oxidation and reduction and ion exchange. As discussed in the Section 1 precipitation, electrodialysis and reverse osmosis suffer from the drawbacks like sludge disposal and membrane fouling.

Adsorption has been shown to be the most promising technique for the removal of mercury from aqueous streams [82]. The most commonly used and efficient absorbents are activated carbon [83]. Because of the high cost of activated carbon researchers tried various low cost absorbents such as fly ash, tree bark, char coal, fertilizer waste, rice husk ash *etc*., for the removal of mercury and achieved high removal efficiency [46]. Adsorption process suffers from frequent regeneration of the adsorbents and disposal of spent regenerates.

Ion exchange is another efficient method for mercury removal from aqueous solution. Anirudhan *et al.* [84] synthesized a novel cation exchange resin from coconut coir pith. The resin was synthesized by grafting poly(hydroxyethylmethacrylate) on to coconut coir pith. They achieved high mercury removal efficiency (about 99%) in the pH range of 5.5-8 and the adsorbent could be reused for three consecutive cycles. Most of the ion-exchange resins are regenarable and can be reused for thousands of cycles before they are replaced. However their useful life shortened drastically due to fouling and the process becomes costlier. All the above mentioned mercury removal processes are ineffective at lower metal concentrations [55].

Solvent extraction of metal ions is one of the effective and energy saving processes for hydrometallurgy and/or treatment of wastewater containing heavy metals. Few literatures are available on solvent extraction of mercury. Baba *et al.* [85] carried out solvent extraction of mercury (II) from hydrochloric acid with 1,2 bis(hexylthio)ethane in 1,2-dichloroethane at 30 ºC. They found that mercury (II) can be extracted into pure 1,2-dichloroethane without any extractant due to the physical partition of the neutral species, $HgCl_2$. However solvent extraction has the disadvantages such as loss of solvent, requirement of large amount of solvent and the difficulties in the recovery of solvent. These disadvantages can be overcome by the use of LM processes as it performs the extraction and stripping process simultaneously in one step with less

quantity of solvent. In addition LM is an effective tool for the separation of metal ions from its aqueous phase when the amount of ion in the solution is trace [86]. Several studies dealt with the use of LM (bulk and emulsion) for Hg^{2+} separation from various aqueous media using different extractants. Bacon and Jung [87] reported a complete removal of mercury through a BLM using macrocyclic ligands as carrier, chloroform as diluent and water as stripping agent. Alpoguz *et al.* [28] studied the kinetics of mercury (II) nitrate transport through a BLM using calixarene nitril derivative as carrier in various solvents such as chloroform, dichloromethane and carbon tetrachloride. The kinetic parameters were investigated in terms of the effect of temperature, stirring rate and carrier concentration. The kinetic parameters and the flux were found to be dependent on the initial carrier concentration and increase steadily with increase in carrier concentration. They observed that the transport of mercury increases with temperature and stirring speed and the highest transport efficiency was achieved with dichloromethane (maximum flux=2.92×10^{-3} min^{-1}) followed by chloroform (maximum flux=2.46×10^{-3} min^{-1}). Boyadzhiev and Bezenshek [88] used a double emulsion technique to extract mercury (II) nitrate from an acidic solution and reported a complete removal of mercury with a 1000 fold concentration increase of the metal in the strip phase under optimum conditions. They used oleic and linolic acid in *n*-paraffins as the membrane phase. Shamsipur *et al*. [24, 27] studied the transport of Hg^{2+} through a BLM comprising tetrathia-crown-4 and potassium dicyclohexyl-18-crown-6 as carriers, chloform as diluents and ethylene diamine tetra acetate (EDTA) as stripping agent. They achieved 99% transport of mercury. Parham and Shamsipur [89] reported a 94% separation of mercury (II) nitrate from a mixture of various metal cations such as Cd^{2+}, Pb^{2+}, Zn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+} *etc*. through BLM using Barium 18 crown-6 as extractant. Safavi and Shams [90] used methyl red in dichloroethane as the LM to extract mercury (II) from a solution

containing other metal ions such as Cd^{2+}, Pb^{2+}, Zn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+} *etc*. and achieved 80% separation in 150 minute. Li *et al.* [26] studied separation of mercury (II) chloride through an ELM using trioctylamine (TOA) in toluene as the membrane phase and achieved 99% extraction in 10 minutes.

All the above reports show great potential of LM for the separation of mercury from aqueous solution. However, very few reports are available on the application of SLM for extraction of mercury. Shamsipur *et al.* [91] used an SLM for the simultaneous separation of silver and mercury ions from aqueous feed employing a two membrane three compartment cell. They used 1,10-phenanthroline sub-unit ($PhenS_2O$) and tetrathia-12-crown-4 (TT12C4) in nitrophenyloctyl ether (NPOE) as the membrane phases, polypropylene as the support, sodium thiosulfate and EDTA as strip phases for Ag^{+} and Hg^{2+} ions, respectively. To the best of our knowledge no reports are available in literature till date on the simultaneous separation of Hg^{2+} and LS from aqueous acidic solution using SLM.

1.4 Importance and objective of the research work

From the review of the literature reported so far it is evident that though attempts have been made by earlier researchers to separate lignin and treat pulp and paper mill wastewater, there are few reports as mentioned earlier regarding application of LM for such treatments. Moreover, very few literatures are available for separation of LS using SLM and to the best of our knowledge no literature is available on separation of LS using ELM. Therefore, there exists a potential for LM based technology to serve dual purpose, using paper mill waste as a source of LS in one hand and an effective wastewater treatment on the other. The scope of using LM techniques for real industrial wastewater from pulp and paper industry is still unexplored by the

scientific community. Intensive work has been reported on the ELM based separation of mercury. A few reports are available on separation of mercury using SLM. In addition, combinatorial approach for simultaneous separation of LS and mercury has never been reported in the literature. Again, though LM based processes based on green or environment friendly solvent such as ionic liquid, vegetable oil *etc*. are gaining more importance now a days for the reasons discussed in Section 1.3.1, little information is available in the literature on the performance of such solvents as LM.

Thus, the present research work aims at all of the above unexplored territories of research problems and provides a systematic approach to implement LM based technology for the removal of LS and mercury from wastewater. Therefore, the overall aim of this thesis is to explore the efficacy of LM based technology for the separation and pre-concentration of LS and mercury from their aqueous solutions. To achieve this overall aim, the thesis finds the following measurable objectives:

- Identification of a suitable organic solvent (membrane phase) that can extract solutes (LS and mercury) from their aqueous solution by a two phase equilibrium study.
- Identification of a suitable carrier agent or more precisely a suitable solvent-carrier combination that enhances the transport of solutes from one aqueous phase (source/feed phase) to the other (strip/receiving phase) through the intermediate membrane phase, by a three phase BLM study.
- Identification of the best operating condition in terms of feed phase pH, initial concentrations of feed phase, concentration of strip phase, carrier concentration and operating temperature which would yield best separation of LS or mercury in a BLM unit.

- Verifying whether the above best operating condition is also applicable for separation of LS using SLM. Selection of support material that would yield a stable SLM is also an integral part of this study.

- Evaluation of the performance of SLM for simultaneous separation of LS and mercury. Further retuning of the best operating condition is also carried out through this study.

- Identification of an environmentally benign solvent (vegetable oil) that could be used in SLM in order to minimize the environmental pollution due to unstable and leakage prone SLMs.

- Study of the performance of an ELM for separation of LS from aqueous solution. In addition to identifying the best operating condition in terms of various process parameters as discussed above, few more process parameters such as surfactant concentration, volume ratio of organic/strip, *etc*. are also carried out.

- A comparative study of BLM, SLM and ELM and their various merits and demerits in separation of LS.

- Case study on a real industrial effluent at the best operating condition obtained as above.

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CHAPTER-II

Materials and Methods

This chapter discusses in detail the three types of liquid membrane set-up viz. bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM) designed to carry out this research work. The experimental procedures followed in each case are described. This chapter also gives information on the materials used in various experiments along with the sources from where they were procured. The analytical instruments used during this research work are also summarized here.

2.1 Chemicals and reagents

Various materials used in the separation of lignosulfonate (LS) and mercury (II) along with their sources are summarized in this section. All reagents used in this work were of GR grade and were used as it is. Aqueous solutions were prepared by using Milli-Q® de-ionized water (Millipore®, USA).

Sodium lignosulfonate (Na_nLS, 90% pure) was obtained from National Chemicals (India) and Tri-octylamine [$(C_8H_{17})_3N$, 98% pure] was procured from Merck® (Germany). All other chemicals such as 1, 2-dichloroethane ($C_2H_4Cl_2$, 99% pure), carbon tetrachloride (99.5% pure), hydrochloric acid (35%), toluene, *n*-heptane, chloroform, sodium chloride and hexane (all 99.5% pure), sodium hydroxide (97% pure) and sodium carbonate (99.9% pure), were obtained from Merck® (India). The surfactants used in the ELM separation of LS such as Span 80 (Sorbitane monooleate) was obtained from Loba Chemicals (India) and polyethylene glycol (PEG) 20,000 from SISCO research laboratories (India).

Tri-octylphosphine oxide ($C_{24}H_{51}OP$, 98% pure) and 2-Ethyl hexanol ($C_{11}H_{20}O_2$, 99% pure) used as carriers for mercury extraction were procured from Alfa Aesar (Lancaster) and Loba Chemical (India) respectively. Coconut oil (parachute, 100% pure)) was procured from Marico India limited. All other chemicals such as mercury (II) chloride ($HgCl_2$, 99.8% pure), sodium bicarbonate (99% pure), cyclohexane (99.5%% pure), stannous chloride ($SnCl_2.2H_2O$, 97% pure) and concentrated nitric acid (70%) were obtained from Merck® (India).

2.1.1 Working solutions for LS separation

A stock solution (1000 mgl^{-1}) of LS was prepared by dissolving 250 mg of sodium lignosulfonate in 250 ml of Milli-Q de-ionized water. The feed phases, in both the equilibrium and mass transfer studies, were prepared from the stock solution by dilution with water up to the desired concentration. The feed phase of higher concentration was prepared following the similar stoichiometry. The receiving (*or stripping*) phase was prepared by dissolving the required quantity of sodium chloride (or sodium hydroxide or sodium carbonate) in 100 ml of Milli-Q de-ionized water. The organic phase in equilibrium studies and liquid membrane in three phase studies were prepared by dissolving appropriate amount of the carrier in various pure solvents.

2.1.2 Working solutions for mercury separation

The stock solution of mercury (II) (10 mgl^{-1}) was prepared by dissolving 13.54 mg of $HgCl_2$ in one liter of de-ionized water. The feed phase of various initial concentrations was then prepared from this stock solution by proper dilution with Milli-Q de-ionized water. The stripping phase was prepared by dissolving the required amount of sodium hydroxide /or sodium bicarbonate in 100 ml of Milli-Q de-ionized water. The organic phase in equilibrium

studies and liquid membrane in three phase studies were prepared by dissolving appropriate amount of the carrier in various pure solvents.

2.2 Analytical instruments

A UV-vis spectrophotometer (Perkin Elmer, Model: Lambda 35) was used for measurement of concentration of LS. The details of working principle and analysis procedure are incorporated in Appendix-AI.1 and AI.2 respectively. For the measurement of pH a CP 901 digital pH meter and/or a EUTECH 510 digital pH meter was used. U-tube viscometer (Model: Stanhope-Seta, Type: A) was used for the measurement of viscosity. A sample calculation is shown in Appendix-AII.

A cold vapor atomic absorption spectrometer (Varian Australia, Model: AA240FS), equipped with a continuous flow VGA-77 vapor generation accessory, was used for the measurement of concentration of mercury in the aqueous phases. Working principle and analysis procedure are incorporated in Appendix-AIII.1 and AIII.2. Following instrumental operating parameters were used while operating the AAS: lamp current 4 mA, wave length 253.7 nm, quartz tube temperature: room temperature and delay time 100 seconds. In this method (as per Varian® standard), samples were acidified with a 5% (v/v) mixture of HCl and HNO_3 and then reacted with a solution of 25% (w/v) $SnCl_2$ in 20% (v/v) HCl to generate mercury vapor [1]. The vapor was carried to the spectrometer by an argon line.

An upright optical microscope (Carl Zeiss, Model: Axiotech 100HD-3D) was used to view the image of precipitate of oxide of mercury in the strip phase.

A tensiometer (Kruss K9, Germany) was used to measure the interfacial tension for dichloroethane-TOA/water system. Working principle and procedure are described in Appendix-AIV.1 and AIV.2.

A sonicator (Elmasonic Germany, model: S30H) having a frequency of 50/60 Hertz was used for preparing emulsion in ELM based separation study.

2.3 Two phase equilibrium set-up and procedure

Two phase equilibrium distribution studies of a solute provide the informations which decide the separation feasibility of the solute through the liquid membrane. It also provides the preliminary operational conditions for such separation. In order to select a suitable organic solvent (diluent) of high separation factor for transferring solutes from aqueous phase to the organic phase, equilibrium study is carried out for both LS and mercury as discussed in the following sections.

2.3.1 Two phase equilibrium distribution for LS [2]

To estimate the two phase equilibrium distribution coefficient, 25 ml of aqueous solution containing 100 mgl^{-1} of sodium lignosulfonate was added to equal volume of organic phase in a conical flux. The mixture was then put under continuous agitation for 6 hours on a shaker at constant speed (100 rpm) to attain equilibrium. The equilibrium concentration of LS in aqueous solution was then measured using UV-vis spectrophotometer at wavelength 280 nm and concentration of LS in organic phase was then calculated from the mass balance of LS in the system with the assumption that LS was neither lost nor consumed in any chemical reaction inside the organic phase. In order to measure the concentration of an unknown sample, a calibration curve was generated for the concentration range 0-100 mgl^{-1} of LS, at wavelength 280 nm. The calibration curve is shown in Fig. 2.1. The details of UV-vis are in appendix. The value of coefficient of determination was found to be, R^2= 0.995. Distribution coefficient (*a.k.a.* separation factor) of LS (*m*) was then calculated as the ratio of LS in organic phase to LS in the aqueous phase at equilibrium. The value of *m* needs to be very high to ensure successful separation by LM based technique. The experiment was repeated

with various solvents such as *n*-heptane, hexane, carbon tetrachloride, chloroform, toluene and dichloroethane. The best performing organic solvent was identified and selected on the basis of high value of separation factor, for further studies to learn the effects of carrier concentration, temperature and pH on the equilibrium LS distribution.

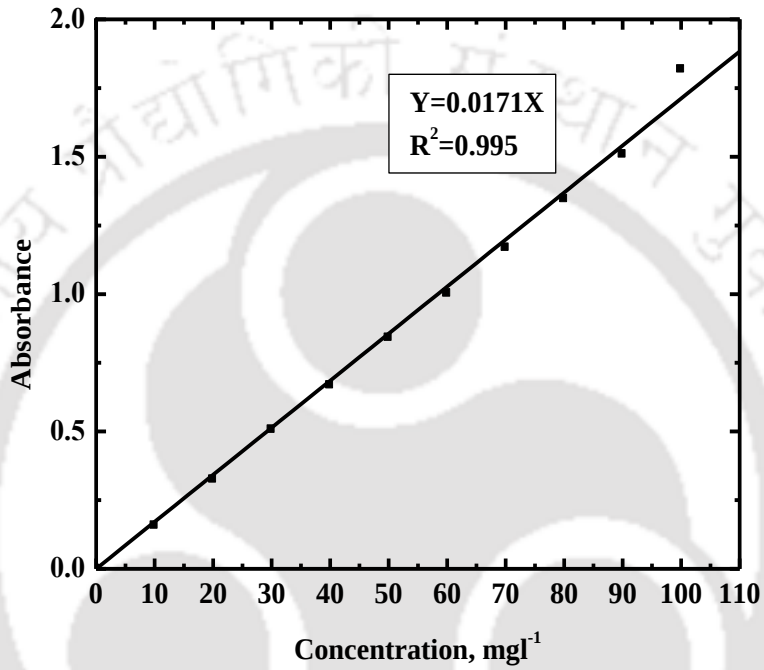

Figure 2.1 Calibration curve for analysis of LS in UV-vis spectrophotometer

2.3.2 Two phase equilibrium distribution for mercury [3]

A similar procedure as described in the previous section was repeated in order to find the two phase equilibrium distribution of mercury in LM. 10 ml stock solution of mercury chloride was added to equal volume of organic phase in a conical flux. The mixture was then continuously agitated at constant speed (100 rpm) for about 6 hours on an orbital shaker. Mercury concentration in aqueous phase was then determined by a cold vapor atomic absorption spectrophotometer (AAS). The details of AAS procedure are in appendix. Assuming no loss of mercury in the process, the mercury concentration in membrane phase

was then determined by mass balance of mercury in the system. Distribution coefficient of mercury (*m*) was then calculated using the method described in Section 2.3.1. The experiments were repeated with different solvents such as *n*-heptane, hexane, toluene, dichloroethane and cyclohexane. The best performing organic solvent was identified and selected on the basis of high value of separation factor, for further studies to learn the effects of carrier concentration, temperature and pH on the equilibrium distribution of mercury.

2.4 BLM set-up and procedure [2, 3]

The laboratory scale BLM setup is usually prepared in a glass beaker. As discussed in the Chapter-I, two different BLM configurations can be set up depending on the density of the membrane phase. In case, the membrane phase is lighter than feed/strip phases, reactor is divided into two parts (compartments) from the bottom erecting a glass wall at the middle with sufficient clearance at the top. Two compartments of the reactor houses the feed and strip phases in such a way that the level of these liquids remain well below the top of the wall. The membrane phase liquid is then poured from the top in such a way that the height of the membrane phase clears the top of the glass wall and thus creates a bridge between the feed and strip phases for possible mass transfer of solutes. On the other hand, if the membrane phase is heavier than the feed/strip phases, the reactor is divided into two parts from the top with a glass wall at the middle with sufficient clearance at the bottom. The membrane phase is placed at the bottom of the reactor in such a way that the liquid level of the membrane phase rises beyond the bottom clearance of the glass wall. Two compartments are thereby formed due to such arrangement which can house the feed and strip phases. Care is taken so that there is no leakage/accidental mixing of these phases in both the cases. This research work deals with the second case where membrane phase is heavier than the feed/strip phases.

The cell of the BLM, used in this study, is shown in the Figs. 2.2 and 2.3. The cell consists of a glass beaker (70 mm ID and 90 mm height), two stirrers (impeller length of 12 mm), and two regulated motors (Sewing motor, model YM-50). The cell is divided into two compartments by a thin glass plate of thickness 2.0 mm with a bottom clearance of 10 mm. The glass plate is fixed at the cell wall with the help of an adhesive for glass. A blank test was carried out to ensure no leakage. In this test, first CCl_4 was put to few mm above the bottom clearance and thereafter one compartment of the cell is filled up with clear water and the other with a coloured (crystal violet) solution. Both the aqueous phases were stirred continuously for 6-7 hours and the intensity of colour in the aqueous phases was then measured with UV-vis spectrometer at 584 nm. The insignificant change in the absorbance confirmed that there was no leakage between feed and the stripping phases. The results of leakage test are incorporated in Appendix-AV. For the BLM separation experiment the organic phase being the heavier one was placed at the bottom and the aqueous phases (*feed or source and strip or receiving*) were separately poured at two compartments. Aqueous phases were continuously stirred by motor driven stirrers and their speeds (rpm) were controlled by voltage regulators. Sufficient care had been taken to prevent unwanted mixing of feed and strip phases. To ensure this, the level of the membrane phase was maintained well above the bottom edge of the separating plate. Moreover, the stirrer speed was regulated in such a way that neither it allows forming any emulsions at the feed/membrane interface nor it disturbs the membrane interface.

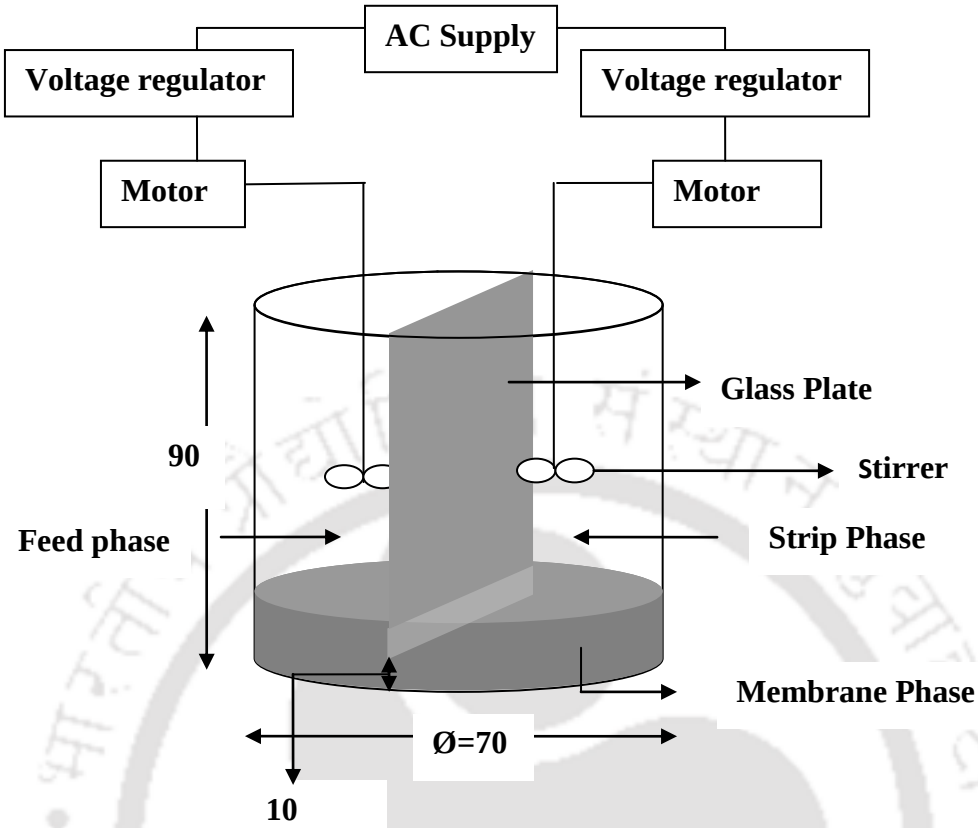

Figure 2.2 Schematic of BLM set-up

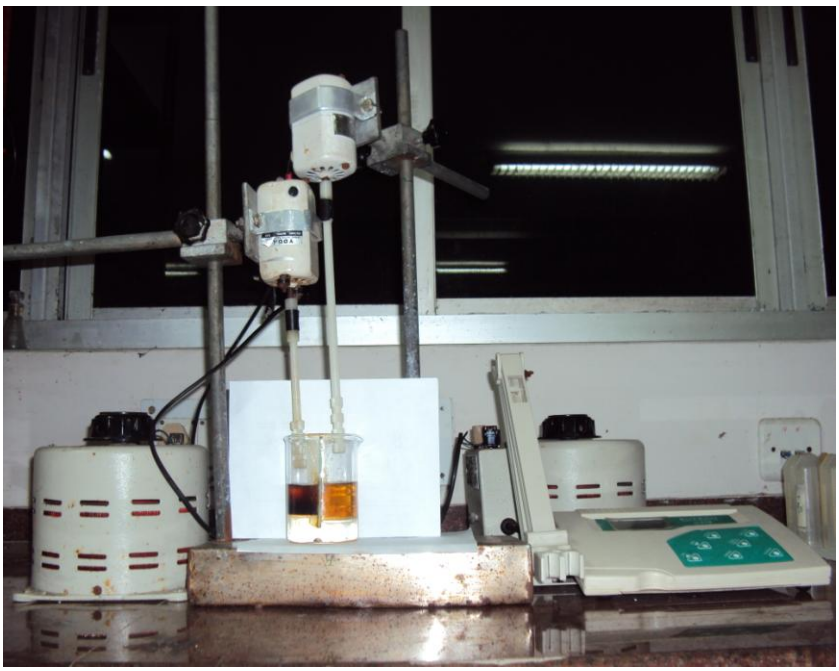

Figure 2.3 Photograph of BLM set-up

The three phase experiments were carried out in the BLM setup as described above. Area of membrane/aqueous interface was 18.2 cm^2 at both sides. LS were transferred through these interfaces. The volumes of feed phase as well as receiving phase were 60 ml each and the volume of organic phase was 50 ml. In case of mercury the volumes of feed, receiving and organic phases were 50 ml each. Continuous stirring ensured the solution to be well mixed and the bulk concentration to be uniform throughout. The pH values of the aqueous phases were continuously monitored and adjusted by adding hydrochloric acid as and when required. One ml of both aqueous phases was collected periodically for further analysis.

2.5 Supported liquid membrane set-up and procedure

Various types of SLM modules such as flat sheet, hollow fiber, spiral wound, *etc*. are discussed in the previous chapter. Among these the simplest one *i.e*. the flat sheet supported liquid membrane is considered for this research work. The SLM set-up and its working procedure are described in the next sections.

2.5.1 SLM set-up [4, 5]

The liquid membrane cell (permeator) is shown in Fig. 2.4. It consists of two equal volume cylindrical tanks made of stainless steel and connected by flanged cylindrical pipes. The pipes are tightly bolted together with a porous support held between the flanges. The pores of membrane (*i.e.* support) are filled with organic solvent (liquid membrane) that acts as a medium of solute transport. The tanks are filled with aqueous solutions of feed and strip phase materials. The solutions are continuously stirred by motor driven stirrers and their speeds (rpm) are controlled by voltage regulators. During the process of separation, solute gets transferred through the membrane from feed phase to the strip phase.

This whole structure is called the permeation cell. The effective membrane contacting area is 490 mm^2. The experiments were performed at 25 ºC. There was no temperature controller

facility with the setup, however, the temperature fluctuation was monitored during the experiment and the variation was found to be within ±1ºC. The experiments were carried out in batch mode.

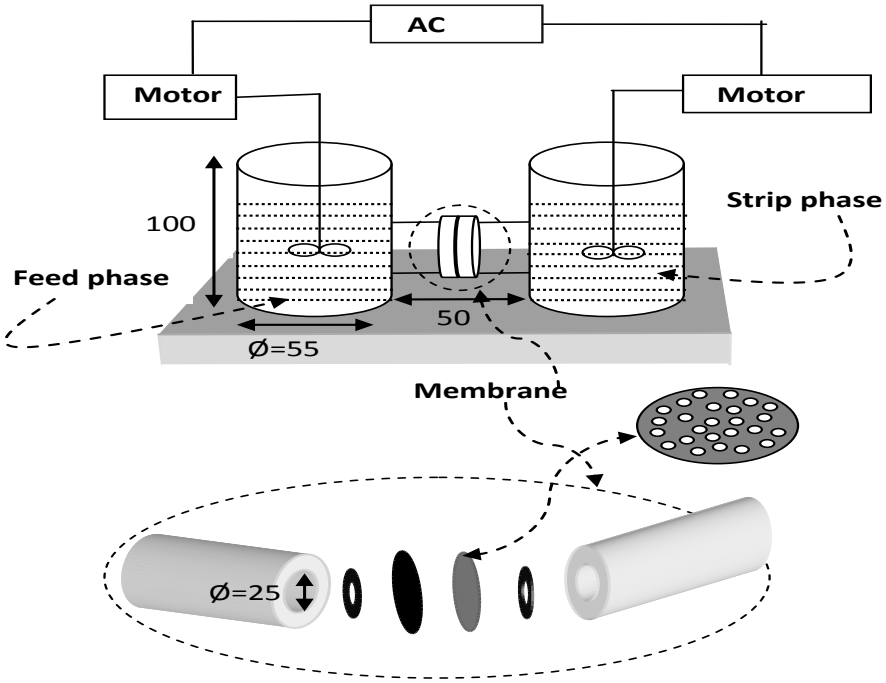

Figure 2.4 Schematic of SLM set-up

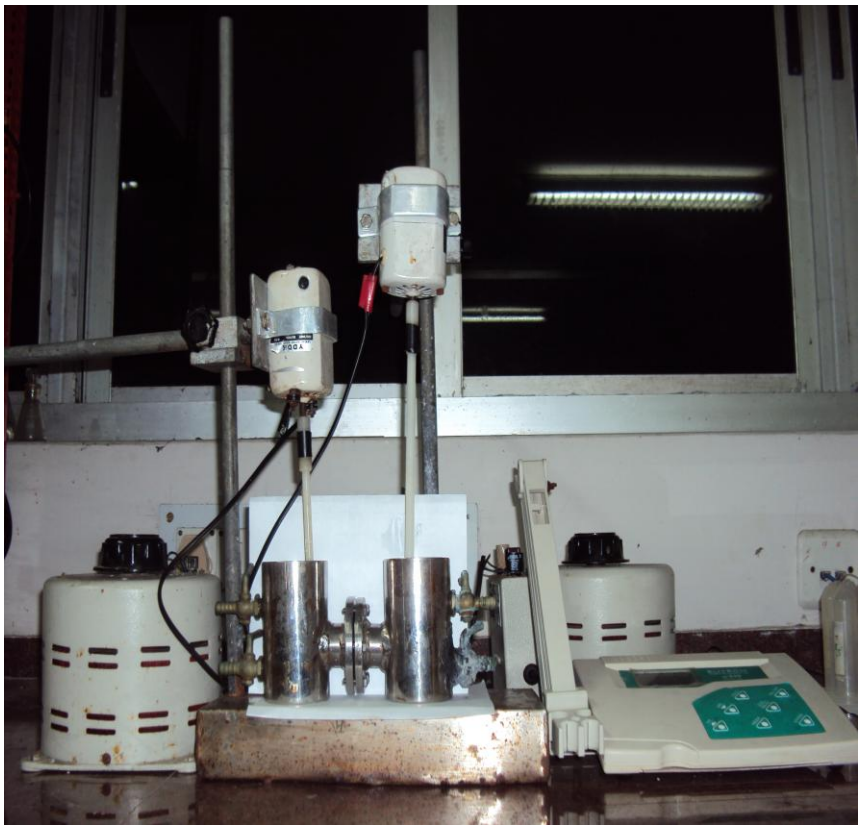

Figure 2.5 Photograph of SLM set-up

2.5.2 Membrane support

Various polymeric membranes were used as support for the organic liquid phase such as polytetrafluroethylene (PTFE), Nylon 6,6, polyvinyldenefluoride (PVDF) and polyethylene (PE). These polymeric membranes were procured from Pall life science (India). The porosity of the support materials was calculated through SEM analysis. SEM pictures of the support materials are presented in Appendix-AVI.1. The thickness of the support materials was calculated from the SEM pictures (Appendix-AVI.2) by measuring the thickness at various points and then taking the average of those values. The value of the tortuosity (τ) was calculated as

$$\tau = \frac{1+V_p}{1-V_p} \qquad (2.1)$$

where, $V_p=1-\varepsilon$ is the volume fraction of the polymeric framework and ε= porosity of the membrane [6].

2.5.3 Preparation of SLM [4, 5]

The micro-porous polymeric support was impregnated with the organic phase by immersing the support in the liquid for about 24 hours. The pores in the polymeric support got filled with the liquid due to capillary action. The support was taken out of the liquid and the liquid on the surface of the support was allowed to drip for few seconds before it was placed in the permeation cell.

2.5.4 Experimental procedure [4]

The volumes of feed phase and strip phase were 140 ml each. It is important to decide upon an ideal stirring speed in order to ensure good mixing and uniform bulk concentration inside the aqueous phases. Stirring minimizes concentration polarization at the membrane interface too. Therefore both the aqueous phases were stirred continuously at a speed of 500 rpm. The pH value of the feed phase was continuously monitored and adjusted by adding hydrochloric acid as and when required. One ml of both the aqueous phases was collected periodically for

further analysis. The LS content of the aqueous phases was determined using UV-vis spectrophotometer as described in Section 2.3.1 and the mercury content using AAS as described in Section 2.3.2.

2.6 Emulsion liquid membrane set-up and procedure

Emulsion membranes can be either water in oil in water (W/O/W) type or oil in water in oil (O/W/O) type. As the present work is related to the treatment of wastewater, the ELM should be water in oil in water type. The description of the W/O/W (water in oil in water) type ELM set-up and the experimental procedure is given in the following sections.

2.6.1 ELM set-up

The ELM set-up is prepared in a 500 ml glass beaker made of Borosil®. A motor driven stirrer as described in Section 2.4 is used to disperse the emulsion phase in the continuous phase present in the beaker. The schematic and photograph of the ELM set-up is shown in the Figs. 2.6 and 2.7.

2.6.2 ELM experimental procedure

The organic phase was first prepared by dissolving required quantity of TOA (as carrier) and surfactants (PEG 20,000 or Span 80) in the solvent dichloroethane. To prepare a stable W/O (water in oil) emulsion, the internal or strip phase (aqueous NaOH solution) was added drop wise to this organic phase under string (1000 rpm) condition until the required volume ratio of organic phase to internal phase was obtained. The blended solution was then kept in a sonicator for 1-3 h until a stable milky white W/O emulsion was obtained. During sonication temperature was maintained in such a way so that it does not exceed beyond 30-40 ºC to avoid demulsification.

Measured quantity of freshly prepared W/O emulsion was then poured slowly into 100 ml of continuous or feed phase (aqueous LS solution) in the ELM set-up. The solution was then

stirred by a motor driven mechanical stirrer at 400-500 rpm to disperse the emulsion phase. The speed of the stirrer was regulated by a voltage regulator. Samples were collected periodically from the continuous phase and allowed to settle by gravity for few minutes to separate the emulsion phase from the continuous feed phase. The emulsion phase, being heavier settled at the bottom. The upper layer of feed phase was filtered and analyzed for measuring concentration of LS. The experiments were performed at 25±1 ºC.

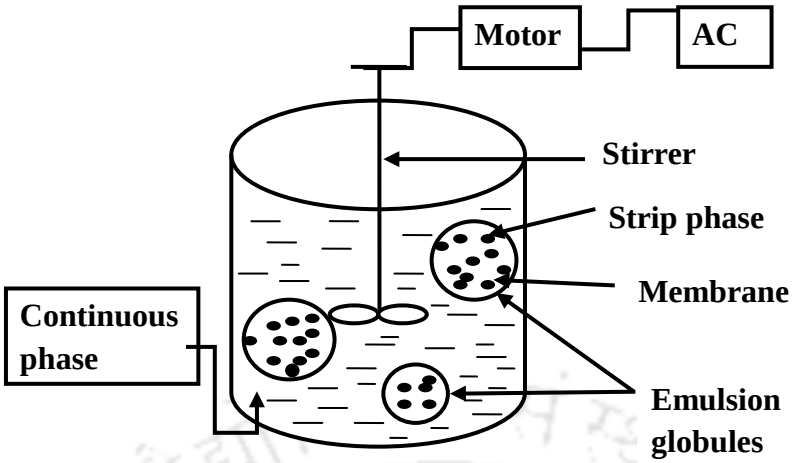

Figure 2.6. Schematic of ELM set-up

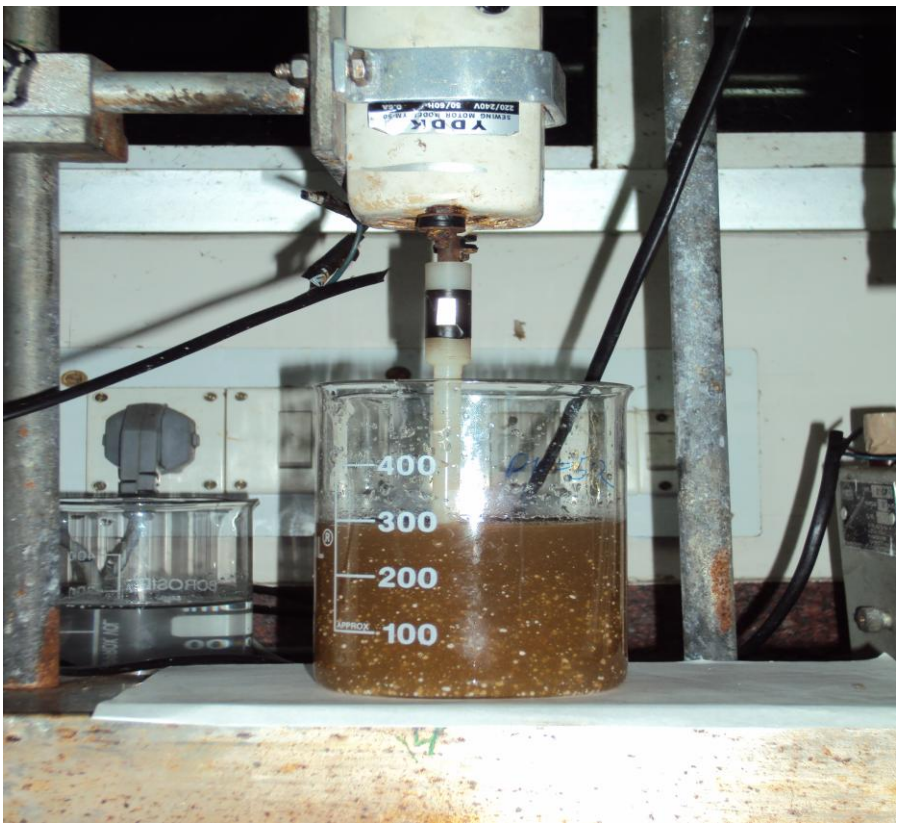

Figure 2.7 Photograph of the ELM set-up

Abbreviations

AAS	atomic absorption spectrometer
BLM	bulk liquid membrane
ELM	emulsion liquid membrane
LS	lignosulfonate
LM	liquid membrane
PEG	polyethylene glycol
PTFE	polytetrafluroethylene
PVDF	polyvinyldenefluoride
PE	polyethylene
SLM	supported liquid membrane
TOA	trioctylamine
TOPO	tri-octylphosphine oxide
VGA	vapor generation accessory

References

[1] Manual of atomic absorption spectrometer (VGA-77), Varian Australia, Model: AA240FS.

[2] K.Chakrabarty, V.Krishna, P.Saha, A.K.Ghoshal, Extraction and recovery of lignosulfonate from its aqueous solution using bulk liquid membrane, J. Membr. Sci., 330 (2009) 135-144.

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[4] K.Chakrabarty, P.Saha, A.K.Ghoshal, Separation of lignosulfonate from its aqueous solution using supported liquid membrane, J. Membr. Sci., 340 (2009) 84 – 91.

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CHAPTER-III

Separation of Pollutants using Bulk Liquid Membrane

This chapter presents the results and discussion on the separation of pollutants using bulk liquid membrane (BLM). Issues regarding separation of LS and separation of mercury (II) from their respective aqueous solutions, are discussed elaborately in this chapter. Initially, a two phase equilibrium study was performed in order to select a suitable membrane phase for efficient transport of solute. The effects of various parameters, such as pH, temperature and carrier concentration, on the equilibrium distribution of pollutants are also studied. Based on the results of equilibrium study, an appropriate optimum operating condition was detected. Further experimentation was then carried out on the three phase separation using BLM. The separation performance was evaluated against various parameters such as stirring speed, carrier concentration, temperature, feed concentration and strip phase concentration. A comparison of the two types of liquid membrane (LM) transport modes (co-and counter) for the separation of pollutants is also highlighted in this chapter.

3.1 Separation of LS

As discussed in the introductory section, very few works have been reported in the literature on the LM based separation of LS. Therefore, an effort has been made to test the efficiency of a low viscous LM for the extraction and recovery of LS from its aqueous solution. The simplest LM separation process is the BLM separation. BLM study provides quick understanding of separation feasibility of a new system and also provides important data required for the upgradation of the system. Therefore, a through experimental investigation

was carried out on the coupled transport of LS through BLM and thereby the best set of solvent, operating conditions and mode of transport that would yield optimum performance of the BLM was identified. This work is reported in the subsequent sections. The work has already been published in the Journal of Membrane Science [1].

3.1.1. Theoretical background [1]

As discussed in the earlier chapter (Chapter-I, Section 1.1.1) LM based separation processes follow various transport mechanisms. However, most of these processes are guided by coupled transport mechanism. In coupled transport, the carrier can lead to transport only when two different elements are present at the same time. The reaction mechanisms in co-and counter transport of LS have been proposed by Kontturi *et al.* [2]. The reaction at the feed/membrane interface follows a two-step mechanism which is same for both types of transport. The reactions are shown as follows:

$$R_3N + HCl \Leftrightarrow R_3NH^+Cl^- \quad (3.1)$$

$$R_3NH^+Cl^- + LSNa_n \Leftrightarrow R_3NHLSNa_{(n-1)} + NaCl \quad (3.2)$$

Where R_3N is trioctylamine and $LSNa_n$ is sodium lignosulfonate. On the other hand, the reaction mechanism at the membrane/strip interface is different for the two transport modes. The co-transport and counter transport mode reactions at membrane/strip interface are represented by reactions (3.3) and (3.4) respectively.

$$R_3NHLSNa_{(n-1)} + NaOH \Leftrightarrow R_3N + LSNa_n + H_2O \quad (3.3)$$

$$R_3NHLSNa_{(n-1)} + NaCl \Leftrightarrow R_3NH^+Cl^- + LSNa_n \quad (3.4)$$

The principles of both these coupled transport mechanisms in case of separation of LS are described in Figs. 3.1 and 3.2 [2-5]. In co-transport mechanism, H^+ and LS ions of feed phase move from the feed phase to the receiving phase by virtue of the concentration gradient of the

ions across the aqueous-organic-aqueous phase (Fig. 3.1). In counter transport, Cl^- and LS ions move counter currently (Fig. 3.2).

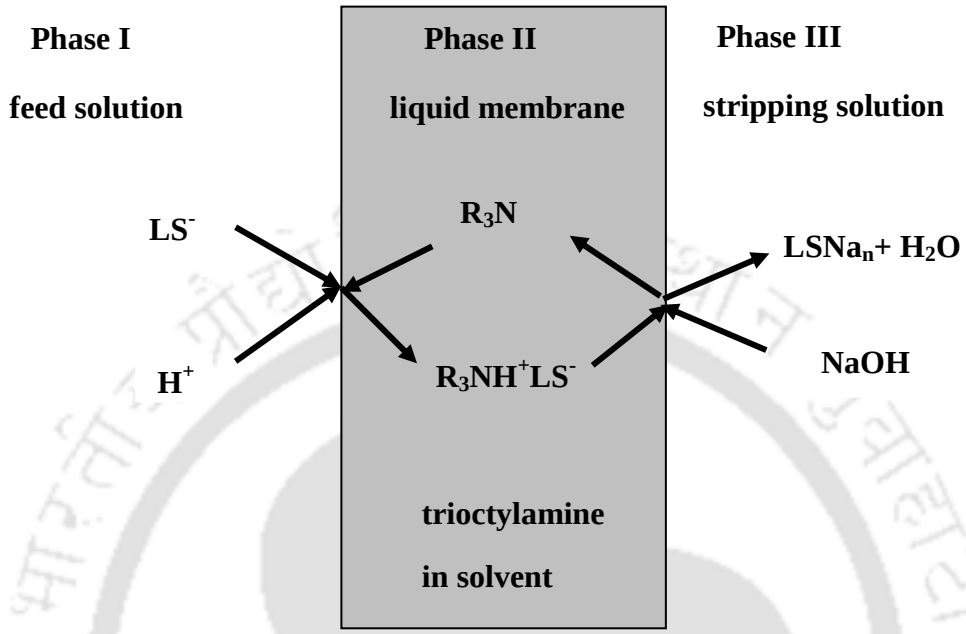


Figure 3.1 Schematic of co-transport mode for LS extraction

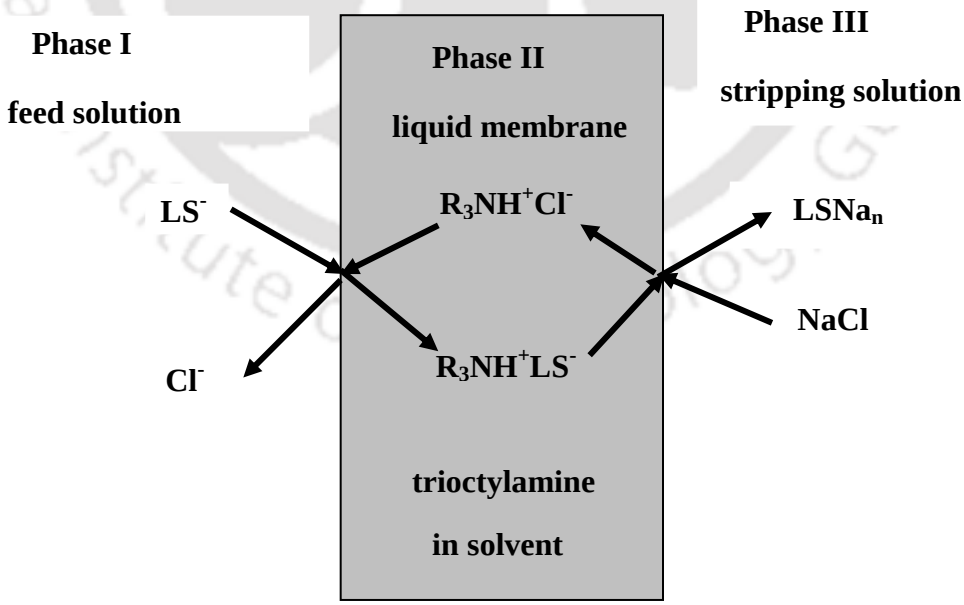


Figure 3.2 Schematic of counter-transport mode for LS extraction

3.1.2 Two phase equilibrium study

Equilibrium study was conducted as described in the Section 2.3.1 of Chapter-II in order to select a suitable LM of high separation factor. Effects of various process parameters such as temperature, pH and carrier concentration on the equilibrium distribution of LS have also been examined with the selected solvent. TOA has been reported as a suitable carrier for such separation process [2] and hence experiments were carried out with TOA as the carrier.

3.1.2.1 Choice of solvent

Selection of a right solvent (or membrane phase) is the prime issue in all kinds of LM based separation processes. The solvent should be chosen in such a way that it is immiscible with the aqueous phase, has low viscosity and volatility and at the same time it should have a high distribution coefficient [3, 4]. The performance of various solvents *viz.* *n*-heptane, hexane, toluene, carbon tetrachloride, chloroform and 1,2-dichloroethane, were examined by estimating distribution coefficients (*m*) of LS in these solvents. The results are reported in Table 3.1. It is observed that separation of LS is negligible when *n*-heptane, hexane and toluene were used as membrane because LS is mostly insoluble in these organic solvents. Considerable separation occurs in 1,2-dichloroethane, followed by carbon tetrachloride and chloroform. Thus, 1,2-dichloroethane has been selected as the suitable solvent for the subsequent studies.

Table 3.1 Equilibrium distribution coefficient (*m*) of LS in various solvents [1]

Experimental conditions	Solvents used	Distribution coefficient (*m*)
Concentration of LS in feed ($C_{LS,o}$): 100 mgl^{-1} pH of feed phase: 2.0 Carrier (TOA) concentration: 0.8 % (v/v) Temperature: 30 °C Stirring speed: 100 rpm Duration of stirring: 6 hrs Volume of feed phase: 25 ml Volume of membrane phase: 25 ml	Dichloroethane	21.5
	Carbon tetrachloride	8.5
	Chloroform	1.25
	n-Heptanes	0.584
	Toluene	0.368
	Hexane	0.247

3.1.2.2 Effect of pH

For a polydispersed macromolecule like LS, pH plays an important role in its separation as the molar mass distribution (MMD) of LS is greatly dependent on the pH value of the solution [6-8]. In order to study the above effect, the two phase equilibrium experiments were repeated with various pH values within the range of 1.5 to 9.0, with and without the presence of carrier. The experimental conditions (other than pH) are same as that given in Table 3.1. The results reveal that the distribution of LS is influenced by pH of feed phase as demonstrated in Fig. 3.3. It is quite clear from the figure that the maximum transport of LS occurs at pH 2. The above fact is justifiable since the reaction mechanism discussed in section 3.1.1 demonstrates that an acidic condition is necessary for the protonation of TOA which eventually enhances the transport of LS into the membrane phase. At higher pH value, the distribution of LS decreases due to incomplete protonation of TOA at the feed/membrane

interface [9]. On the other hand at much lower pH, the distribution coefficient is observed to be having a decreasing trend. The above fact could be attributed to the following two reasons:

- In highly acidic condition, LS molecules with higher molar mass on average, is not ionized [8] and therefore, reaction (3.2) is not favored.
- Increase in chloride ion at lower pH inhibits the formation of amine complex, as reaction (3.1) is at equilibrium.

Hence, a pH equal to 2 has been selected for the subsequent experiments

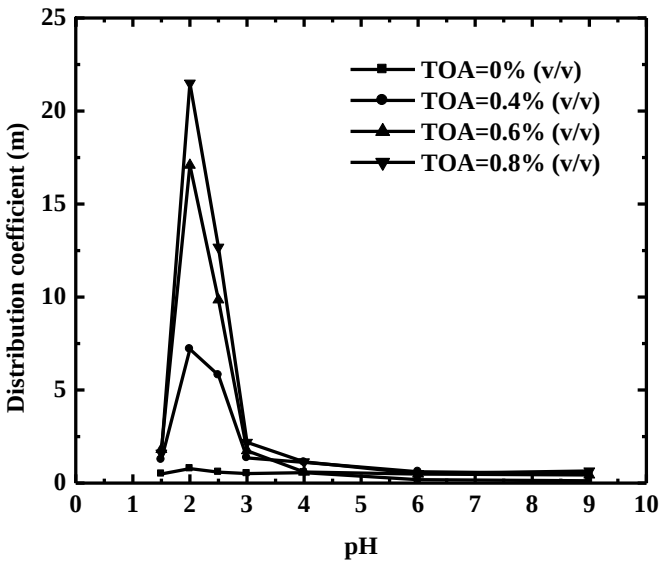


Figure 3.3 Effect of pH on the equilibrium distribution of LS

3.1.2.3 Effect of Temperature

The effect of temperature, on the equilibrium distribution coefficient of LS in the LM, was examined at 298, 303, 308, 313, 318 and 323 K. The experimental conditions (other than temperature) are same as that given in Table 3.1. The experimental results are shown in Fig. 3.4. It is observed that an increase in temperature enhances the distribution coefficient of LS initially till it reaches an optimum at 313 K. However, the distribution coefficient drops

sharply above 313 K. The initial increase in the distribution coefficient is possibly due to the fact that increase in temperature favours feed/membrane interface reaction. Nevertheless, effective charge of LS drops to zero above 313 K [10, 11]. Hence the transport of LS due to carrier (reaction 3.2) drops sharply above 313 K as it loses its charge and is found to be almost zero at relatively higher temperature (323 K).

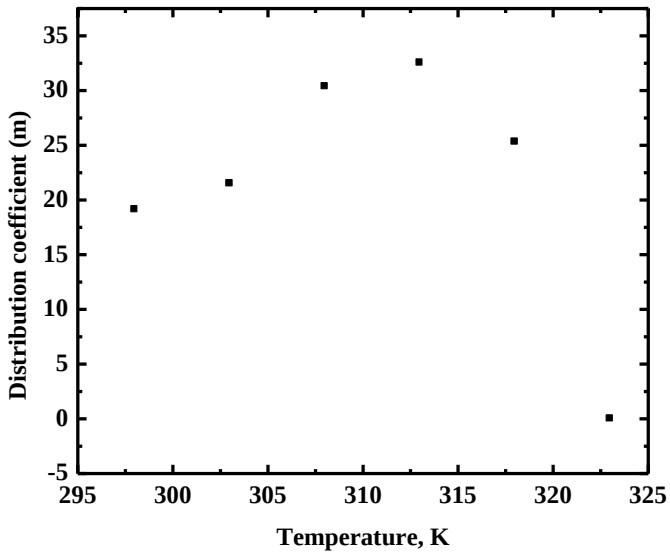


Figure 3.4 Effect of temperature on the equilibrium distribution of LS

3.1.2.4 Effect of carrier concentration

The effect of carrier concentration on the equilibrium distribution of LS was studied in the range of 0 to 6 % (v/v) TOA. The experimental conditions (other than carrier concentration) are same as that given in Table 3.1. The results are reported in Fig. 3.5. It is observed that the distribution coefficient is very low (<1) in absence of any carrier in the membrane phase. The equilibrium distribution coefficient increases with increase in carrier concentration and attains a maximum at 2 % (v/v) TOA. This is indicative of poor solubility of the LS in the membrane phase. Once the carrier is added to the membrane phase, LS reacts with the carrier and results in formation of a LS-amine complex (reaction 3.2) in the membrane phase. Thus,

the mass transfer through the feed/membrane interface is enhanced as well as controlled by the chemical reaction at the interface that yields high distribution coefficient. The maximum distribution coefficient at 2 % (v/v) TOA indicates that saturation capacity of the membrane phase for the complex is reached (Figs. 3.5(a) and 3.5(b)). Therefore, with further increase in the carrier concentration, the saturation capacity of the membrane phase for the complex is marginally reduced due to presence of more amount of carrier. This in effect reduces the transport of LS in the membrane phase (Fig. 3.5(b)). The above fact is also manifested through the lower distribution coefficient at higher concentration of the carrier. However, it is worth mentioning here that this optimum carrier concentration would vary depending on the initial feed phase concentration of LS, the ratio of volumes of feed phase to membrane phase, and other physicochemical properties such as temperature, pH *etc*.

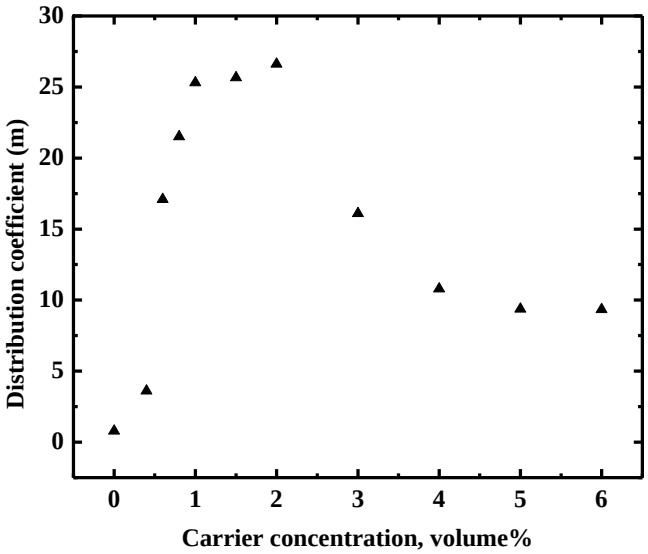


Figure 3.5(a) Effect of carrier concentration on the equilibrium distribution of LS

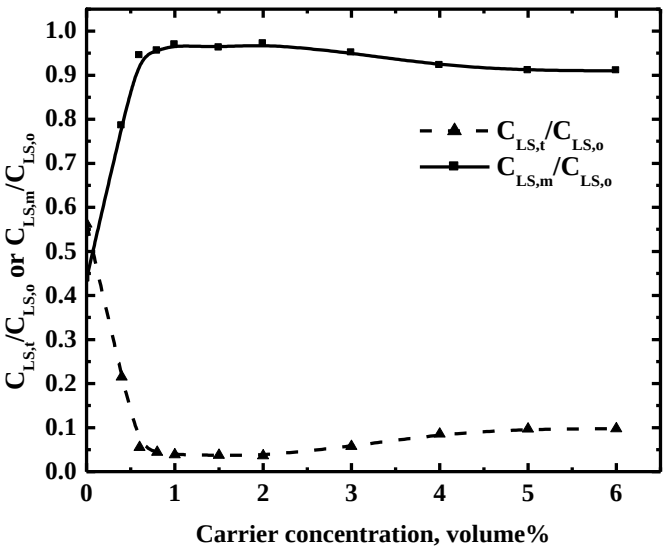


Figure 3.5(b) Effect of carrier concentration on the concentration of LS in feed and membrane phases

3.1.3 Three phase studies

The effects of various process variables, such as stirring speed, temperature and concentrations of carrier, feed and strip phases, on the transport of LS were studied in the BLM set-up as discussed in Section 2.4 of Chapter-II. Co-transport mode of mass transfer is observed when NaOH or Na_2CO_3 are used as a stripping agent, while counter-transport is observed if NaCl is used for stripping. In this work, counter transport mode was studied first and then the stripping performance was compared with co-transport mode. NaCl solution of required concentration in acidic condition (pH=2.2) was used as receiving phase. The effects of process variables on the transport of LS were evaluated by measuring the concentration profile of LS with time and also by change in the fluxes J_F (flux of feed phase) or J_S (flux of strip phase), calculated as follows:

$$J_F = \frac{V_F\left[C_{LS\ F,t_2} - C_{LS\ F,t_1} \right]}{A\ t_2 - t_1} \tag{3.5}$$

$$J_s = \frac{V_S\left[C_{LS\ S,t_2} - C_{LS\ S,t_1} \right]}{A\ t_2 - t_1} \tag{3.6}$$

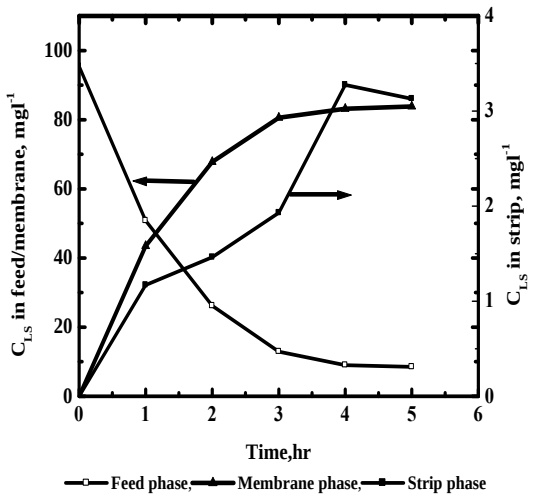
Where, V_F = volume of feed phase, V_S= volume of strip phase, $(C_{LS})_F$ = concentration of LS in feed phase, $(C_{LS})_S$= concentration of LS in strip phase, A= surface area of the membrane phase, and t_1, t_2, are the time of measurements.

J_F and J_S are calculated at one hour interval.

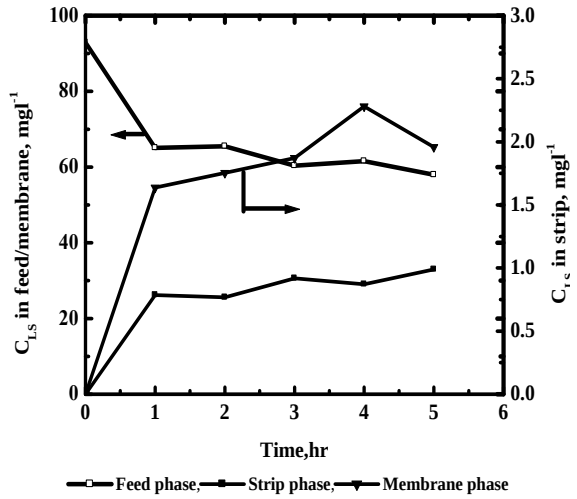
3.1.3.1 Effect of stirring

Effects of hydrodynamic conditions on the LS transport have been studied at various stirring conditions of the phases involved. To identify the control regime in extraction and stripping, experiments were carried out by stirring either of the phases or both the phases as and when

required. Stirring speed was maintained at 500 rpm. The results are shown in the Fig. 3.6 (a, b, c, d, and e) and Table 3.2. Time profiles of concentration of LS in all the three phases are recorded in these figures for various stirring conditions. It is observed that, after an experimental run of 5 hours duration, the separation achieved is 91% when only feed phase was in stirred condition (Fig. 3.6a). However, the separation was only 22% when only strip phase was in stirred condition (Fig. 3.6b). The extent of separation increased to 95% when both the aqueous phases were stirred (Fig. 3.6c) and the same drops down to 23% in completely unstirred condition (Fig. 3.6d). Above study indicates that the stirring of the feed phase significantly increases the transport of LS; however stirring of the strip phase has little effect on the extraction process. The recovery of LS at the receiving phase increases from 1.1% in unstirred condition to 2.5% when strip phase is stirred. This fact reveals that stripping process is not controlled by the hydrodynamic conditions. It is also evident that stirring of organic phase has little effect on the extraction and recovery of LS (Fig. 3.6e). In Fig. 3.7, the rate of extraction (J_F) and the rate of stripping (J_S) of LS are plotted at various stirring speeds (0, 500 and 700 rpm) of the aqueous phases. The results reveal that the flux J_F increases considerably with the increase in stirring speed within the range studied; while the flux J_S is not affected much. This indicates that the rate of extraction is controlled by the diffusion of LS across the feed/membrane interface [12, 13]. Although extraction increases with increasing speed, emulsions are formed at the interface when stirring was increased to 700 rpm. Hence a stirring speed of 500 rpm was maintained, as it gives good separation without forming noticeable emulsion.



(a)



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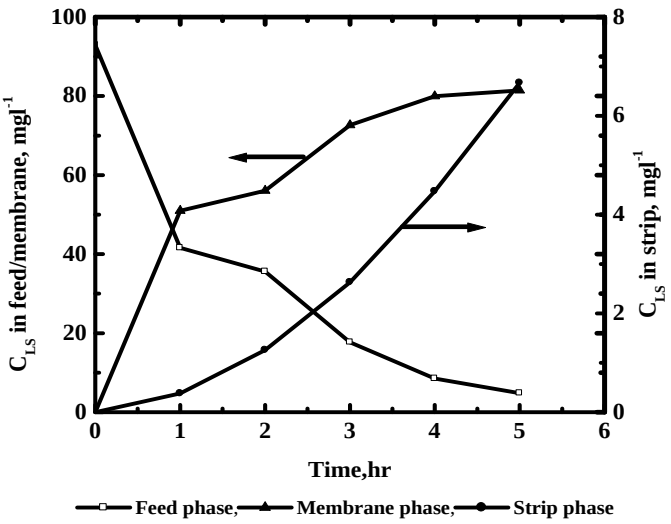
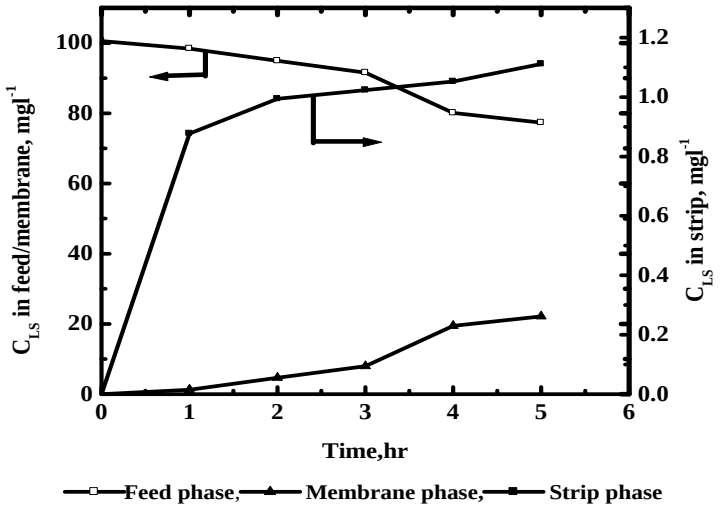
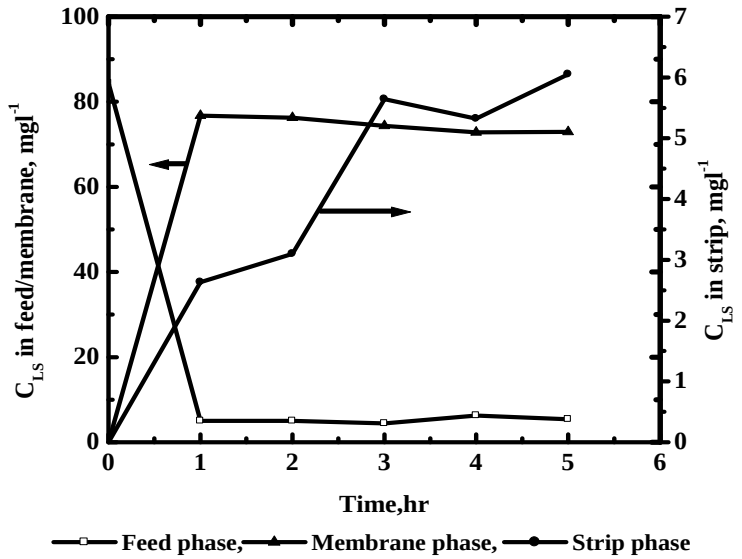


(c)

Figure 3.6 Effect of stirring (a) feed phase stirred (b) strip phase stirred (*c)* aqueous phases stirred *(carrier concentration=1vol. %, temperature=298 K, pH=2, stirring speed =500 rpm, V_F= V_S= 60 ml, V_O=50 ml)*



(d)



(e)

Figure 3.6 Effect of stirring (d) without stirring (e) all phases stirred *(carrier Concentration=1vol. %, temperature=298 K, pH =2.0, stirring speed=500 rpm, V_F =V_S= 60 ml, V_O = 50 ml).*

Table 3.2 Effect of stirring of various phases, stirring speed= 500 rpm

Stirring condition	$C_{LS,o}$ (mgl^{-1})	Time (hr)	$(C_{LS})_F$ (mgl^{-1})	$(C_{LS})_S$ (mgl^{-1})	Percentage extraction (wt %)	Percentage recovery (wt %)
Feed phase stirred	95.4	5	8.5	3.13	91	3.4
Strip phase stirred	92.9	5	72.1	1.96	22	2.5
Aqueous phases stirred	92.9	5	4.79	6.67	94.8	7.2
All phases stirred	84.4	5	5.4	6.05	93.7	7.1
Without stirring	100.5	5	77.34	1.11	23	1.1

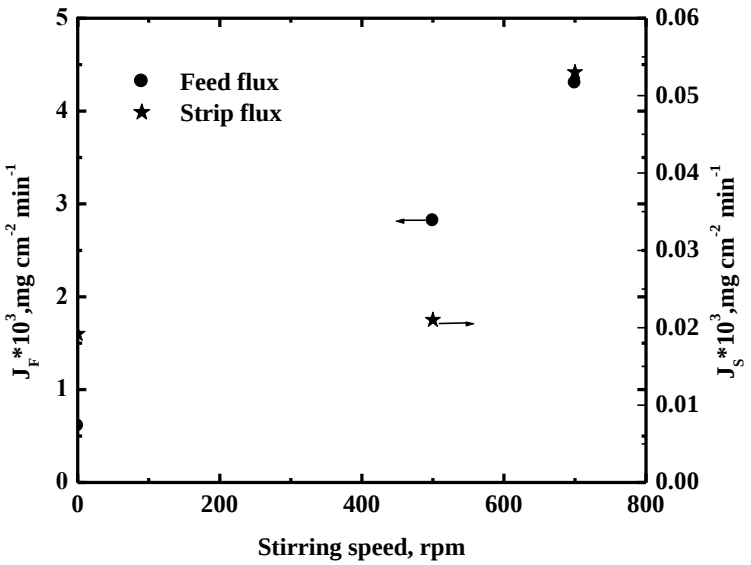


Figure 3.7 Effect of stirring speed on the mass flux of LS (*$C_{LS,o}$=84 mgl^{-1}, carrier concentration=1% (v/v), temperature=298 K, pH=2, V_F=V_S=60 ml, V_O=50 ml, stirring speed= 0-700 rpm, aqueous phases stirred).*

3.1.3.2 Effect of carrier concentration

It is a well known fact that in carrier mediated transport, carrier is used to enhance the trans-membrane transport of the solute. According to the available literatures [13, 14], the optimum carrier concentrations for their respective applications had been in the range of 0-10%. In the present case, the influence of carrier concentration in the organic phase has been studied at concentrations ranging from 1 to 10 % (v/v) TOA. It has been observed from the equilibrium study (Fig. 3.5) that the equilibrium distribution of LS remains quite low without the presence of any carrier. Fig. 3.8 shows that an increase in carrier concentration enhances the effectiveness of the LM in terms of increased rate of transport of LS. However, the rate of increase gradually slows down when the carrier concentration is 4% (v/v) or more. Again, with increase in carrier concentration, the rate of stripping of LS is also increased and attains a maximum value at 4% (v/v). Contrary to the two phase studies (Section 3.1.2.4), requirement of the carrier is more (4 % (v/v) in place of 2 % (v/v)) for the three phase studies to attain maxima. This is because three phase studies are operated within much shorter time compared to the time required for reaching the equilibrium (two phase study). As discussed in Section 3.1.2.4, when the concentration of carrier is increased from 1 to 4 % (v/v) the flux J_F is controlled by the chemical reaction at the feed/membrane interface and hence it increases. However, decrease in the effect of the carrier at its concentration beyond 4 % (v/v) further justifies that the feed phase mass transfer is controlled by the rate of reaction [12]. The flux J_S is limited by the stripping reaction at the membrane/strip interface [12]. The decrease of flux J_S, above 4 % (v/v) carrier concentration is due to increase of viscosity (Table 3.3) of the membrane phase [5, 12]

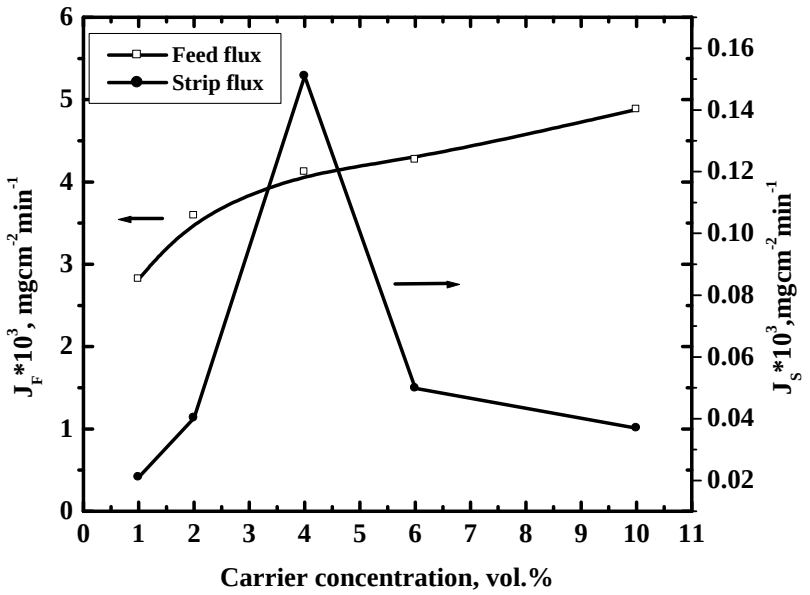


Figure 3.8 Effect of carrier concentration on the mass flux of LS *($C_{LS,o}$=84 mgl^{-1}, temperature=298 K, pH =2, V_F=V_S=60 ml, V_O=50 ml, aqueous phases stirred, stirring speed = 500 rpm).*

Table 3.3 Viscosity of membrane phase (dichloroethane and TOA) for various carrier (TOA) concentration at 25^{o}C [1]

Carrier (TOA) concentration, vol.%	Viscosity, cp
0	0.8717
1	0.8767
2	0.8781
3	0.885
4	0.8899
6	0.9068
8	0.9211

3.1.3.3 Effect of initial feed concentration

The influence of initial feed concentration on the transport of LS was studied in the concentration range of 93 to1486 mgl^{-1}. Figures 3.9(a) and 3.9(b) show the effect of initial feed concentration on extraction and recovery of LS respectively. It is observed from Fig. 3.9(a) that with increase in initial feed concentration the initial rate of the transport of LS is higher but the transport continues for a longer time. At the same time, with increase in initial feed concentration recovery of LS also increases (Fig. 3.9(b)). Figure 3.9(a) clearly shows that after 3 hours of experiments the separation achieved in case of initial feed concentrations 93, 422 and 847 mgl^{-1} is about 90-98% on weight basis. Similar separation for initial feed concentrations above 1000 mgl^{-1} is achieved after 4 hours of experiment. In fact, in counter transport mode of transfer of LS using NaCl as stripping agent we have observed that though the extraction of LS is 98%, its recovery is only 5-10%. This might be due to the ineffectiveness of the stripping agent (NaCl) to decomplex the LS-amine complex. As the rate of stripping is slow compared to the rate of extraction, a level of saturation is attained in the membrane phase at high initial feed concentration and hence more time is needed for achieving high percentage of extraction (>90 wt%). Almost overlapping concentration profiles after one hour of experiment (Fig. 3.9(a)) at higher concentrations (1042 and 1486 mgl^{-1}) is an indication of saturation of the carrier by feed LS and transport rate is limited by carrier concentration. Exactly similar behavior is not observed in the stripping phase concentration (Fig. 3.9(b)) due to low rate of stripping as mentioned earlier.

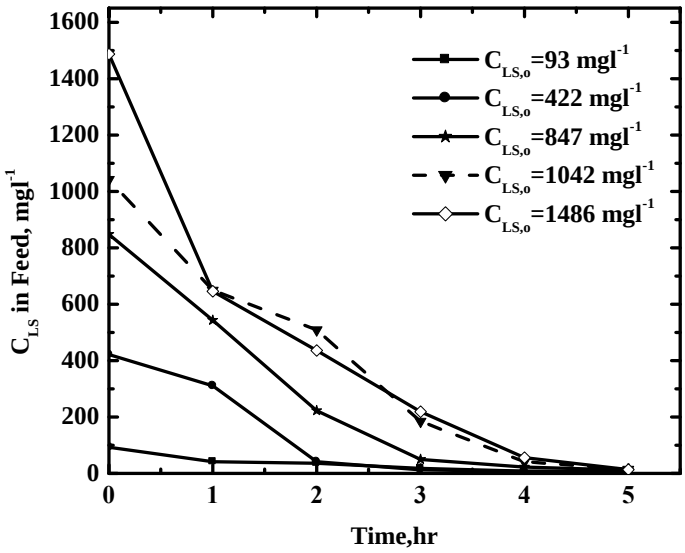


Figure 3.9(a) Effect of initial feed concentration on extraction of LS (*temperature=298 K, pH =2, V_F=V_S =60 ml, V_O=50 ml, stirring speed=500 rpm, carrier (TOA) concentration=4% (v/v)).*

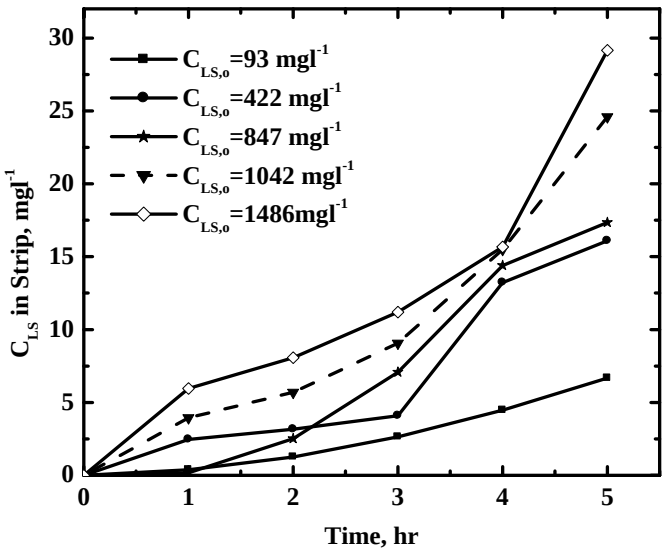


Figure 3.9(b) Effect of initial feed concentration on recovery of LS (*temperature =298K, pH=2, V_F = V_S =60 ml, V_O=50 ml, stirring speed=500 rpm, carrier (TOA) concentration=4% (v/v)).*

3.1.3.4 Effect of temperature

The effect of temperature on the transport of LS was tested at 298 K, 303 K, 308 K and 318 K. The results are shown in Fig. 3.10. It is clear from the figure that with increase in temperature the rate of both extraction and stripping of LS increases. This is due to the fact that an increase in temperature enhances diffusion of LS and TOA complex as well as the feed/membrane and membrane/strip interface reactions. However, reverse trend is observed at relatively higher temperature. It may be observed that at temperature 318 K, the strip phase flux continues to increase, whereas the feed phase flux reduces. Both the phenomena further justifies that feed phase and strip phase fluxes are controlled by the feed/membrane and membrane/strip phase reactions respectively. As discussed in Section 3.1.2.3, feed/membrane interface reaction (reaction 3.2) is not favorable at temperature above 313 K as the effective charge of LS drops to zero at that temperature [10, 11]. Therefore, the feed phase flux started decreasing at higher temperature though the strip phase flux is increased.

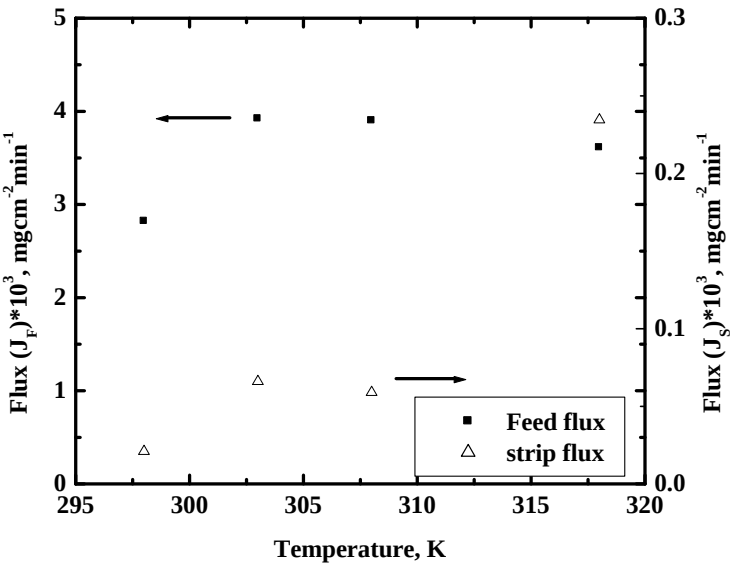


Figure 3.10 Effect of temperature on the mass flux of LS *($C_{LS,o}$=88 mgl^{-1},carrier (TOA)concentration=1vol. %, pH=2, V_F=V_S =60 ml, V_O=50 ml, aqueous phases stirred, stirring speed=500 rpm).*

3.1.3.5 Effect of strip phase concentration

The effect of strip phase (NaCl) concentration on the recovery of LS was studied in the range of 0.1M-0.8M. The results are reported in Fig. 3.11. It is observed that with increase in NaCl concentration in the strip phase the flux J_S increases too, and hence the recovery of LS increases and attains optimum at 0.3M. The decrease of recovery at higher salt concentration is due to salting out effect, which is defined as the decrease of aqueous solubility of various compounds in presence of inorganic salts [14, 15].

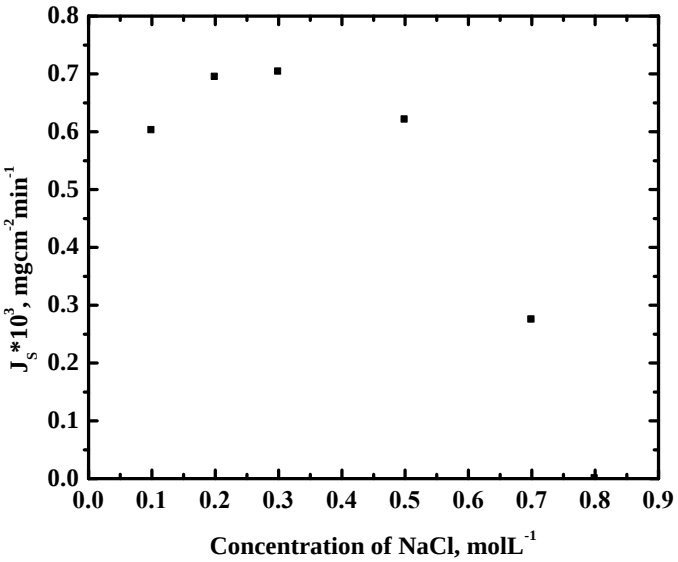


Figure 3.11 Effect of sodium chloride concentration on the mass flux of LS after 3 hours of experiment. (*$C_{LS,o}$= 100 mgl^{-1}, carrier (TOA) concentration=1% (v/v), V_F = V_S = 60 ml, V_O=50 ml, aqueous phases stirred, stirring speed =500 rpm).*

3.1.3.6 Co-transport mode of LS transport

Understanding the limitation of NaCl as stripping agent, two more stripping agents namely, aqueous sodium carbonate (Na_2CO_3) and aqueous sodium hydroxide (NaOH) were used to study the recovery of LS and strip flux. In this co-transport mode of LS transport aqueous NaOH and aqueous Na_2CO_3 were used as a strip phase separately. The effect of NaOH concentration on the recovery of LS is studied at optimum carrier (TOA) concentration.

Further, a comparative assessment is made between the performance of co-and counter transport modes of LS transfer, while aqueous NaOH and aqueous Na_2CO_3 solution were used as strip phases for co-transport and aqueous NaCl solution was used as strip phase for the counter-transport. The influence of NaOH concentration on the recovery of LS was studied in the range of 0.1M-1.25M. The results are reported in Figs. 3.12(a) and 3.12 (b). It is observed that with increase in NaOH concentration the recovery of LS increases. It is also noted that recovery of LS increases with time and it reached about 70% when NaOH concentration is 1.25M. The reaction (3.3) discussed in Section 3.1.1 also indicates that with increasing NaOH concentration recovery of LS should increase. Strip flux is also found to be quite high (about 70% of feed flux) for 1.25M solution of NaOH (Fig. 3.12b) *i.e.* when the feed flux is 16.98×10^{-3}mg cm^{-2} min^{-1} the strip flux is 11.95×10^{-3}mg cm^{-2} min^{-1}. A comparison of the two transport modes at the same operating condition is also reported in Fig. 3.13. It is clear from the figure that recovery of LS is higher in co-transport mode. The performance of NaOH and Na_2CO_3 as stripping agents in co-transport mode is almost same till about two hours of operation. However, at later stages Na_2CO_3 showed relatively better performance. This is due to differences in the reactions at the membrane/strip interface.

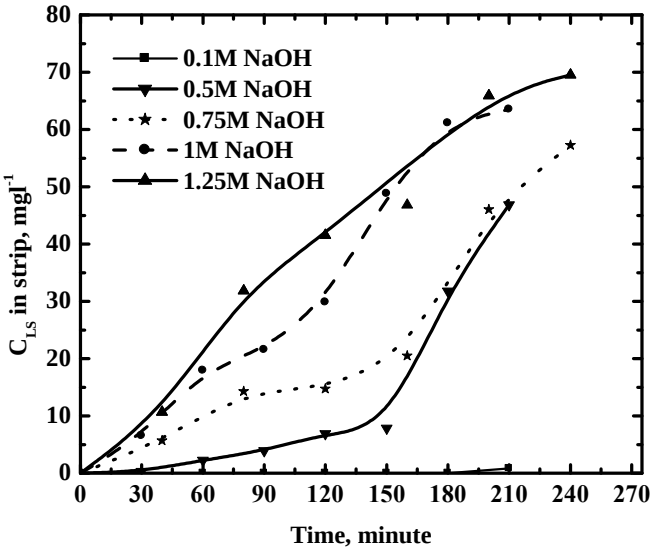


Figure 3.12(a) Effect of NaOH concentration on the recovery of LS *($C_{LS,o}$=108 mgl^{-1}, carrier (TOA) concentration=4 % (v/v), pH =2, V_F=V_S =60 ml, V_O=50 ml, stirring speed=500 rpm).*

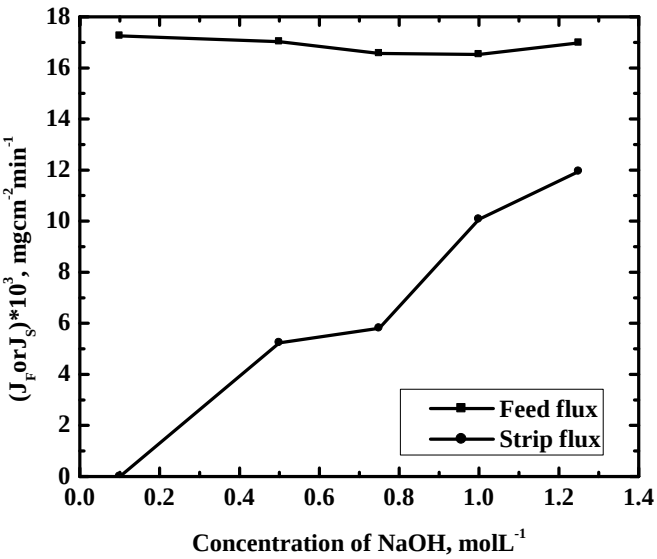


Figure 3.12(b) Effect of NaOH concentration on the mass flux of LS *($C_{LS,o}$=108 mgl^{-1}, carrier (TOA) concentration = 4 % (v/v), pH =2, V_F =V_S =60 ml, V_O=50 ml, stirring speed =500 rpm).*

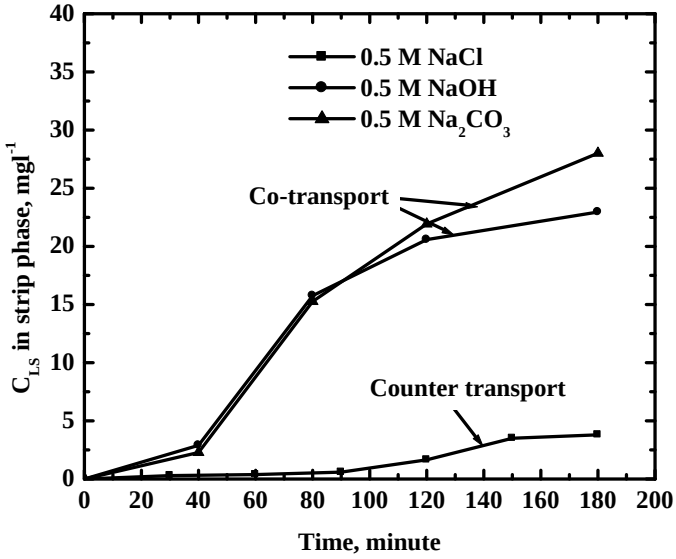


Figure 3.13 Comparison of co- and counter transport mode of LS transfer, *($C_{LS,o}$ =108 mgl^{-1}, carrier (TOA) concentration = 1% (v/v), strip concentration = 0.5M, feed pH = 2.0, V_F = V_S = 60 ml, V_O = 50 ml, aqueous phases stirred, stirring speed = 500 rpm).*

3.1.4 Summary of the separation of LS using BLM

- The solvent-carrier combination dichloroethane-TOA has the highest distribution coefficient for the separation of LS.
- Transport of LS can be enhanced by increasing the carrier concentration, temperature and stirring speed of feed phase.
- The LS extraction process is controlled by the diffusion of LS across the feed/membrane interface.
- The co-transport mode of LS transfer is better than the counter transport mode so far as recovery is concerned.

- The separation achieved under the experimental conditions studied is around 90-98%, however, recovery is only 5-10% in counter transport.

- The recovery is about 70% in co-transport mode using 1.25 M NaOH as stripping agent.

- Recommended proposition and conditions for BLM separation of LS are: solvent= dichloroethane, carrier=TOA, feed phase pH=2, carrier concentration=4% (v/v), stirring speed=500 rpm (aqueous phase stirred), stripping agent=NaOH, strip phase concentration=1.25M.

3.2 Separation of mercury (II)

A similar approach as in Section 3.1 was undertaken to examine the efficiency of a low viscous LM for the extraction and recovery of mercury from its aqueous solution through BLM. The results of the BLM study are discussed in the following sections. The relevant work has been already published in Industrial Engineering and Chemistry Research [16]

3.2.1 Theoretical background

In Section 3.1, co-transport mode showed better performance than counter transport mode. Hence, co-transport mode is studied in case of separation of mercury. In this mechanism, the transport of mercury and the H^+ ions occur in the same direction by virtue of the concentration gradient of the ions across the aqueous-organic-aqueous phases. The coupled transport scheme for mercury is presented in Fig. 3.14 [17]. TOA has been found to be the most promising carrier agent in the separation of mercury (will be discussed later in Section 3.2.2.1). Therefore, the reaction mechanism is described considering TOA as the carrier. The reaction mechanism for the separation of mercury is as follows.

Complexation of Hg (II) by chloride ions in the feed solution

$$Hg^{+2} + 4Cl^{-} \leftrightarrow HgCl_4^{-2} \quad (3.7)$$

Reaction of TOA (denoted as R_3N) at the feed /membrane interface with HCl in the feed solution:

$$R_3N_{org} + H^+Cl^-_{aq} \Leftrightarrow R_3NH^+Cl^-_{org} \quad (3.8)$$

In the feed, $HgCl_4^{2-}$ is exchanged with Cl^- of $R_3NH^+Cl^-$ in the membrane phase:

$$2R_3NH^+Cl^-_{(org)} + HgCl_4^{2-} \Leftrightarrow (R_3NH)_2HgCl_{4(org)} + 2Cl^-_{(aq)} \quad (3.9)$$

The stripping reaction:

$$(R_3NH)_2HgCl_{4(org)} + OH^- \Leftrightarrow R_3N_{(org)} + HgCl_4^{2-}{}_{(aq)} + 2H_2O \quad (3.10)$$

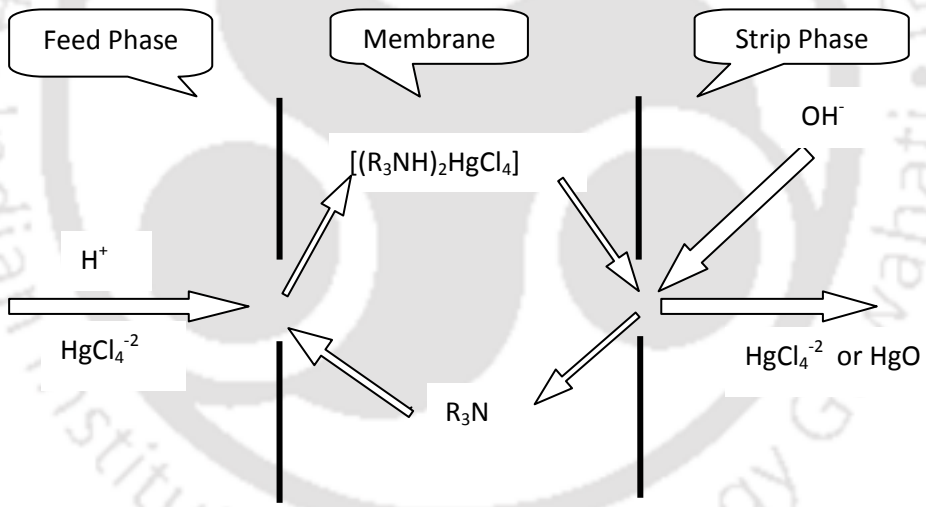


Figure 3.14 Schematic of co-transport mode of extraction of mercury

3.2.2 Two phase equilibrium study

A suitable LM of high separation factor was identified by performing the experiments as per procedures reported in the Section 2.3.2 of Chapter-II, through two phase equilibrium studies.

With the selected solvent, effects of various process parameters such as carrier concentration and pH on the equilibrium distribution of mercury have also been examined.

3.2.2.1 Choice of solvent-carrier combination

Various solvents *viz. n*-heptane, hexane, toluene, cyclohexane and dichloroethane, were first employed and tested for the extraction of mercury. Various carriers *viz.* TOA, tri-octylphosphine oxide (TOPO) and 2-Ethylhexanol were then employed to study the equilibrium distribution of mercury ions in the aqueous and membrane phases. The values of distribution coefficients are reported in Table 3.4. The distribution coefficients (*m*) of mercury in these solvents in absence of any carrier are also reported in table in order to compare the effects of various carrier agents. It is observed that transport of mercury is not significant when *n*-heptane and toluene were used as membrane. Significant separation is observed with hexane, followed by dichloroethane and cyclohexane. Since vapor pressures of hexane and cyclohexane at 25 $^{\circ}$C are 201 and 130 mbar respectively, they prove to be more volatile than the dichloroethane having vapor pressure 105 mbar at 25 $^{\circ}$C. Therefore hexane and cyclohexane have not been considered and dichloroethane has been selected as the suitable solvent for the subsequent studies. It is observed that TOA as carrier is the most promising one as it gives the highest distribution of mercury in the LM when compared to other carriers. Hence, 1,2-dichloroethane-TOA combination has been selected as the solvent-carrier combination in the BLM for further experiments.

Table 3.4. Effects of various solvents and carriers on the equilibrium distribution coefficient (*m*) of mercury.

Experimental condition	Solvents	Distribution coefficient (*m*)			
		No carrier	TOA	TOPO	2-Ethylhexanol
Feed: 500 ppb Hg solution Carrier concentration: 1% (v/v) Stirring speed:100 rpm Temperature: 303 K Time: 6 hours	Hexane	5.6	119.6	29.1	0.87
	Dichloroethane	2.9	26.97	0.96	9.05
	Cyclohexane	1.04	6.01	5.2	2.6
	Toulene	0.47	4.62	0.62	1.2
	n-Heptane	0.87	2.10	1.3	3.06

3.2.2.2 Effect of carrier

The effect of concentration of carrier **(**TOA) in the organic phase on the equilibrium distribution of mercury was studied in the range of 0 to 5 % (v/v). The results are reported in Fig. 3.15. It is observed that the optimum carrier concentration attains at 1.5 % (v/v) TOA. It is also observed that when the carrier is imparted to the membrane phase, the formation of mercury-amine complex (reaction 3.9) in the membrane phase takes place which thereby increases the mass transfer through the feed/membrane interface and eventually yields higher distribution coefficient. The optimality in the distribution coefficient at 1.5 % (v/v) TOA indicates the saturation capacity of the membrane phase for the complex. It is also observed that the saturation capacity of the complex in the membrane phase reduces due to the presence of excess amount of carrier. This downfall of membrane phase capacity for the complex is reflected from the lower distribution coefficient obtained at higher carrier concentration. However, the optimum carrier concentration should also depend upon the ratio of membrane phase volume to feed phase volume and the initial feed phase concentration [1].

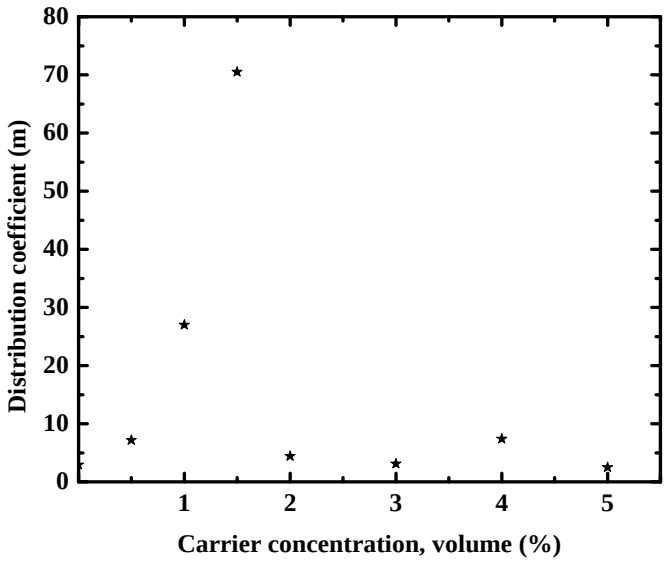


Figure 3.15 Effect of carrier concentration on the equilibrium distribution of mercury (*V_F=V_O=10 ml, time=6 h, stirring speed=100 rpm, temperature=303 K*).

3.2.2.3 Effect of pH

In order to understand the effect of pH of the feed phase on separation, two phase equilibrium experiments were performed with pH variation in the range of 1 to 6 in the presence of carrier, TOA. The experimental results are reported in Fig. 3.16. It is observed that at pH 2.5, the distribution coefficient of mercury is maximum. The reaction mechanism (Section 3.2.1) indicates that acidic condition is needed for the protonation of TOA as it binds with mercury in anionic form only, which in turn justifies the maximum transport of mercury. At much lower pH, increase in proton concentration in the feed solution forms H_2HgCl_4 which doesn't dissociate enough to form adequate $HgCl_4^{-2}$ that forms the complex with the cation R_3NH^+ [18]. Hence, extraction is not effective at very low pH. Again, at much higher pH protonation of TOA to form R_3NH^+, that makes the complex with $HgCl_4^{-2}$, becomes inadequate. Therefore, pH=2.5 is selected for the subsequent studies.

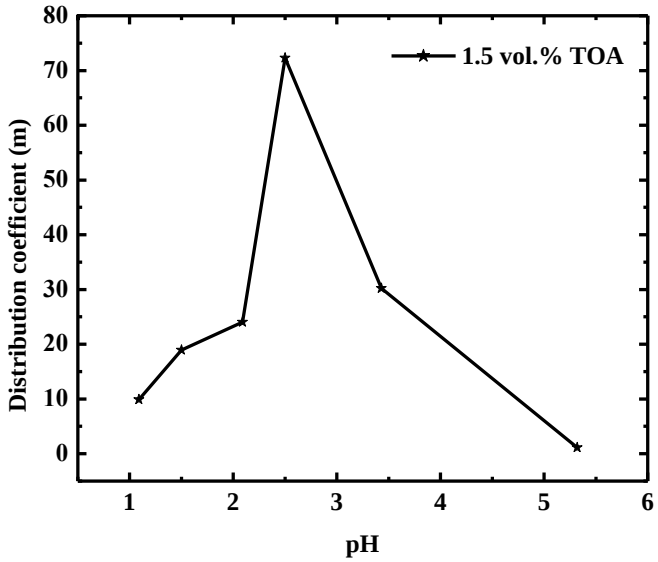


Figure 3.16 Effect of pH on the equilibirum distribution of mercury (*V_F=V_O=10 ml, carrier (TOA) concentration = 1.5 % (v/v), time=6 h, speed= 100 rpm, temperature= 303 K***).**

3.2.3 Three phase study

The BLM set-up discussed in Section 2.4 of Chapter-II was used to study the influence of various process variables, such as feed and strip phase concentrations and carrier concentration on the transport of mercury. The effects of process variables on the transport of mercury were estimated in terms of % extraction and % recovery.

3.2.3.1 Effect of strip phase concentration

The effect of NaOH concentration on the transport of mercury was studied in the range of 0.1M – 1M. The results of both extraction and recovery are shown in Figs. 3.17 (a) and (b). The NaOH behaves as a strip-extractant in the stripping phase. From Fig. 3.17 (a), it is observed that the percentage extraction after 80 minutes lies between 78% to 94% for variation of NaOH concentration between 0.1 M to 1 M. Percentage extraction after 80 minutes for 0.5M-1M NaOH are almost same, which is around 90%. According to Le

Chatelier principle, an increase in hydroxyl ions results in faster decomposition of mercury complex and removal of protons from amine molecule. That results in higher recovery. The percentage recovery is found to increase for some time and then starts decreasing. The apparent downfall of recovery at higher concentration (Fig. 3.17 (b)) is due to precipitation of mercury as HgO in the strip phase [17]. However, both percentage extraction and recovery were found to be more for 0.5M NaOH strip solution.

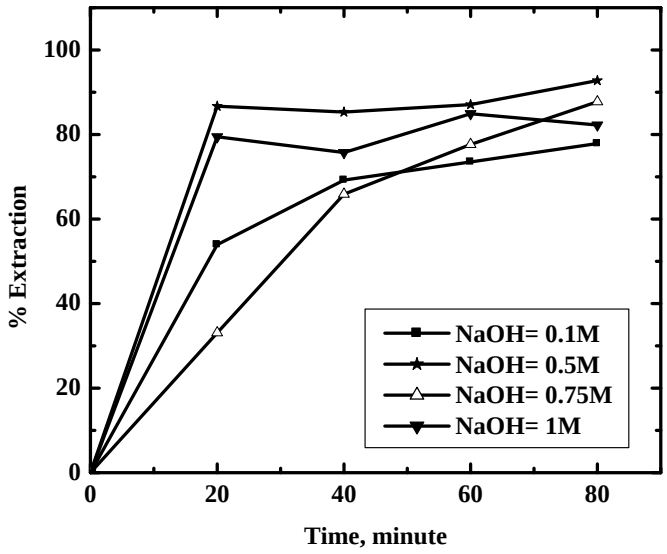


Figure 3.17(a) Effect of strip phase concentration on extraction of mercury (C_{Hg} *=500 µgl*$^{-1}$*,*V_F*=*V_O*=*V_S*=50 ml, carrier (TOA) concentration=1.5% (v/v), pH=2.5, time =80 min, speed=400 rpm, temperature=303 K).*

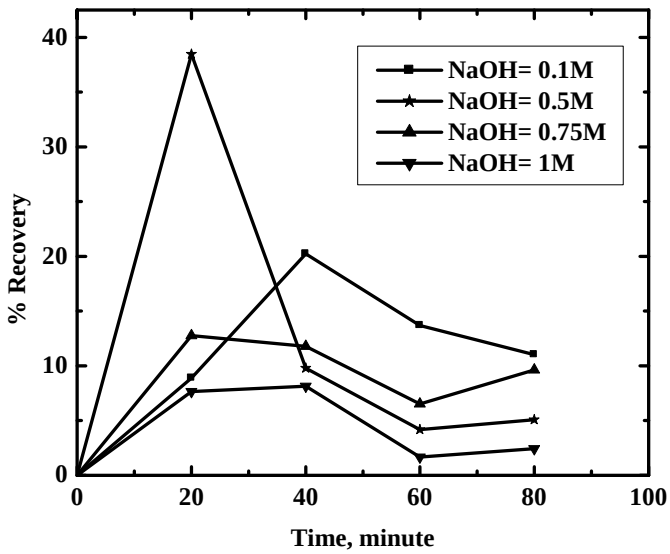


Figure 3.17(b) Effect of strip phase concentration on recovery of mercury (C_{Hg} *=500 µgl*$^{-1}$*,*V_F*=*V_O*=*V_S*=50 ml, carrier (TOA) concentration=1.5% (v/v), pH=2.5, time =80 min, speed=400 rpm, temperature=303 K).*

3.2.3.2 Effect of carrier concentration

The actual transport phenomena in BLMs are quite complex and are strongly influenced by the both carrier concentration and physiochemical properties of carrier in the membrane phase. The percentage extraction of mercury ions increased with increase in TOA concentration from 1 to 1.5 % (v/v), as shown in Figs. 3.18 (a) and (b). However, when the TOA concentration exceeded 1.5% (v/v), both % extraction and % recovery decreased (Fig. 3.18). This phenomenon occurred due to the enhanced viscosity of membrane phase with increase in TOA concentration. Higher viscosity retards the diffusion speed of the complex and affects the mass transfer process through the membrane phase [1, 12]. Hence, similar to the two phase study, 1.5 % (v/v) TOA has been found to be optimum carrier concentration for the three phase study too.

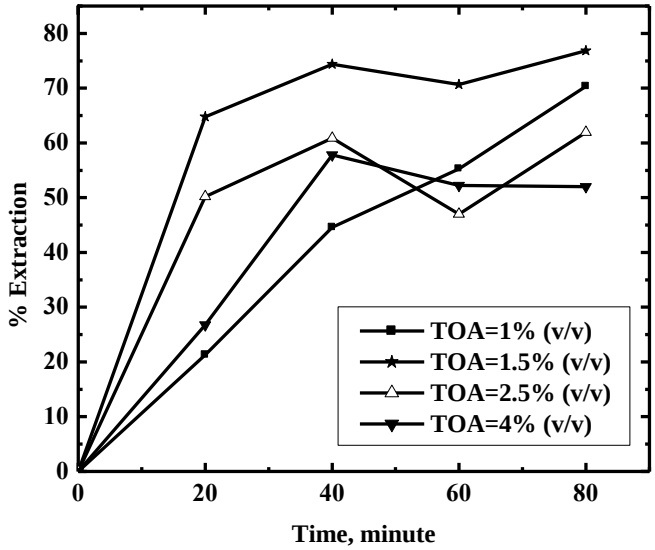


Figure 3.18(a) Effect of carrier concentration on extraction of mercury (*C_{Hg} = 500 µgl^{-1}, V_F=V_O=V_S=50 ml, carrier (TOA) concentration=1.5% (v/v), pH=2.5, time = 80 min, speed =400 rpm, strip concentration=0.5 M).*

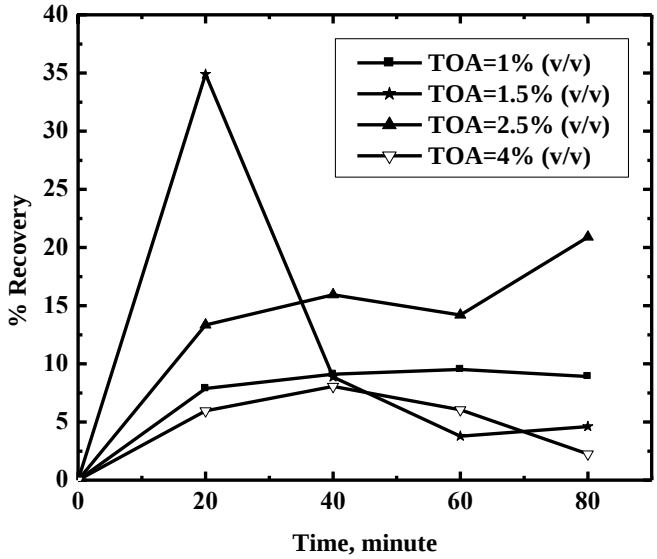


Figure 3.18(b) Effect of carrier concentration on recovery of mercury (*C_{Hg} = 500 µgl^{-1}, V_F=V_O=V_S=50 ml, pH=2.5, strip concentration=0.5 M, time=80 min, speed =400 rpm, temperature=303 K).*

3.2.3.3 Effect of initial feed concentration

The relation between the feed phase concentration and the percentage of extraction and recovery of mercury is shown in Figs. 3.19 (a) and (b). The effect of initial feed concentration was examined over concentration range of 200 μgl^{-1} to 4 mgl^{-1}. From the figure it is seen that with increase in feed concentration, the initial rate of transport of mercury increases. But the feed concentration above 1 mgl^{-1} shows a declining trend which may be attributed to the fact that at higher concentration, complexed mercury ions get accumulated at feed/membrane interface and consequently leads to a longer diffusion path of complex and/or lowers the complexation rate. Observing the percentage of recovery behavior (Fig. 3.19 (b)), it can be concluded that lower concentration of mercury in feed leads to a higher recovery. But as the concentration of mercury in feed increases, the recovery decreases due to the slower diffusion of complex from feed to strip as the path becomes longer. However, on adequate supply of mercury at the strip side, precipitation reaction is enhanced. This can be explained by the combined effect of diffusion through the membrane phase and the precipitation of mercury to HgO at the strip side. At lower initial feed concentration the diffusion rate of the complex through the membrane is higher and at the same time it provides inadequate mercury ion to facilitate the precipitation reaction.

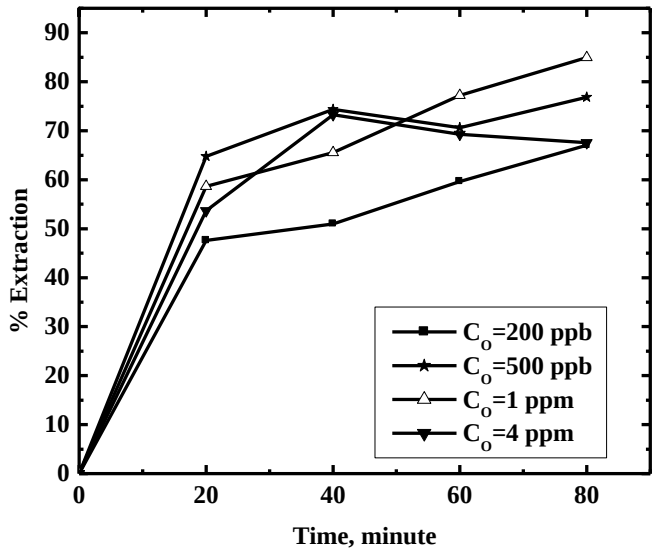


Figure 3.19(a) Effect of initial concentration on extraction of mercury (*C_{Hg} =500 µgl^{-1}, V_F =V_O =V_S=50 ml, carrier (TOA) concentration=1.5% (v/v), pH=2.5, time = 80 min, speed =400 rpm, strip concentration=0.5 M)*

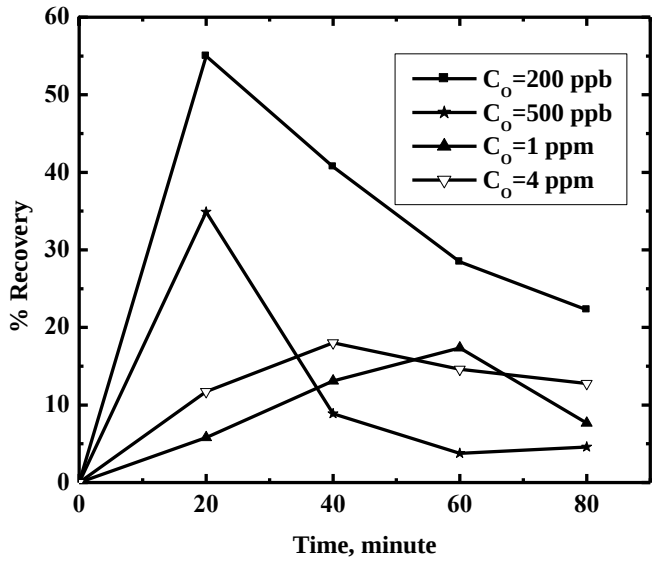


Figure 3.19(b) Effect of initial concentration on recovery of mercury (*C_{Hg} =500 µgl^{-1}, V_F=V_O=V_S=50 ml, pH=2.5, strip concentration=0.5 M, time=80 min, speed =400 rpm, temperature=303 K).*

3.2.4 Summary of the BLM separation of mercury

- TOA-dichloroethane is proved to be the best solvent-carrier combination for the separation of mercury
- Extraction of mercury is a highly pH dependent phenomenon. A pH of 2.5 is found to be optimum for the above separation.
- The same LM (TOA-dichloroethane) is found to be suitable for the separation of mercury and LS.
- Recommended proposition and conditions for BLM separation of mercury are: solvent: dicholoroethane, carrier: TOA, carrier concentration: 1.5% (v/v), stripping agent: NaOH and strip phase concentration: 0.5M.

Abbreviation

BLM bulk liquid membrane

LM liquid membrane

LS lignosulfonate

TOA trioctylamine

TOPO tri-octylphosphine oxide

Nomenclature

A membrane area, cm^2

$(C_{LS})_F$ concentration of LS in the feed, mg l^{-1}

$(C_{LS})_S$ concentration of LS in the strip, mg l^{-1}

$C_{LS,o}$ initial concentration of LS, mg l^{-1}

$C_{LS,t}$ concentration of LS in the feed phase at time t, mg l^{-1}

$C_{LS,m}$ concentration of LS in the membrane phase, mg l^{-1}

C_{Hg} initial concentration of mercury in the feed, µgl^{-1}

J_F flux of feed phase, mg cm^{-2} min^{-1}

J_S flux of strip phase, mg cm^{-2} min^{-1}

V_F volume of feed phase, ml

V_S volume of strip phase, ml

V_O volume of organic phase, ml

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CHAPTER-IV

Separation of Pollutants using Supported Liquid Membrane

This chapter presents the results and discussion on the separation of pollutants lignosulfonate (LS) and mercury (II) using supported liquid membrane (SLM). Issues regarding separation of LS and separation of mercury from their respective aqueous solutions are discussed elaborately in this chapter. Separation of mixture of LS and mercury from aqueous solution is also discussed here. Dichloroethane-TOA is used as the LM phase. This chapter also describes a theoretical model based on the experimental findings for the permeation of LS through SLM.

4.1 Separation of LS using flat sheet SLM

From the discussion of the previous chapter (Chapter-III) it is evident that LS can be extracted efficiently with BLM using dichloroethane as solvent and TOA as carrier. About 98% of LS can be extracted from feed phase to membrane phase and about 70% of the extracted LS can be recovered in the stripping phase using co-transport mode at optimum process conditions [1]. In order to convert the above LM separation module into a more application oriented form, an attempt has been made to develop an SLM for the separation of LS using dichloroethane as solvent and TOA as a carrier agent. Various polymeric supports such as polytetrafluoroethylene (PTFE) of different pore sizes, polyvinyldene floride (PVDF) and Nylon 6,6 were tested in order to select a suitable support for the SLM. The parameters such as carrier concentration, strip phase concentration, ionic strength of feed phase, *etc*. can have significant impact on the transport of LS through SLM and hence they were thoroughly

studied. An elaborate discussion on the experimental findings is presented in the subsequent sections. The experiments were carried out in the SLM set-up as described in Section 2.5.1 of Chapter-II. This part of the research work has been already published in the Journal of membrane science [1, 2].

4.1.1 Theoretical Background

The mechanism by which LS is extracted from an aqueous solution, using dichloroethane as solvent and TOA as a carrier agent can be represented by the following set of reactions:

$$xR_3N\ \ org\ \ + xHCl \Leftrightarrow xR_3NH^+Cl^- \tag{4.1}$$

$$xR_3NH^+Cl^- + LSNa_{\ n}\ \ aq\ \ \Leftrightarrow (R_3NH)_x LSNa_{\ (n-x)}\ \ org\ \ + xNaCl\ \ aq \tag{4.2}$$

where R_3N (org) is TOA in organic phase and $LSNa_n$(aq) is sodium lignosulfonate in aqueous phase. The overall reaction can be written as follows:

$$LSNa_n\ \ aq\ \ + xR_3N\ \ org\ \ + xHCl \Leftrightarrow R_3NHLSNa_{\ n-x}\ \ org\ \ + xNaCl\ \ aq \tag{4.3}$$

The equilibrium constant K_{eq} for the above reaction (Eq. 4.3) can be written as

$$K_{eq} = \frac{[R_3NHLSNa_{\ n-x}\ ][NaCl]^x}{[LSNa_n][R_3N]^x[HCl]^x} \tag{4.4}$$

Rearranging Eq. (4.4) we have,

$$[LSNa_n] = \frac{[R_3NHLSNa_{\ n-x}\ ][NaCl]^x}{K_{eq}[R_3N]^x[HCl]^x} \tag{4.5}$$

Taking logarithm at each side and rearranging Eq. (4.5) we have,

$$Log\ \ \ LSNa_n\ \ \ = Log\left\{\frac{[R_3NHLSNa_{\ n-x}\ ][NaCl]^x}{K_{eq}[HCl]^x}\right\} - xLog\ \ \ R_3N \tag{4.6}$$

At a constant pH, [HCl] remains constant. It also can be assumed that the variation in [$NaCl$] would be negligible within the concentration range of TOA studied. Therefore, [$NaCl$] can be considered as constant. Hence a plot of $Log\ [LSNa_n]$ versus $Log\ [R_3N]$ gives a straight

line with the slope of {-*x*}. The extraction equilibrium data were taken from the BLM separation of LS (Chapter-III) [1] and $Log\ [LSNa_n]$ and $Log\ [R_3N]$ have been plotted in Fig. 4.1. The value of {-*x*} is found to be {-0.866} which is nearly equal to {-1}. It indicates that one mole of LS requires one mole of TOA for extraction to take place.

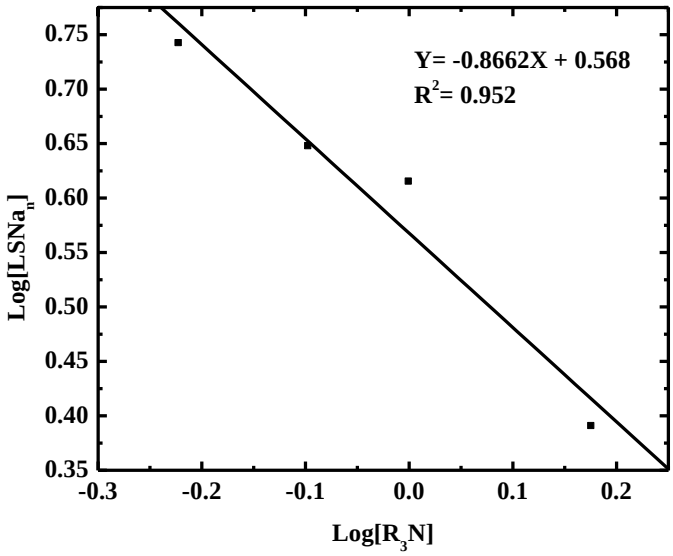

Figure 4.1 Stoichiometric plots for the equilibrium extraction of LS using TOA as carrier and dichloroethane as solvent.

4.1.2 Permeation model for LS transport across SLM

The permeation models for the transport of various metal ions have been reported elsewhere [3-4]. A similar approach has been incorporated in this work to develop a permeation model for the transport of LS. The said permeation model is based on the following assumptions:

- The mass transfer of LS across the SLM occurs through diffusion mechanism only.
- The chemical reaction takes place at the feed/membrane and membrane/strip interfaces. The speed of reaction is very high compared to the speed of diffusion process. Hence, the interfacial flux due to chemical reaction is neglected.

The mechanism of coupled co-transport of LS across the SLM is shown in Fig. 4.2. Here the transport of LS and protons takes place from the feed phase to the strip phase due to their concentration gradients. This transport process is considered to be composed of various elementary steps [4, 5-7] that include diffusion of LS, protons and chloride ions from the bulk of feed phase to the feed/membrane interface followed by reaction at the interface; diffusion of LS-carrier (TOA) complex from the feed/membrane interface to the membrane/strip interface followed by stripping of LS at the membrane/strip interface and diffusion to the bulk of stripping phase; and finally diffusion of the free carrier back to the feed/membrane interface.

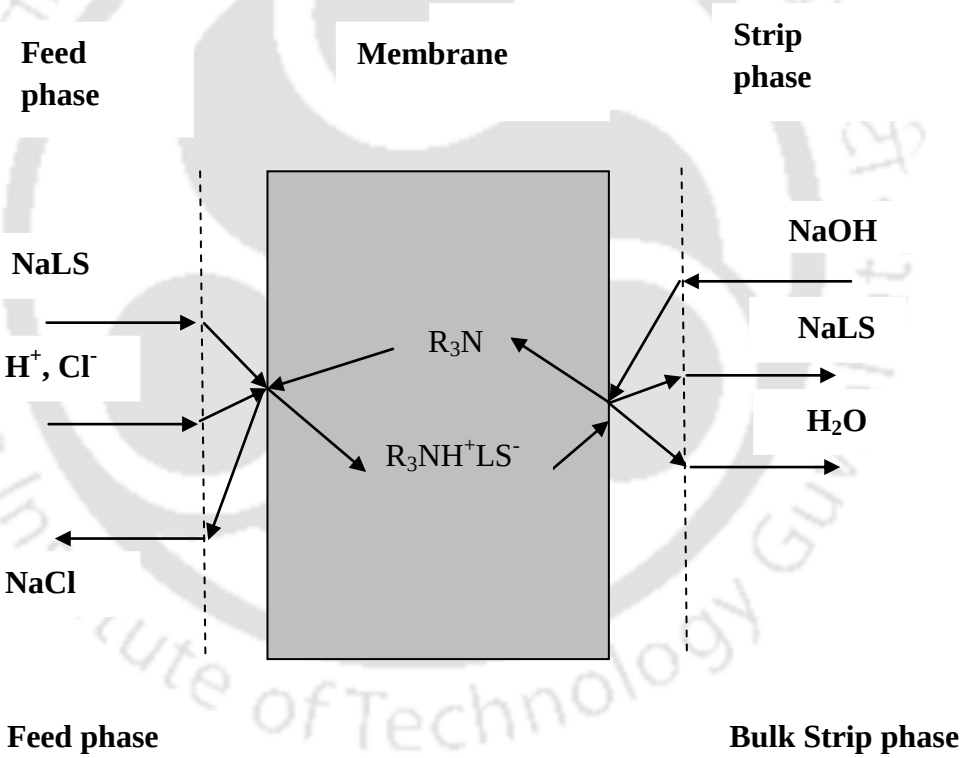

Figure 4.2 Schematic of co-transport mode of LS transfer through SLM

The extraction constant (K_{ext}) for the extraction of LS by TOA represented by Eq. (4.3) can be re-written considering $x = 1$, as follows:

$$K_{ext} = \frac{[R_3NHLSNa_{n-1}][NaCl]}{[LSNa_n][R_3N][HCl]} \tag{4.7}$$

Diffusion of LS from the bulk of the feed phase to the aqueous layer in the feed/ membrane interface can be written as follows:

$$J_{aq.} = \frac{D_{LS}}{\delta}\left[LSNa_{n\ f} - LSNa_{n\ fm} \right] \tag{4.8}$$

Or,

$$J_{aq.} = \Delta aq.^{-1}\left[LSNa_{n\ f} - LSNa_{n\ fm} \right] \tag{4.9}$$

where, $\Delta aq. = \frac{\delta}{D_{LS}}$ aqueous phase resistance, $[LSNa_n]_f$ and $[LSNa_n]_{fm}$ are the concentrations of LS at bulk feed phase and feed/membrane interface, respectively. Diffusion of LS-TOA complex through the membrane phase can be written as follows:

$$J_{org.} = \frac{D_{complex} \times \varepsilon}{l\tau^2}\left[R_3NHLSNa_{n-1} \right]_{fm} - \left[R_3NHLSNa_{n-1} \right]_{ms} \tag{4.10}$$

Or,

$$J_{org.} = \Delta org.^{-1}\left[R_3NHLSNa_{n-1} \right]_{fm} - \left[R_3NHLSNa_{n-1} \right]_{ms} \tag{4.11}$$

Where, $\Delta org.$ = organic phase resistance due to diffusion through the membrane, $\left[R_3NHLSNa_{n-1} \right]_{fm}$ and $\left[R_3NHLSNa_{n-1} \right]_{ms}$ are the concentrations of LS-TOA complex at feed/membrane and membrane/strip interfaces, respectively.

The distribution of LS between the membrane phase and strip phase is much lower than that between the feed phase and membrane phase. Hence the concentration of LS-TOA complex in the membrane phase at the strip side may be neglected compared to that at the feed phase side [5]. Thus Eq. (4.11) can be simplified to

$$J_{org.} = \Delta org.^{-1}\left[R_3NHLSNa_{n-1} \right]_{fm} \tag{4.12}$$

As the chemical reaction expressed by Eq. (4.3) is assumed to be fast compared to the diffusion rate, local equilibrium at the interface is reached and concentration at the interface can be related by Eq. (4.7) [5]. Combining Eq. (4.7) and Eq. (4.12), it can be written as

$$J_{org.} = \frac{K_{ext}\ LSNa_{n\ fm}\ HCl\ \ R_3N}{\Delta org.\ NaCl} \tag{4.13}$$

Or,

$$LSNa_{n\ fm} = \frac{J_{org.}\Delta org.\ NaCl}{K_{ext}\ R_3N\ \ HCl} \tag{4.14}$$

At steady state, $J_{aq} = J_{org} = J$ and by rearrangement of Eqs. (4.9), and (4.14) the expression for flux J is obtained as,

$$J\Delta aq. = LSNa_{n\ f} - \left[\frac{J\Delta org.\ NaCl}{K_{ext}\ R_3N\ \ HCl} \right] \tag{4.15}$$

Or,

$$J = \frac{K_{ext}\ HCl\ \ R_3N\ \ LSNa_{n\ f}}{\Delta org.\ NaCl + \Delta aq.K_{ext}\ HCl\ \ R_3N} \tag{4.16}$$

The permeability coefficient P can be written as

$$P = \frac{J}{LSNa_{n\ f}} = \frac{K_{ext}\ HCl\ \ R_3N}{\Delta org.\ NaCl + \Delta aq.K_{ext}\ HCl\ \ R_3N} \tag{4.17}$$

Or,

$$\frac{1}{P} = \Delta aq. + \frac{\Delta org.}{K_{ext}\ HCl\ \ R_3N\ \ NaCl}^{-1} = \Delta aq. + \frac{\Delta org.}{\left\{\frac{[R_3NHLSNa_{n-1}]}{[LSNa_n]}\right\}} \tag{4.18}$$

Or,

$$\frac{1}{P} = \Delta aq. + \frac{\Delta org.}{m} \tag{4.19}$$

Where, m is the distribution coefficient of LS at various carrier concentrations and at a pH of 2 maintained during the experiments, as the separation of LS was found to be maximum [1] at pH 2. Thus, by plotting P^{-1} versus m^{-1} of the Eq. (4.19) for various $[R_3N]$ at constant pH a straight line with slope $\Delta org.$ and intercept $\Delta aq.$ would be obtained. The mass transfer coefficients for aqueous and organic phases can thereby be found out from $\Delta aq.$ and $\Delta org.$

4.1.3 Calculation procedure for flux and permeability

The flux of transport of LS, J can be expressed by the following equation:

$$J = -\frac{V_F}{A}\frac{d\ LSNa_n}{dt} \tag{4.20}$$

where, A is the effective area of the membrane and V_F is the volume of feed phase. Similarly, the permeability coefficient, P can be expressed as follows:

$$P = \frac{J}{LSNa_n} = -\frac{V_F}{A\ LSNa_n}\frac{d\ LSNa_n}{dt} \tag{4.21}$$

Or,

$$\frac{d\ LSNa_n}{LSNa_n} = -\frac{PA}{V_F}dt \tag{4.22}$$

Simple integration of the Eqs. (4.20) and (4.22) for the specified duration of experiment would respectively yield

$$J = \frac{V_F\ \ LSNa_{n\ 0} - LSNa_{n\ t}}{At} \tag{4.23}$$

and

$$P = \frac{V_F \left\{ \ln \frac{LSNa_{n\ 0}}{LSNa_{n\ t}} \right\}}{At} \tag{4.24}$$

where, t is the elapsed time during the experiment, $LSNa_{n\ 0}$ and $LSNa_{n\ t}$ are the concentrations of LS at initial time ($t=0$) and at time t, respectively.

4.1.4 Selection of support materials

Various polymeric membranes such as PTFE, Nylon 6, 6 and PVDF were tested as support in order to design a suitable SLM for the separation of LS. The physical characteristics of all these support materials are summarized in Table 4.1.

The efficiency of various support materials in the separation and recovery of LS is shown in Figs. 4.3(a) and 4.3(b). PVDF (0.2 µm) and PTFE of 0.2µm pore size shows almost similar result for extraction as well as recovery of LS. In case of PTFE membrane having bigger pore size (0.45 µm), both the separation and recovery of LS is low. This may be due to larger pore size because of which the support is unable to hold the organic phase for longer time. Nylon 6,6 (0.2 µm) is easily impregnated by dichloroethane and shows better separation as well as recovery of LS compared to the other supports studied. Hence Nylon 6,6 is chosen as the support for the separation of LS in the present case and the SLM configuration "Nylon 6,6–TOA- dichloroethane" is selected for the subsequent studies.

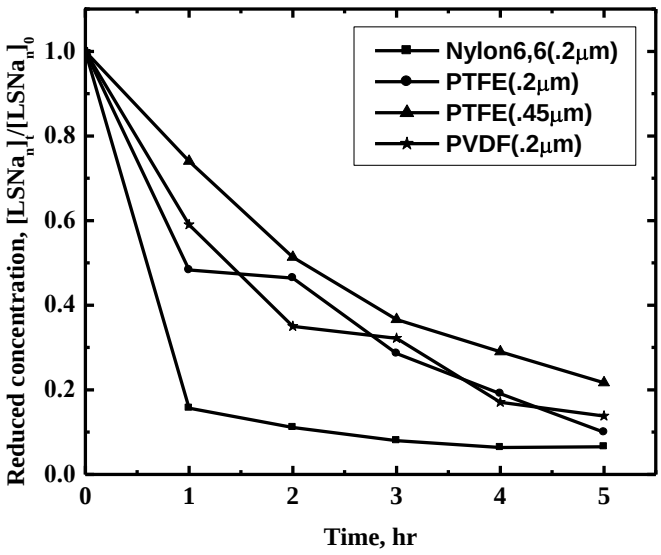

Figure 4.3 (a) Reduced concentration of LS through SLM of various polymeric supports (*V_F=V_S=140 ml, carrier concentration=4 vol%, pH=2, strip phase= 0.5M NaOH***).**

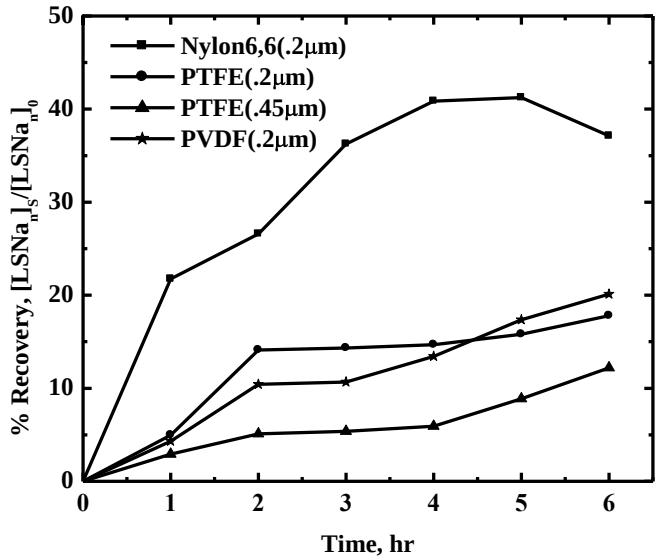

Figure 4.3 (b) Percentage recovery of LS through SLM of various polymeric supports (*V_F=V_S=140 ml, carrier concentration=4% (v/v), pH=2, strip phase= 0.5M NaOH***).**

Table 4.1 Physical characteristics of the support materials

Support material	Pore size (μm)	Thickness, l (μm)	Porosity, ε	Tortuosity, τ
PTFE	0.2	77.2	51%	2.92
PTFE	0.45	75.9	75%	1.67
PVDF	0.2	88.5	30%	5.6
Nylon 6,6	0.2	102	40%	4.0
PE	0.2	107	67%	1.98

4.1.5 Effect of carrier concentration

The influence of the composition of LM on the transport of LS was studied using various carrier (TOA) concentrations in the range of 1-5 % (v/v) in the membrane phase. The results are shown in Figs. 4.4(a) and 4.4(b). As the carrier concentration is increased from 1 to 4 % (v/v), both the extraction and recovery of LS increase. They reach a maximum at about 4 % (v/v) TOA and then the extraction and recovery decrease with increase in TOA concentration (5% (v/v)). Panja *et al*. [8] have explained this "maximal phenomenon" by introducing the term "dominant effects". This effect is observed due to (i) the concentration gradient of the carrier-complex species, (ii) the viscosity of the membrane phase, and (iii) hindered diffusion of carrier complex caused by aggregation of the complex. From the BLM separation of LS (Chapter-III, Table 3.3) it is observed that with increase in concentration of TOA the viscosity of the organic phase increases [1]. Since diffusivity is inversely proportional to viscosity, an increase of viscosity causes reduction of diffusivity and eventually increases the membrane phase resistance to transport [9]. Thus, increase of viscosity of the membrane phase is likely the main cause for such "maximal phenomenon".

At lower concentration of TOA, the transport of LS is expected to be enhanced with increase of carrier concentration. Because more number of TOA molecules get associated with LS and form complex (Eqs. 4.1 and 4.2), it is transported through diffusion. The optimum

concentration of TOA observed in BLM study for effective separation of LS has been reaffirmed in SLM study too.

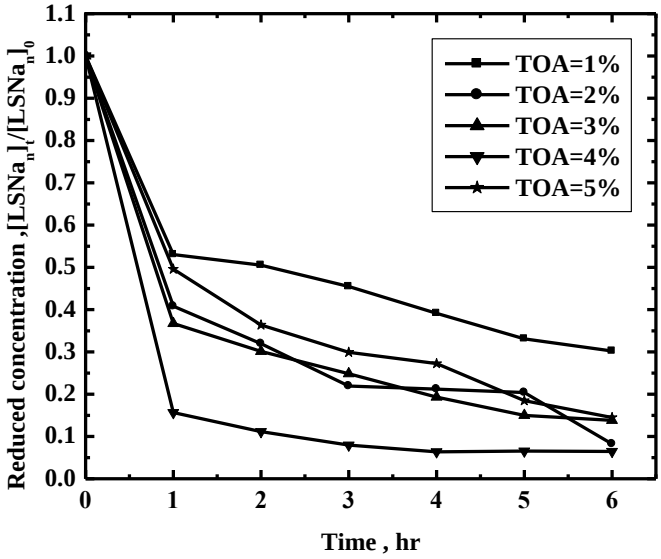

Figure 4.4(a) Reduced concentration of LS through SLM at various carrier concentrations (*V_F=V_S=140 ml, carrier concentration=1-5% (v/v), pH=2, strip phase=0.5M NaOH***).**

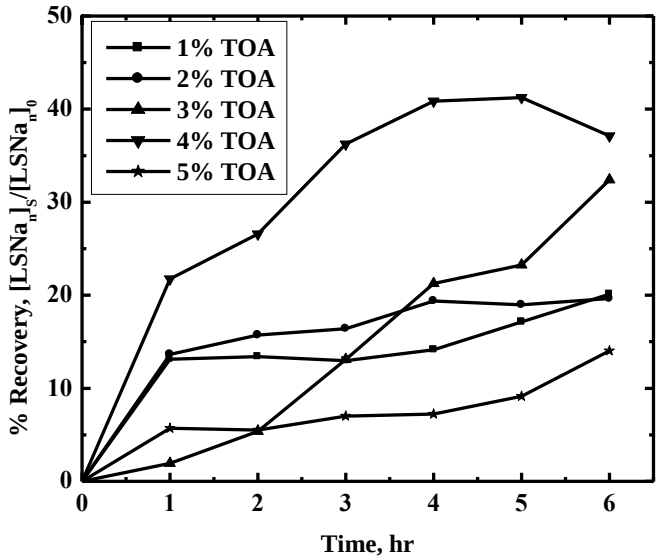

Figure 4.4(b) Percentage recovery of LS through SLM at various carrier concentrations (*V_F=V_S=140 ml, carrier concentration=1-5 % (v/v), pH=2, strip phase=0.5M NaOH***).**

4.1.6 Effect of salt concentration in the feed phase on the flux of LS

Experiments were conducted to study the influence of the variation of salt concentration of feed phase on the flux of LS. During this study, the strip phase concentration of NaOH was fixed at 0.5M and TOA concentration in membrane phase was maintained at 4 % (v/v) for the obvious reasons explained in the Section 4.1.5. The salt concentration of feed phase was varied by dissolving various quantities of NaCl in the feed phase. The experimental results are shown in Fig. 4.5.

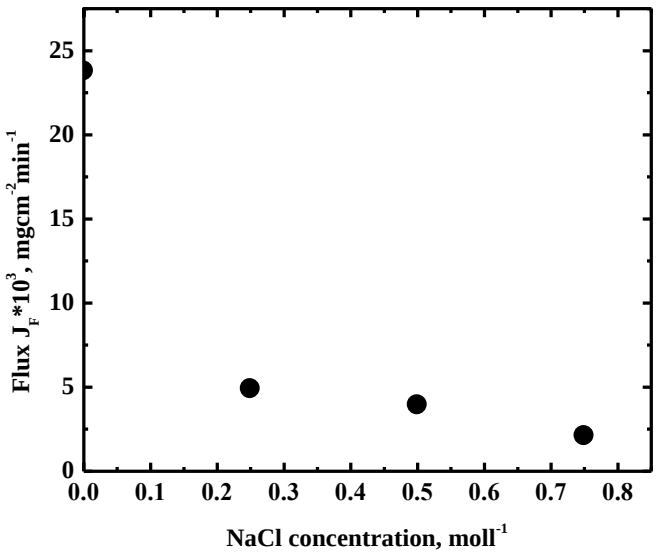

Figure 4.5 Effect of salt concentration in feed phase on the flux of LS ***(V_F=V_S=140 ml, carrier (TOA) concentration=4 % (v/v), pH=2, strip phase=0.5M NaOH).***

It is observed that with increase in NaCl concentration in the feed phase, the flux of LS decreases. As the NaCl concentration in feed phase increases, the difference of ionic strength between the feed and strip phase increases. This phenomenon creates an osmotic pressure differential [10]. Osmotic pressure is a motive force for the water transport through the SLM and causes instability in SLM. Because of this pressure, part of the support pores may get

devoid of membrane liquid and direct channeling between feed and strip phases occurs. This results in decrease of LS flux. Figure 4.5 reveals that the difference in ionic strength between feed and strip phases occurring due to increase in NaCl concentration affect the system considerably.

4.1.7 Effect of strip phase concentration

The influence of NaOH concentration in the strip phase on the transport of LS was studied in the range of 0.25-1.25M. The results are reported in Fig. 4.6.

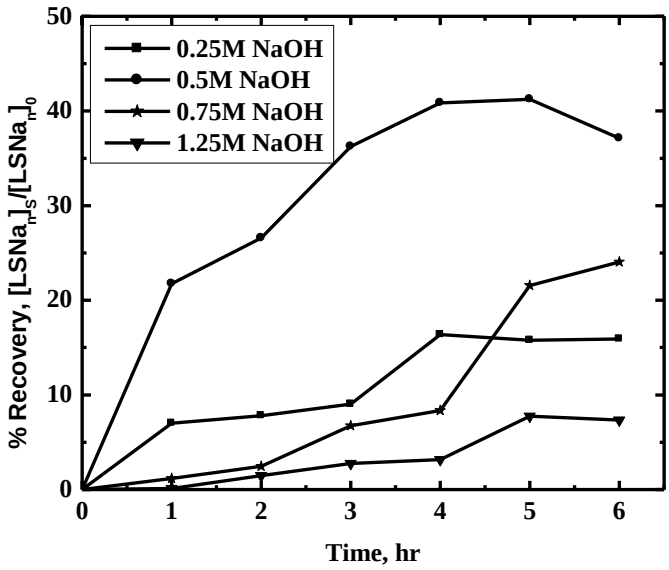

Figure 4.6 Effect of strip phase concentration on the transport of LS through SLM (*V_F=V_S=140 ml, carrier(TOA) concentration=4% (v/v), pH=2*).

From the figure it is observed that with the increase in NaOH concentration up to 0.5M the recovery of LS increases. However, further increase in NaOH concentration shows adverse effect on LS transport. This phenomenon is different from the one observed in the previous study with the separation of LS through BLM [1], where recovery of LS increased and never showed any adverse effect with increase of NaOH concentration. The decrease of recovery of LS at high concentration in SLM may be due to following two reasons:

- *Increase in difference of ionic strength between the feed and strip phases:* As described in Section 4.1.6 the system performance is considerably affected by the presence of a difference in ionic strengths of feed and strip phases. The increase of recovery of LS from 0.25M to 0.5M NaOH concentration reveals that the ionic concentrations in the two phases (feed and strip) are balanced within this range. However, beyond 0.5M NaOH the difference in ionic strength increases and creates an osmotic pressure differential. This phenomenon eventually results in decrease of LS flux.

- *Decrease of interfacial tension in the strip side at high concentration:* According to the progressive wetting mechanism, the aqueous phase from low interfacial tension side progressively penetrates the membrane pores [10]. With increase in sodium hydroxide concentration in strip side (0.1M-1M) the interfacial tension decreases (Table 4.2). Therefore strip solution may penetrate the support pores causing the loss of membrane liquid and thereby reducing the LS flux. The interfacial tension data for various combinations of feed/membrane system are reported in Appendix-IV (Table AIV.1).

Table 4.2 Interfacial tension for dichloroethane -TOA (4% v/v) mixture/water system

Organic phase	Aqueous phase	Interfacial tension (γ), (mN/m)
Dichloroethane and TOA	Water	21.0
	0.1M NaOH	20.07
	1M NaOH	19.56

4.1.8 Stability of SLM

The supports used in SLMs are generally porous in which the organic solution or membrane liquid is held within its pores by capillary action. After prolonged use, the efficiency of these membranes deteriorates. And that happens due to one or cumulative effect of more than one phenomena such as chemical degradation, loss of carrier and/or solvent, formation of emulsion, *etc*. [10]. Sometimes stability of these membranes may be affected due to the chemical degradation of the support material. Therefore experiments were performed to study the stability of these SLMs in terms of membrane liquid loss from the support pores and integrity of the support materials. The chemical resistance of Nylon 6,6 membranes against TOA/dichloroethane was tested over a period of 45 days by keeping it dipped in a solution of 4% (v/v) TOA in dichloroethane. Experiment performed with 100 mgl^{-1} of LS as feed at a pH of 2 showed that the fluxes for 24 hours immersion period and 45 days immersion period are 9.72×10^{-3} and 10.4×10^{-3} $mgcm^{-2}$ min^{-1}, respectively. Hence, the integrity of the support material was not affected during this period.

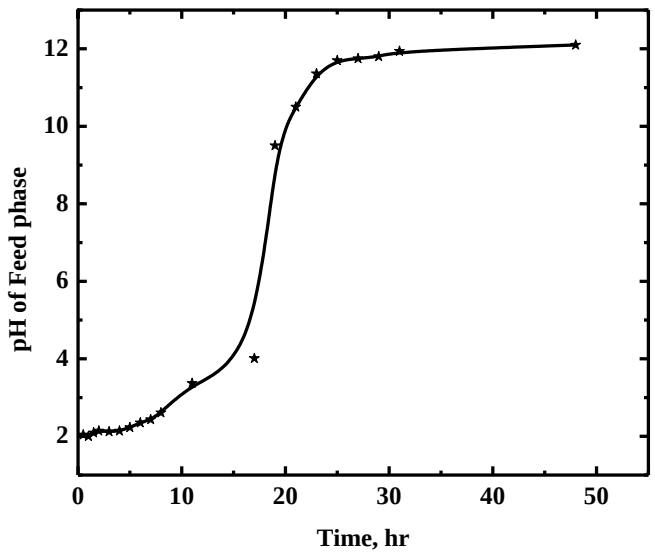

Figure 4.7 Life time of SLM (*V_F=V_S=140ml, carrier (TOA) concentration=4 %(v/v), pH=2, strip phase=0.5M NaOH).*

The stability of a SLM can be estimated from the concept of membrane liquid loss [10]. When the membrane liquid in the support pores is totally lost to the adjacent aqueous phases, serious leakage and direct channeling between feed and strip phase occurs. The pH value of feed solution becomes closer to that of strip solution at the point of total loss. The experiment was carried out with 100 mgl^{-1} of LS solution as feed phase at an initial pH of 2 and of 0.5M NaOH solutions (pH=12.86) as strip phase. The results are reported in Fig. 4.7. It is observed that rate of increase of pH is very slow up to 10^{th} hours but beyond that it changes rapidly. Changes of pH at the initial period (0-10 h) are basically due to the protonation of the amine molecules. However rapid changes of pH after 10^{th} hour indicate membrane liquid loss from the pores of the support. The total liquid loss occurs after a period of 48 hours. This reveals that the membrane is stable till 10^{th} hour but its life time is more than 48 hours. It may be noted that all the results reported here in various sections are up to duration of 6 hours.

4.1.9 Determination of mass transfer coefficient

To evaluate the values of mass transfer resistances, m^{-1} values were plotted against P^{-1} as described in Section 4.1.2 and according to Eq. (4.19) a straight line with a slope $\Delta org.$ and intercept $\Delta aq.$ was obtained. Steady permeability, P at various carrier concentrations are tabulated in Table 4.3 and the Fig. 4.8. The changes of permeability with time at various carrier concentrations are reported in Fig. 4.8.

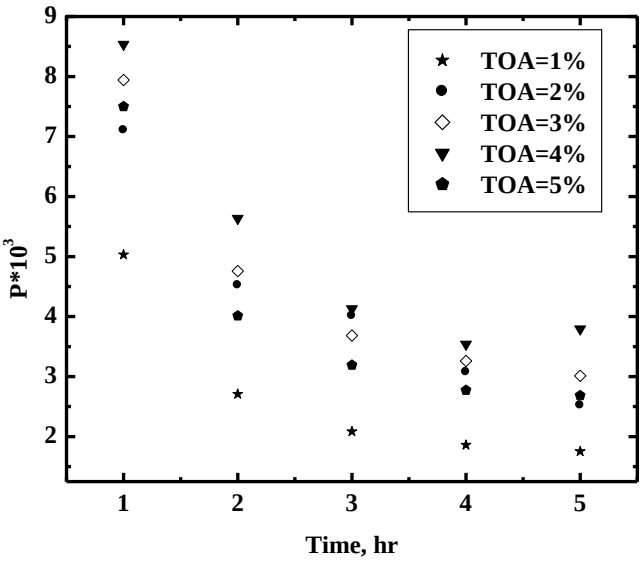

Figure 4.8 Changes of permeability with time at various carrier concentrations

Table 4.3 Steady permeability at various carrier concentrations (*V_F=V_S=140 ml, pH=2, strip phase=0.5M NaOH*).

Carrier concentration, (v/v) %	Permeability, P×10^3(cm s^{-1})
1	1.75
2	2.52
3	3.01
4	3.79
5	2.68

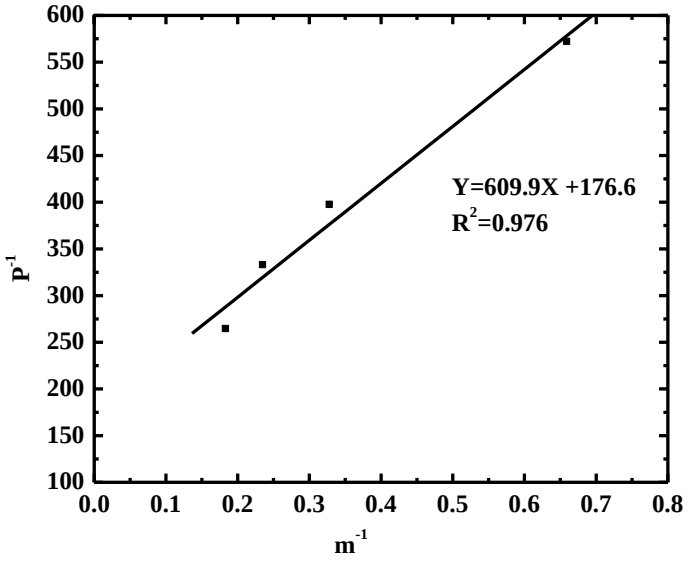

Figure 4.9 P^{-1} vs. m^{-1} for experimental data.

It was observed that, permeability of LS decreases with time and reaches almost a steady value (termed as steady permeability) after four hours. This is due to the fact that the stripping process is slower than the extraction process as discussed in the earlier work (Chapter-III) with BLM [1]. From Fig. 4.9 the values of $\Delta org.$ and $\Delta aq.$ were found to be 609.9 and 176.6 s cm^{-1}, respectively. The mass transfer coefficients in aqueous and organic phases were calculated as $\Delta aq.^{-1}=5.602\times10^{-5}$ m s^{-1} and $\Delta org.^{-1}= 1.639\times10^{-5}$ m s^{-1}, respectively. The estimated value of diffusion coefficient in the membrane with micropores ($D_{org}=l/\Delta org.$) is 1.67×10^{-9} m^2s^{-1}. The diffusion coefficient of LS-TOA complex in the bulk organic phase *i.e.* $D_{complex}$ was evaluated from the organic phase resistance as follows:

$$D_{complex} = \Delta org.^{-1} l\tau^2 / \varepsilon \qquad (4.25)$$

The value of $D_{complex}$ was found to be 6.68×10^{-8} m^2 s^{-1}. In SLM system, the diffusivity of LS-TOA complex in the membrane (D_{org}) was found to be lower than that of the bulk diffusion

coefficient. This is due to diffusional resistance caused by micro-porous thin membrane placed between the feed and stripping phase.

4.1.10 Separation of LS from industrial black liquor (a case study)

The above SLM configuration (Nylon 6,6–dichloroethane–TOA) was applied to industrial black liquor collected from sulphite pulping unit of a pulp and paper plant, in order to study the efficiency of the above SLM in the extraction of LS. The experiments were carried out with diluted (500 times of the original liquor) black liquor (pH=10) and the pH was adjusted to 2 by adding HCl. The carrier concentration and strip phase concentration were maintained at 4% (v/v) and 0.5M NaOH, respectively. The results are shown in Fig. 4.10. It is observed that about 73% of LS can be extracted from the industrial black liquor and 26% of it can be recovered. The extraction as well as recovery of LS obtained with real black liquor is little less than that obtained with synthetic LS solution (extraction was 90% and recovery was 43%). This may be due to the different molar mass distribution of the industrial LS or interference of the other ingredients present in the industrial black liquor.

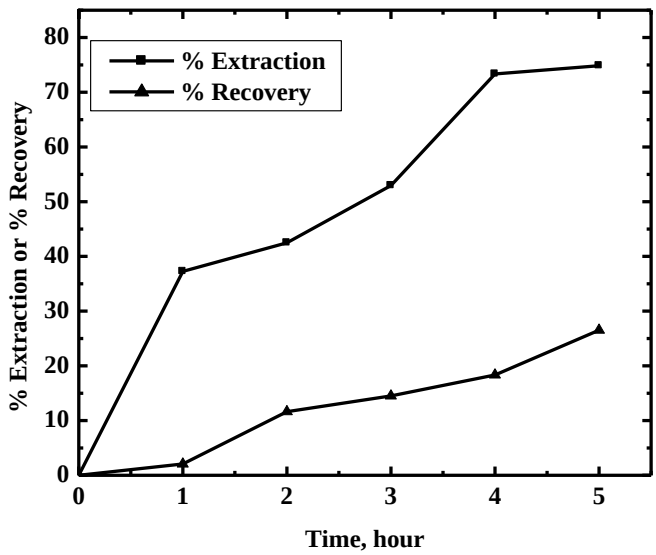

Figure 4.10 Separation of LS from industrial black liquor (*V_F=V_S=140 ml, pH=2, strip phase=0.5M NaOH, TOA= 4% (v/v), stirring speed=500 rpm).*

4.1.11 Summary of the SLM separation of LS [2]

- The SLM combination of "Nylon 6,6–TOA-dichloroethane" is found to be an efficient SLM for the extraction and recovery of LS.
- The SLM was found to be reasonably stable up to 10 hours of operation.
- The separation of LS achieved at optimum condition is 90%, however the recovery is 43% with 0.5M NaOH as strip phase.
- From experimental data, it is inferred that LS permeation can be well described by permeation model similar to metal ions.
- The LS permeation process is an aqueous diffusion film controlled process. Similar conclusion is also drawn on BLM separation of LS (Chapter-III, Section 3.1.3.1) as well.
- The mass transfer coefficients were calculated as 1.639×10^{-5} m s^{-1} and 5.602×10^{-5} ms^{-1} for the organic and aqueous phases, respectively.

4.2 Separation of mercury using SLM

From the review of the literature on the separation of mercury, it is observed that there is great potential of LM for the separation of mercury from aqueous solution. However, very few reports are available on the use of SLM for extraction of mercury. The BLM separation of mercury as discussed earlier (Chapter-III, Section 3.2) shows that the LM comprising of TOA and dichloroethane is a suitable combination for the separation of mercury. About 90% extraction of mercury was achieved with this LM at optimum condition. Therefore a systematic investigation on the transport of mercury from aqueous solution through an SLM containing TOA as carrier and dichloroethane as solvent has been discussed in this section.

Based on the findings of the SLM separation of LS as discussed in the Section 4.1 [2], Nylon 6, 6 has been used as the support material for the SLM and aqueous NaOH as the strip phase. The influence of various parameters such as feed pH, strip concentration, carrier concentration and feed concentration on the transport of mercury are studied and discussed in the subsequent sections. The experiments were conducted according to the procedure described in Section 2.5.4 of Chapter-II. This work has been published in the Journal of membrane science [11].

4.2.1 Effect of feed phase pH

The pH gradient between the source and receiving phases is an important driving force for the permeation of metal ions through LM. The effect of feed phase pH on the transport of mercury ions was studied by varying the pH in the range of 2-4. Hydrochloric acid was used to maintain the feed phase pH in the above range. In the presence of hydrochloric acid in the feed phase, the transport of mercury through the SLM follows the similar reaction mechanism as described in Chapter-III, Section 3.2.1.

The principle of co-transport mechanism in case of mercury transport is described in Chapter-III, Section 3.2. Here transport of the species *i.e.* H^+ and mercury occur in the same direction. The transport process is driven by the concentration gradient of H^+ and mercury. The effect of feed phase pH on the extraction and recovery of mercury is shown in Fig. 4.11. It is observed that a pH of 2.5 yields the best results. As discussed in Section 3.2 of Chapter-III, hydrochloric acid is required to protonate the amine molecules and to convert the $HgCl_2$ to $HgCl_4^{2-}$. At a pH higher than 2.5, availability of H^+ ion is not adequate to protonate the amine molecules and hence the transport of mercury decreases. The decrease of transport of mercury at a pH below 2.5 could be due to the following reasons. Increased acidic condition can lead to the formation of H_2HgCl_4 in place of $HgCl_4^{2-}$. Thus formation of amine complex (reaction 3.8) is inhibited. In addition TOA is an alkaline extractant and it reacts with metal

ions in a basic or low acidic solution [12]. Hence the extraction of mercury is low at a pH below 2.5.

However, the optimum pH changes with the change of initial feed concentration as discussed later.

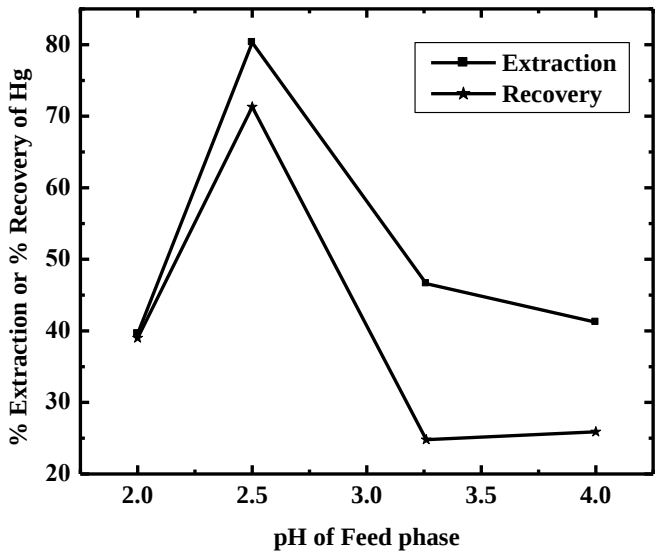

Figure 4.11 Effect of feed phase pH on the transport of mercury (*feed concentration=250µgl^{-1}, strip phase=0.1M NaOH, carrier concentration=4% (v/v), experiment time= 60 minute, speed=500 rpm).*

4.2.2 Effect of strip phase concentration

Strip phase concentration plays an important role in the transport of mercury from feed side to strip side through SLM. If the metal complex is not properly stripped, the membrane phase becomes saturated with the complex and permeation rate decreases. The effect of strip phase concentration on the transport of mercury was studied by varying the NaOH concentration in the range of 0.01-0.2M. The effect of NaOH concentration on the recovery and extraction of mercury is shown in Fig. 4.12. From the figure it is observed that with increase in NaOH concentration recovery as well as extraction of mercury increases and reaches maximum at

NaOH concentration of 0.1M. From Eq. (3.9) and according to Lé Chatelier principle, when the concentration of hydroxide ion increases, extraction and recovery of mercury ions into the stripping solution would increase too. However, above 0.1M NaOH concentration the recovery of mercury decreases abruptly. This is because; the addition of OH^- ions to salt of mercury yields a precipitate of HgO or Hg [13]. Because of this precipitation, membrane pores get clogged and transport of mercury gets affected. Sample of strip solutions before and after experiment were viewed under microscope as shown in Figs. 4.13(a) and 4.13(b) respectively. These figures reveal the presence of some precipitate in the strip solution collected at the end of experiment. To identify the precipitate a concentrated solution of mercury chloride (500 mgl^{-1}) has been prepared and mixed with a 0.5M NaOH solution. It has been observed (visual observation) that a yellow colored precipitate was formed within a fraction of second. This yellow precipitate is due to the formation of HgO. The microscopic view of this solution is also shown in Fig. 4.13(c).

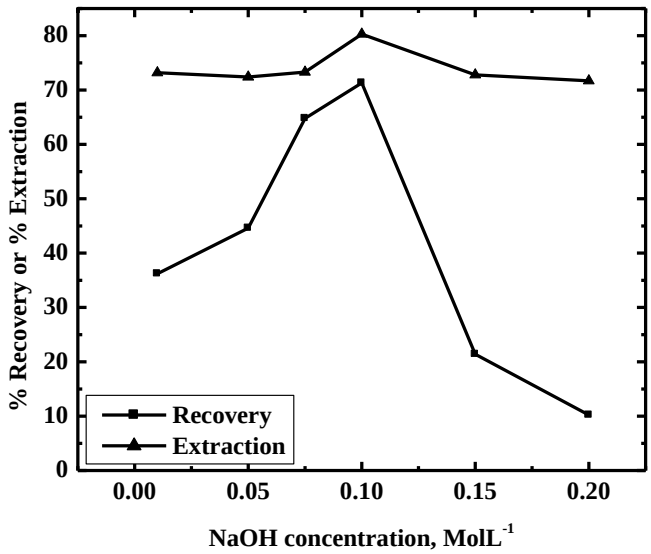

Figure 4.12 Effect of strip phase concentration on the transport of mercury (*feed concentration=250 µgl^{-1}, feed phase pH=2.5, carrier concentration=4 %(v/v), experiment time=60 minute, speed=500 rpm***).**

Figure 4.13(a) Microscopic view of 0.1M NaOH solution.

Figure 4.13(b) Microscopic view of strip solution at the end of experiment (*feed concentration =250 µgl^{-1}, pH=2.5, TOA=4% (v/v), strip phase= 0.1M NaOH***).**

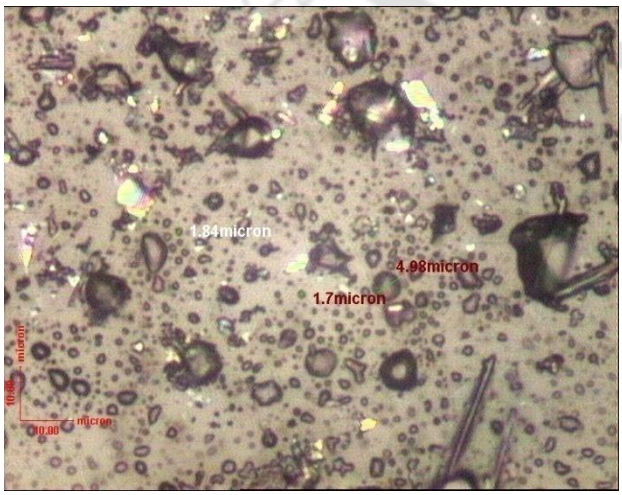

Figure 4.13(c) Microscopic view of 0.5M NaOH solution when 500 mgl^{-1} mercury chloride solutions were added to it.

4.2.3 Effect of carrier concentration in the membrane phase

The concentration of carrier in the membrane phase has a significant effect on the transport of metal ions through SLM. According to Eq. (3.8), the transport of metal ions should increase with increase in carrier concentration. This fact has been studied in the TOA concentration range of 1- 6% (v/v) and the results have graphically been represented by Fig. 4.14. The figure shows that the percentage extraction of mercury increases with increase in carrier concentration, however, the rate of increase gradually slows down when the carrier concentration is 4 % (v/v) or more. Again, the percentage recovery of mercury increases with increase in carrier concentration and attains an optimum at a carrier concentration of 4 % (v/v). The above fact can be attributed to the viscosity of the LM that increases with increase in concentration of TOA (carrier) [1]. As diffusivity is inversely proportional to viscosity; an increase in LM viscosity causes reduction of ion diffusivity which eventually decreases percentage recovery of mercury. Hence, the subsequent experiments were carried out with a TOA concentration of 4% (v/v).

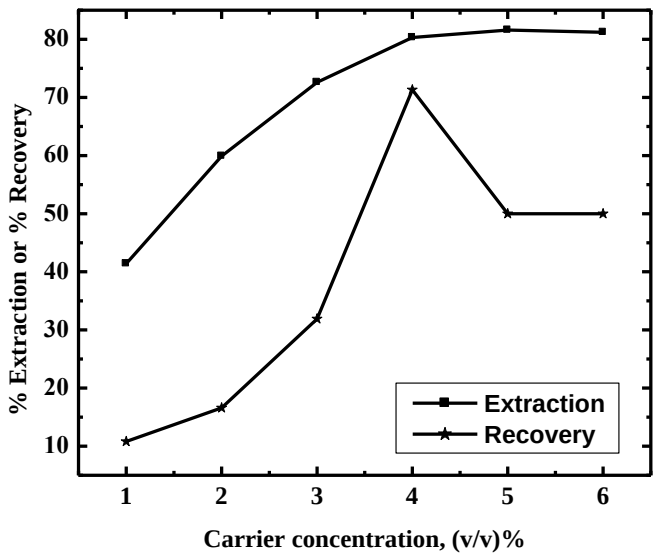

Figure 4.14 Effect of carrier concentration on the transport of mercury (*feed concentration=250 µgl^{-1}, strip phase=0.1M NaOH, pH=2.5, experiment time=60 minute, speed=500 rpm***).**

4.2.4 Effect of initial feed concentration

The effect of initial feed concentration on the transport of mercury was studied at two different conditions.

- By varying the mercury concentration in the range of 1.525-8.89 mgl^{-1} and at a pH of 1.5 (optimum pH for 8.89 mgl^{-1}).
- By varying the mercury concentration in the range of 0.25–10.3 mgl^{-1} at a pH of 2.5 (optimum pH for 0.25 mgl^{-1}).

Aqueous NaOH (0.1M) solution was used as the strip phase and TOA (4% v/v) as carrier. Fig. 4.15(a) shows the effect of initial feed concentration on the transport of mercury for the first case *i.e.* at a pH of 1.5. From the figure it is observed that at higher initial feed concentration (8.89 mgl^{-1}) the extraction of mercury is about 88%, however it decreases to 62.9% at the initial feed concentration 1.525 mgl^{-1}. The above fact could be attributed to the following two reasons:

- As discussed in Section 4.2.1, the mercury extraction process is a highly pH dependent phenomenon. With changes of initial mercury concentration in the feed, the amount of HCl requirement (pH) also changes. In the above study we have carried out all the three experiments at the same pH *i.e.* 1.5.
- As opposed to the higher initial feed concentration, the amount of chloride ions remains excess at lower initial feed concentration. Excess chloride ions inhibit the formation of amine complex as reaction (3.7) is at equilibrium [1]. Therefore the percentage extraction of mercury is low at lower initial feed concentration.

Figure 4.15(b) shows the influence of feed concentration on the transport of mercury carried out at a higher pH of 2.5. From the figure, it is observed that with increase of initial feed

concentration, the extraction of mercury decreases. This phenomenon is just opposite to that found in the first case *i.e.* at a pH of 1.5. In this case, the extraction decreases at higher feed concentration due to insufficient amount of chloride ions, which is required to convert $HgCl_2$ to $HgCl_4^{2-}$. These facts reveal that the optimum feed phase pH changes with the feed concentration and the membrane under optimum feed phase pH is equally effective both at high and very low feed concentrations.

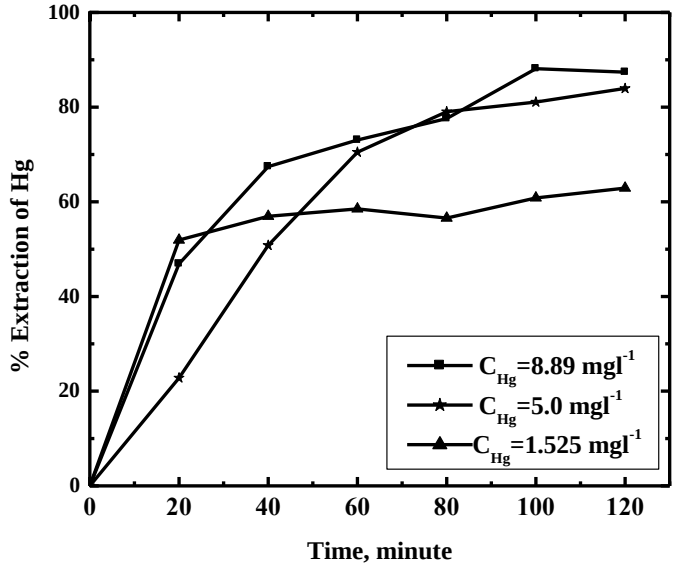

Figure 4.15(a) Effect of initial feed concentration on extraction of mercury at feed phase pH of 1.5 (*strip phase=0.1M NaOH, carrier concentration=4 %(v/v), speed=500 rpm***).**

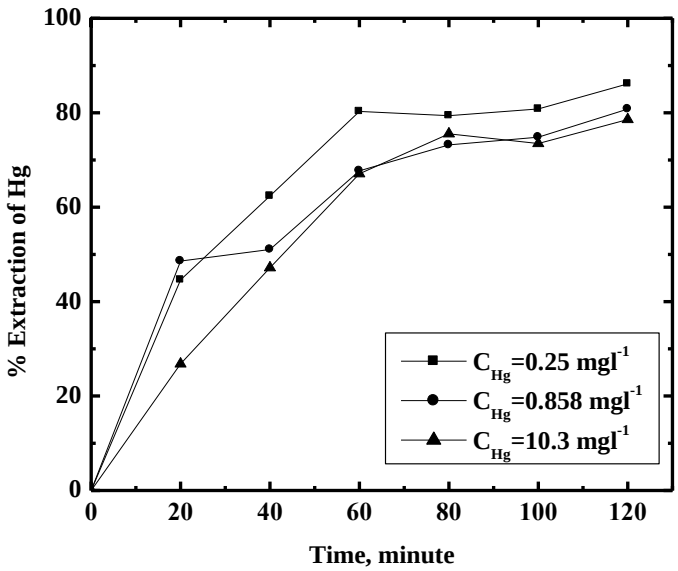

Figure 4.15(b) Effect of initial feed concentration on extraction of mercury at feed phase pH of 2.5 (*strip phase=0.1M NaOH, carrier concentration= 4 %(v/v), speed= 500 rpm***).**

4.3 Separation of mixture of mercury and LS

From the previous study on the separation of LS and mercury through SLM, it is evident that the same SLM configuration is suitable for the separation of both LS and mercury. Industries like pulp and paper generates wastewater containing both LS and mercury. In order to assess the suitability of the above SLM configuration for such effluent, performance of the above SLM in the separation of mixture of mercury and LS was investigated by varying various parameters such as strip concentration, feed phase pH, carrier concentration and feed composition. The experimental results are described in the following sections. The mixed feed **(**mixture of Hg^{2+} and LS) was prepared by dissolving 10 mg of LS and 1.354 mg of $HgCl_2$ in 100 ml of Milli-Q® deionized water. Thereby, a mixed feed composition of 100 mgl^{-1} LS and 10 mgl^{-1} Hg^{2+} is generated. The relevant work is published in the Journal of Membrane Science [11].

4.3.1 Separation of the mixture at various strip phase concentration

The influence of the strip phase concentration on the separation of mixture of LS and mercury was carried out by varying the NaOH concentration in the range of 0.1 to 0.5M and at a feed phase pH of 1.5. Figure 4.16 shows the effect of strip phase concentration on the transport of mixture of LS and mercury. From the figure, it is observed that extraction of LS increases with increase of NaOH concentration up to 0.2 M NaOH; however extraction of LS reduces at higher strip phase concentration (0.5M). This is due to the precipitation of mercury at higher NaOH concentration that clogged the membrane pores. The separation of mercury is maximum at 0.1 M NaOH. For the same reason as described above, the extraction of mercury reduces at higher NaOH concentration. It is worth mentioning here that in case of separation of pure LS solution with SLM the maximum extraction (90%) was achieved at 0.5 M NaOH [12]. As the extraction of both mercury and LS is almost equal at a strip phase concentration of 0.2M NaOH, further studies are carried out at this strip phase concentration.

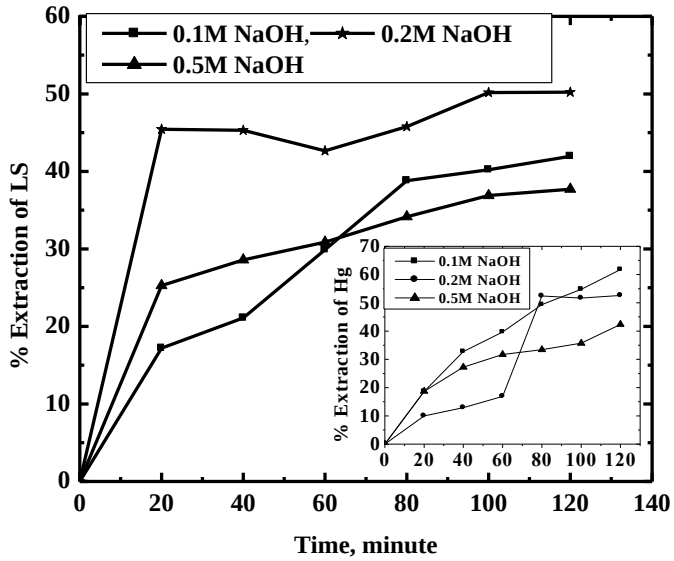

Figure 4.16 Separation of mixture of mercury and LS at various strip phase concentrations (*feed composition: 10 mgl^{-1} Hg and 100 mgl^{-1} LS, pH=1.5, carrier concentration=4% (v/v), strip concentration=0.1 to 0.5 M NaOH, experiment time=120 minutes, speed=500 rpm).*

4.3.2 Separation of the mixture at various feed phase pH

The effect of feed phase pH on the separation of LS-mercury mixture was studied in the pH range of 1 to 2.5 at a strip phase concentration of 0.2M NaOH. The results are shown in Fig. 4.17. From the figure, it is observed that the extraction of both LS and mercury attain maximum at a feed phase pH of 1.5. At highly acidic condition, LS molecules are not ionized and hence lower extraction is achieved [1]. The decrease of extraction at a pH of 2.5 is due to insufficient protonation. The reason for the decrease of extraction of mercury at highly acidic condition is same as explained in Section 4.2.1.

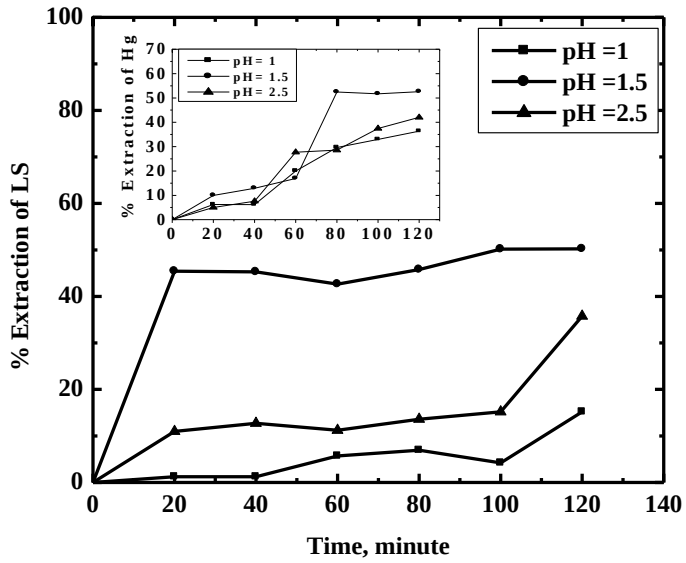

Figure 4.17 Separation of mixture of mercury and LS at various feed phase pH (*feed composition: 10 mgl^{-1} Hg and 100 mgl^{-1} LS, feed pH 1 to 2.5, carrier concentration=4% (v/v), strip concentration=0.2M NaOH, experiment time=120 minutes, speed=500 rpm).*

4.3.3 Separation of the mixture at various carrier concentrations

The effect of carrier concentration on the transport of mixture of LS and mercury was carried out by varying the carrier concentration from 4% to 8% (v/v), as 4% carrier concentration was found to be optimum in case of separation of pure solutions. The feed pH was maintained at 1.5 and strip concentration at 0.2M NaOH. The influence of carrier concentration on the separation of mixture is shown in Fig. 4.18. The figure shows that the extraction of the mixture also attains maximum at a carrier concentration of 4%. The reason for decrease of extraction beyond 4% (v/v) carrier concentration is due to the increase of membrane phase viscosity as described in Section 4.2.3.

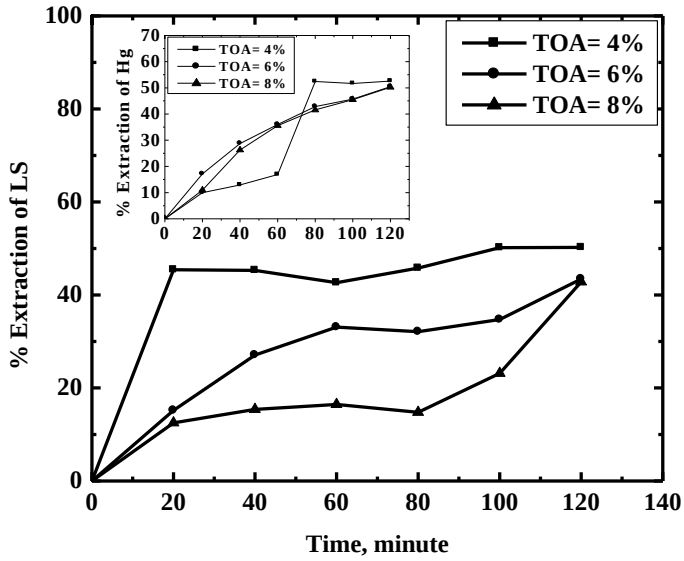

Figure 4.18 Separation of mixture of mercury and LS at various carrier concentration (*feed composition: 10 mgl^{-1} Hg and 100 mgl^{-1} LS, pH=1.5, strip concentration=0.2 M NaOH, experiment time=120 minutes, speed=500 rpm***).**

4.3.4 Separation of the mixture at various feed compositions

Separation of the mixture at two different feed compositions (LS=100 mgl^{-1} and Hg=10 mgl^{-1}; LS= 100 mgl^{-1} and Hg= 1.3 mgl^{-1}) has been studied in this section. The pH of the feed phase was maintained at 1.5 and strip phase concentration at 0.2M NaOH. The results are presented in Fig. 4.19. The figure shows that the extraction of LS for both the feed compositions is almost same. This indicates that the extraction of LS is independent of the Hg^{2+} concentration in the range of the present study. However, the extraction of mercury decreases at lower mercury concentration. The decrease of extraction of mercury is due to the higher acidity of the feed phase as described in Section 4.2.4.

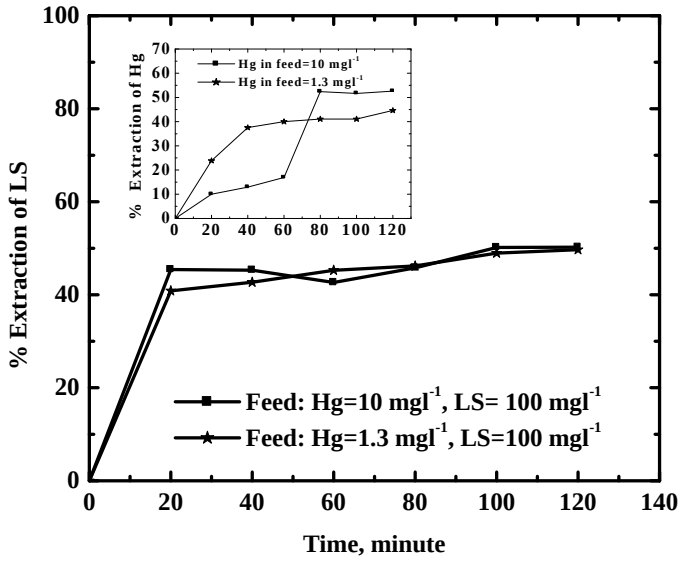

Figure 4.19 Separation of mixture of mercury and LS at various feed compositions (*feed pH=1.5, carrier concentration=4% (v/v), strip concentration=0.2 M NaOH, experiment time=120 minute, speed=500 rpm).*

4.4 Summary of the SLM separation of mercury and its mixture with LS

- The SLM "Nylon 6,6-TOA-dichloroethane" can efficiently separate mercury from its aqueous solution. About 81% separation of mercury is achieved at optimum conditions.
- The efficiency of the SLM in the extraction of mercury is almost same at high as well as at low feed concentration, provided the feed phase pH is well maintained.
- The separation of mercury and LS from their mixture is about 52.6 % and 50.2 %, respectively.
- The mixture of mercury and LS behaves exactly in a similar way as their pure solution.
- However the extraction is low in comparison to their pure solution due to increased number of ions against the fixed area of the feed membrane interface.

Abbreviations

BLM	bulk liquid membrane
LS	lignosulfonate
LM	liquid membrane
PTFE	polytetrafluroethylene
PVDF	polyvinyldenefluoride
SLM	supported liquid membrane
TOA	trioctylamine

Nomenclature

C_{Hg}	initial concentration of mercury in the feed (μgl^{-1} or mgl^{-1})
D_{LS}	diffusivity of LS(ms^{-1})
$D_{complex}$	diffusitivity of carrier complex (m^2s^{-1})
J_F	flux of LS in aqueous phase ($mgcm^{-2}min^{-1)}$
J_{org}	flux of LS in organic phase ($mgcm^{-2}min^{-1}$)
K_{eq}	equilibrium constant
k_s	mass transfer coefficient in aqueous phase (ms^{-1})
k_m	mass transfer coefficient in organic phase (ms^{-1})
$LSNa_n(aq)$	sodium lignosulfonate
$[LSNa_n]_0$	initial feed concentration (mgl^{-1})
$[LSNa_n]_t$	feed concentration at time t (mgl^{-1})
$[LSNa_n]_S$	concentration of LS in strip phase at time t (mgl^{-1})
l	thickness of membrane (μm)
m	distribution coefficient
V_F	volume of feed phase (ml)
V_S	volume of strip phase (ml)
δ	thickness of aqueous film
ε	porosity
τ	tortuosity

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CHAPTER-V

Liquid Membrane Separation with Environmentally benign Diluent

This chapter focuses on the possibility of using environment friendly diluent for the separation of lignosulfonate (LS) and mercury (II) through supported liquid membrane (SLM). Coconut oil is chosen as a representative diluent for such study. The solubility of LS and its compounds in coconut oil are found to be very poor and hence, only the separation of mercury through such SLM is investigated in this work. This chapter also presents the results and discussion of the various experiments performed on the separation of mercury with the help of such vegetable oil based SLM. Finally a comparison between organic solvent and coconut oil as diluent in the separation of mercury is presented.

5.1 Introduction

From the literature reported in the introductory discussion (Chapter-I, Section 1.3.1), it was observed that most of the LM based processes use organic solvents as the diluents. These solvents are generally flammable, volatile, toxic and their use leads to environmental and safety risks. One common problem, seldom encountered with SLM, is the instability of the membrane due to loss of liquid that oozes out from the membrane pores. The volatility of these organic solvents thereby increases its loss and that eventually makes the SLM more unstable. Moreover, the toxicity due to the strayed solvent is never desirable for obvious reasons. Thus, it is essential to look for environment friendly solvent for successful operation of SLM based unit. The room temperature ionic liquids (RTILs) are considered as green solvent due to their non-flammable nature and negligible vapor pressure. These ionic liquids

are generally expensive and their toxicity data are not available [1]. Moreover, the choice of a solvent also depends upon economic considerations. Vegetable oils are ideal replacement for the conventional volatile organic diluents. These vegetable oils are considered to be non-hazardous, naturally occurring, easily available, non-toxic, low cost, easily biodegradable and renewable sources. Very few literatures are available on the use of vegetable oil as diluent in LM processes. Separation of dyes and copper through SLM have been reported [2, 3] where vegetable oils such as palm oil, sunflower oil and coconut oil were used as diluents. Coconut oil has been observed to be stable diluent for the separation of Cu^{2+} from copper plating wastewater and about 60-70% removal of copper could be achieved.

In this study, the feasibility of using coconut oil as a diluent in the SLM for the removal of mercury is explored. Coconut oil and TOA were used as diluent and extractant respectively for the separation of mercury from its aqueous solution. An experimental investigation was carried out to describe the performance of coconut oil in the separation of mercury as diluent. Various polymeric support materials such as PE (polyethylene), PTFE (polytetrafloroethylene), PVDF (polyvinyldenefluoride) and Nylon 6, 6, were tested to select a suitable support for the SLM. The fundamental parameters such as feed pH, strip phase concentration, carrier concentration, feed concentration and feed to strip ratio that affect the transport of mercury through the SLM were investigated. Stability of the SLM was tested and finally, the performance of coconut oil in the separation of mercury as diluent was compared with two other organic solvents, *viz.* dichloroethane and heptane. The relevant work has already been published in the Journal of Membrane science [4].

5.2 Experimental

The experiments were carried out in the SLM set-up described in Chapter-II, Section 2.5.1. The SLM was prepared by immersing the micro-porous polymeric support in the LM containing coconut oil and TOA for 24 hours as described in Chapter-II, Section 2.5.3. The experiments were performed according to the procedure described in Chapter-II, Section 2.5.4.

5.3 Results and discussion

5.3.1 Choice of support material

The efficiency of various polymeric supports (Table 4.1, Chapter-IV) soaked in TOA and coconut oil was studied through a series of experiments. In each experiment, the initial concentration of Hg^{2+} in feed phase was 10 mgl^{-1} and its pH was 1.5. The carrier (TOA) concentration in the membrane was 4% (v/v) and concentration of NaOH at the strip phase was 0.1M. Each experiment was run for 3 h. The results are shown in Fig. 5.1. The separation of mercury is maximum with PTFE (0.2 µm) followed by PTFE (0.45 µm). PVDF, PE and Nylon 6,6 yield similar results but their performance is poorer than PTFE. The performance of PTFE (0.45 µm) is poorer than that of PTFE (0.2 µm) because larger pores of PTFE (0.45 µm) are unable to hold the LM for longer time [5]. To examine the physical stability of the support materials, they were dipped in the LM phase for a longer duration. After a period of 4 days few dark spots were observed on the PTFE membranes. This is due to physical deterioration of the membrane materials. Therefore, amongst the equally performing membranes *viz.* PVDF, PE and Nylon 6,6; PVDF is selected as the support for the separation of mercury for the remaining studies. The PVDF membrane support is found to be a stable support where both chemical degradation and solvent loss are observed to be marginal. The complete experimental analysis on this fact has been presented in the later part of this

Chapter (Section 5.3.6). Thus SLM configuration "PVDF-TOA-coconut oil" is selected for the subsequent studies.

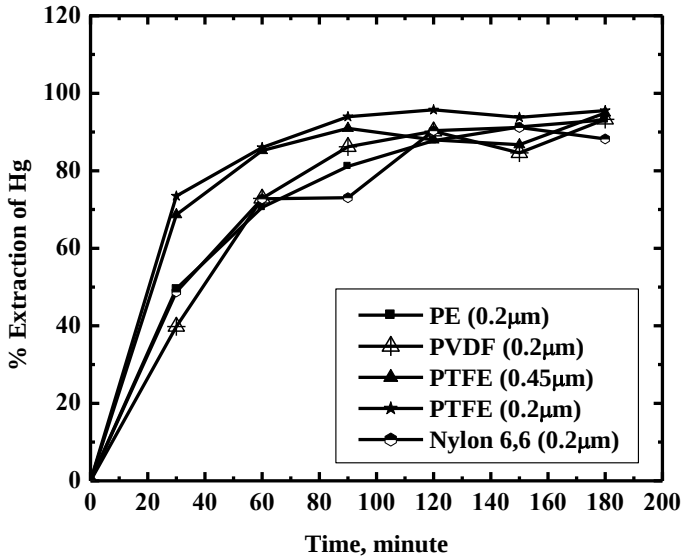

Figure 5.1 Percentage extraction of mercury through SLM of various polymeric supports (*feed concentration=10 mgl^{-1}, feed phase pH=1.5, volume of aqueous phases=140 ml, carrier (TOA) concentration=4% (v/v), strip phase=0.1 M NaOH, experiment time=3h, speed=500 rpm).*

5.3.2 Effect of feed phase pH

The transport process of mercury through SLM in presence of a base carrier such as TOA is driven by a concentration gradient of hydrogen ions. Thus, feed phase pH plays an important role in the transport of mercury through SLM. In order to assess the role, the pH of the feed phase was varied from 0.6 to 3.5. HCl was used to maintain the pH in the above range. The co-transport mode of mercury through the LM is described in Chapter-III and schematically represented in Fig 3.14. Here transport of the species i.e. hydrogen and mercury occur in the same direction. The experiments were carried out with 5 different pH values *viz.*, 0.6, 1, 1.5, 2.5 and 3.5 and the results are shown in Fig. 5.2. It is observed that effect of pH in the range of study on the extraction of mercury is insignificant. This is unlike the previous observation

[6] on extraction of mercury (Chapter-IV, Section 4.2.1) using dichloroethane as the organic phase, where the optimum pH had been 2.5 after 1h of experiment with 80 % extraction of mercury. Figure 5.2 shows that the percentage extraction of mercury is about 90-95% at a pH of 1 after 1.5h of experiment. Nonethless, subsequent experiments were performed maintaining a feed phase pH of 1.

It is worth mentioning here that coconut oil is basically long and medium chain triglycerides. The hydrolysis of triglycerides produces free fatty acid. However, the hydrolysis reaction occurs only at a high temperature (260-280ºC) [7]. The present reaction condition is far away from the reaction condition for hydrolysis. Therefore, contribution of such hydrolysis (if any at the ambient condition) towards the transport of mercury has been neglected in the present study.

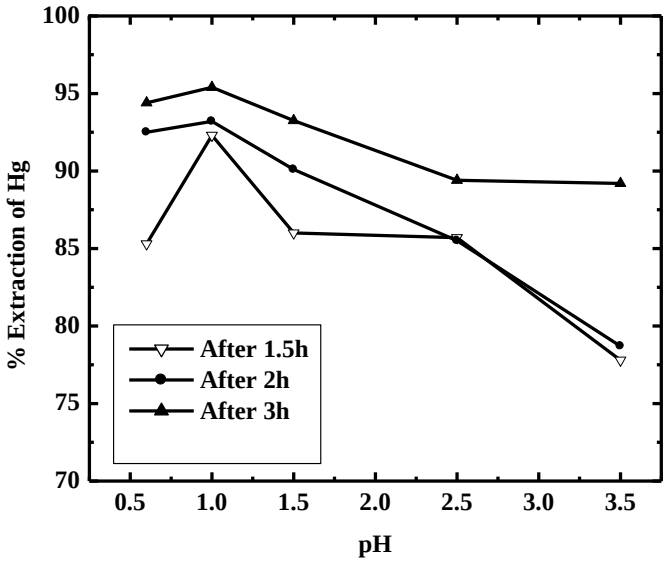

Figure 5.2 Effect of feed phase pH on extraction of mercury (*feed concentration=10 mgl^{-1}, volume of aqueous phases=140 ml, carrier (TOA) concentration=4% (v/v), strip phase=0.1 M NaOH, experiment time=3h, speed=500 rpm).*

5.3.3 Effect of strip phase concentration

The reaction at the membrane/strip interface plays an important role in the transfer of metal ions through LM. If the metal complex is not completely stripped, the membrane phase gradually becomes saturated with the complex and that may lower the permeation rate. The influence of the strip phase concentration on the extraction of mercury was studied by varying the NaOH concentration from 0.05M to 0.5M. Figure 5.3 reveals that with increase of NaOH concentration from 0.05 to 0.1M in the strip phase the extraction of mercury increases sharply. Extraction of mercury increases marginally with further increase of concentration of NaOH in the strip phase beyond 0.1M. As discussed earlier (Chapter-IV, Section 4.2.2) at a higher concentration of NaOH, more number of OH^- ions are added to the salt of mercury and it yields a precipitate of HgO or Hg [6, 8]. Because of this precipitation, membrane pore gets clogged and extraction rate decreases. Since, beyond a strip phase concentration of 0.1M NaOH no significant increase of extraction of mercury is observed, the subsequent experiments were carried out at a strip phase concentration of 0.1M NaOH.

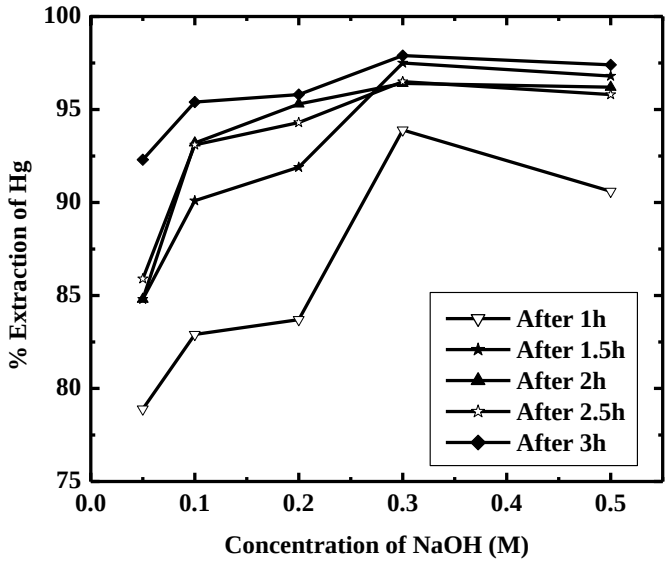

Figure 5.3 Effect of strip phase concentration on extraction of mercury (*feed concentration=10 mgl^{-1}, feed phase pH=1, volume of aqueous phases=140 ml, carrier (TOA) concentration=4 %(v/v), experiment time= 3h, speed=500 rpm).*

5.3.4 Effect of carrier concentration

The concentration of carrier in the membrane phase has significant effect on the transport of metal ions through SLM [9, 6]. The effect of carrier concentration on the transport of mercury was studied by varying the TOA concentration in the range of 0 to 6% (v/v). The results are presented in Fig. 5.4. Effect of carrier is observed to be distinct at the initial period of the experiments. Percentage extraction of mercury without carrier is much lower than that in presence of carrier till the first 90 minutes of the experiments. However, in the long run difference in percentage extraction with and without carrier is marginal, *e.g.* the separation achieved without carrier is about 91% after 3 h of operation whereas a carrier concentration of 1% and 4% would yield 93.2% and 95% extraction respectively after the same 3 h of operation. This phenomenon is unlike to the earlier observation (Chapter-IV, Section 4.2.3) with an SLM with dichloroethane as the solvent and TOA as the carrier, where presence of

carrier did improve the extraction performance [6]. Thus, coconut oil has been found to be a promising and environment friendly diluent that can be used without a carrier for the extraction of mercury from polluted water. The high rate of transport of mercury even without the carrier may be attributed to the following reasons.

Coconut oil is a mixture of saturated (91%) and monosaturated (7%) fatty acids such as lauric, palmitic, caprylic, oleic, linoleic *etc.* The composition of common coconut oil is presented in Appendix-VII (Table AVII.1). Oleic and linoleic acids are proved to be a good carrier of mercury if they are present in cationic form [10]. Mercury at increased acidic condition of feed phase (pH=1) is expected to be in the form of H_2HgCl_4 [6]. Some component of the coconut oil may form a co-ordination complex with the H_2HgCl_4 at the feed/membrane interface and diffuses through the LM towards the membrane/strip interface. At the membrane/strip interface it releases H_2HgCl_4 as $HgCl_4^{2-}$ to the strip solution and the free component diffuses back to the feed/membrane interface. However, there is no direct evidence of the component responsible for such transformation. It may be noted from the figure (Fig. 5.4) that the performance of coconut oil with carrier after 1.5h of experiment has been marginally better than that of coconut oil without the carrier. This might be due to the formation of amine complex with the present $HgCl_4^{-2}$ at the feed/membrane interface. This is an additional contribution to the transport along with the coconut oil without carrier. As there was no significant increase of extraction of mercury beyond 1.5h in the range of carrier concentration studied, further experiments were carried out at a lower carrier concentration of 1%.

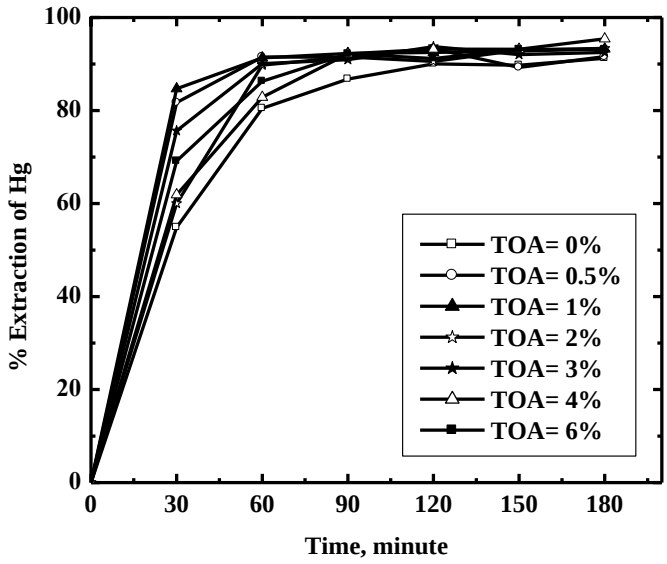

Figure 5.4 Effect of carrier concentration on extraction of mercury (*feed concentration=10 mgl^{-1}, feed phase pH=1, volume of aqueous phases=140 ml, strip phase=0.1M NaOH, experiment time=3h, speed=500 rpm).*

5.3.5 Effect of feed concentration and feed dose

The effect of initial feed concentration on the transport of mercury through SLM was studied by varying the feed concentration in the range of 0.43 mgl^{-1} to 10.5 mgl^{-1}. The results are shown in Fig. 5.5. From the figure it is observed that with decrease of initial feed concentration the extraction of mercury also decreases. At higher initial feed concentration (10.5 mgl^{-1}) the percentage extraction of mercury is about 93.2%, however it decreases to 75% when the initial feed concentration decreases to 0.43 mgl^{-1}. A similar trend was also observed in the previous work (Chapter-IV, Section 4.2.4) on separation of mercury using dichloroethane as diluent [6]. The above fact could be attributed to the following two reasons:

- The extraction process depends on the feed phase pH. With changes of initial mercury concentration in the feed the amount of HCl requirement (pH) also changes. In the above study all the experiments were carried out at the feed phase pH of 1 which

yielded maximum extraction of mercury (Fig. 5.2) for the initial feed concentration of 10 mgl^{-1}.

- At lower initial feed concentration amount of excess chloride ions is more compared to at higher initial feed concentration. Increase in chloride ions possibly inhibits the interfacial reaction at the feed/membrane interface. Therefore the percentage extraction of mercury is low at lower initial feed concentration.

To analyze the enrichment of the strip phase with mercury concentration the same strip phase was reused for repeated experiments with several dose of fresh feed phase. The experiment was continuously repeated at the selected conditions (*viz.* feed phase concentration=14.6 mgl^{-1}, pH of 1, strip phase concentration=0.1M NaOH) for six runs without changing the strip phase. As major amount of the mercury has been found to be separated within 1h in the previous experiments, hence each run of fresh feed for a duration of 1h has been considered. The results are shown in Fig. 5.6. From the figure it is observed that the percentage extraction of mercury in each run is almost same. It reveals the practical applicability of such SLM in concentrating mercury from a dilute feed stream to the strip phase. Thus TOA-coconut oil LM has efficiency of uphill transport and achieves a concentration in the strip phase much more than the feed phase.

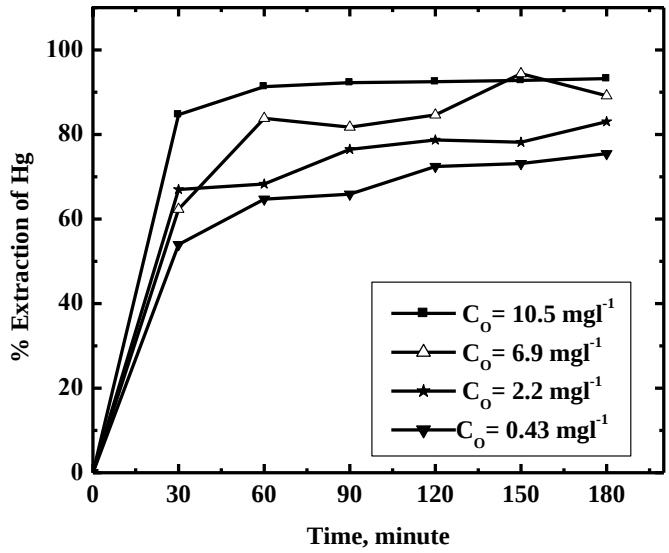

Figure 5.5 Effect of initial feed concentration on the extraction of mercury (*strip phase=0.1M NaOH, feed phase pH=1, volume of aqueous phases=140 ml, carrier concentration=1 %(v/v), experiment time=3h, speed=500 rpm).*

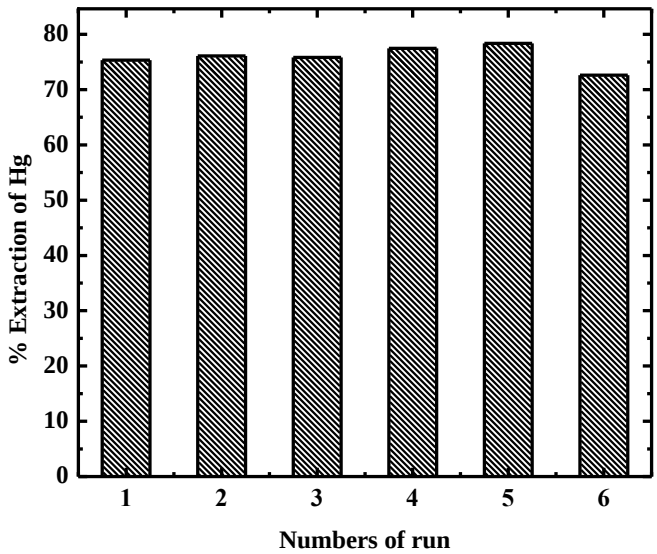

Figure 5.6 Effect of feed dose (*strip phase=0.1M NaOH, feed concentration=14.6 mgl^{-1}, feed phase pH=1, volume of aqueous phases=140 ml, carrier concentration=1 %(v/v), speed= 500 rpm***).**

5.3.6 Stability of SLM

A major drawback of the SLM based processes is its low stability. Because of this drawback, most of the SLM based processes cannot be scaled up to the industrial level. As discussed in Chapter-IV, Section 4.1.8, the efficiency of these membranes deteriorates after prolonged use. And that happens due to several phenomena such as chemical degradation, loss of membrane solvent and/or carrier, formation of emulsion, *etc*. [5, 11]. In order to study integrity of the support materials, the chemical resistance of PVDF membranes against TOA/coconut oil was tested over a period of 15 days by keeping it dipped in a solution of 1% (v/v) TOA in coconut oil. Experiment was performed with feed phase concentration of 10 mgl^{-1} and pH of 1. The strip phase concentration is fixed at 0.1M NaOH. Figure 5.7(a) shows that there was no significant change in the extraction even after immersion time of 15 days. This revealed that the integrity of the support material was not affected during this period.

In order to study the stability of the SLM from the concept of membrane liquid loss [10] as discussed in Chapter-IV, Section 4.1.8. Experiment was performed with feed phase concentration of 10 mgl^{-1} and pH of 1.07. The strip phase concentration was fixed at 0.1M NaOH (pH=12.67). The results are reported in Fig. 5.7(b). From the figure it is observed that even after 98 hours of operation, the change of feed phase pH is very small. The minor change in pH (by 0.4) is basically due to protonation of the amine molecules. This reveals that the "TOA-coconut oil" LM in the PVDF membrane support have reasonably good stability.

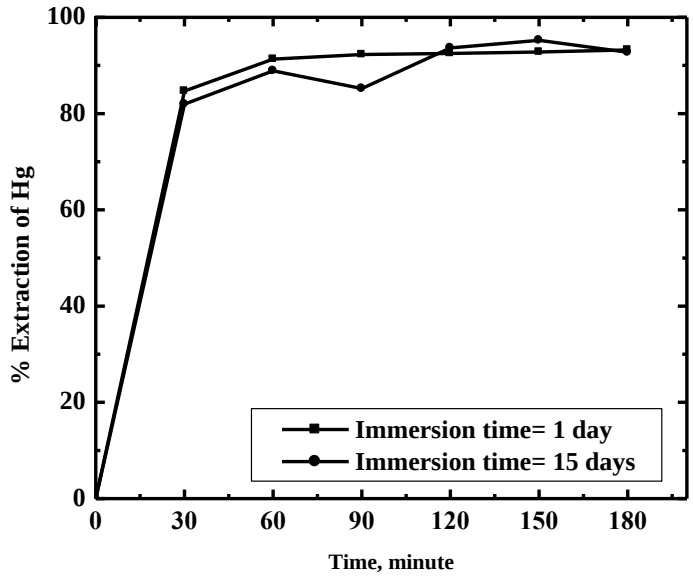

Figure 5.7(a) Integrity of the support material (*strip phase=0.1M NaOH, feed concentration=10 mgl^{-1}, feed phase pH=1, volume of aqueous phases=140 ml, carrier concentration=1 %(v/v), speed=500 rpm).*

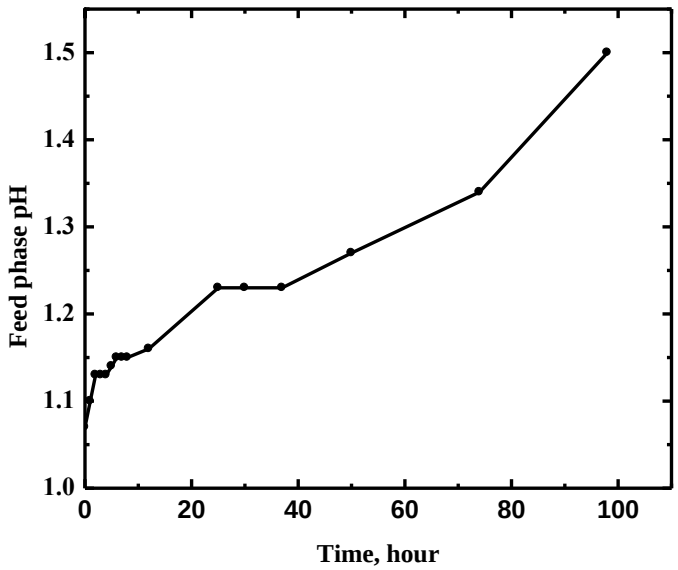

Figure 5.7(b) Stability of SLM (*strip phase=0.1M NaOH, feed concentration=10 mgl^{-1}, feed phase pH=1, volume of aqueous phases=140 ml, carrier concentration=1 %(v/v), speed=500 rpm).*

5.3.7 Organic solvent versus vegetable oil as diluents in the extraction of mercury

In this section, a comparative analysis between the efficiencies of the three diluents, *viz*., environmentally benign coconut oil and organic solvents dichloroethane and heptane, has been presented. The experiment was performed with feed concentration of 10 mgl^{-1} and pH of 1. The strip phase concentration and carrier concentration were fixed at 0.1M NaOH and 1% TOA respectively. The results are presented in Fig. 5.8. From the figure, it is observed that the extraction of mercury is maximum with coconut oil followed by dichloroethane and heptane. Hence, coconut oil is found to be the most efficient and environment friendly diluent among the three, for the separation of mercury.

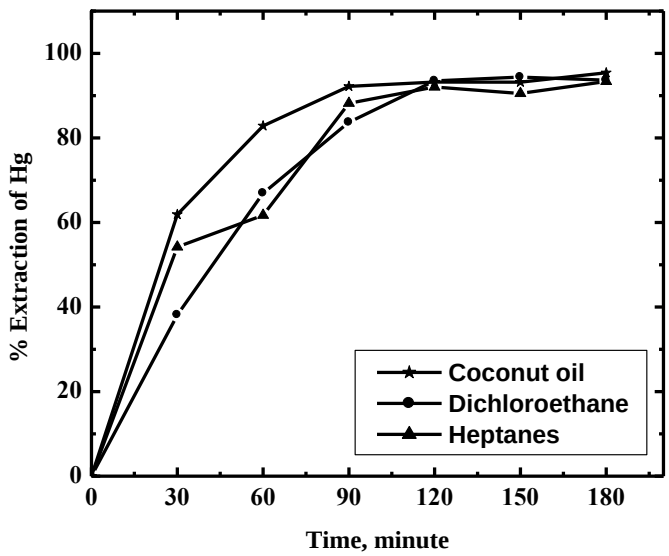

Figure 5.8 Performance of various diluents in the transport of mercury through the SLM (*feed concentration=10 mgl^{-1}, feed phase pH=1, strip phase=0.1M NaOH, volume of aqueous phases=140 ml, carrier concentration=4 %(v/v), speed=500 rpm).*

5.4 Summary of coconut oil based SLM separation

- The solubility of LS-amine complex in coconut oil is very low. Hence coconut oil based SLM process is not suitable for the separation of LS.
- The SLM configuration "PVDF-coconut oil-TOA" is found to be the best option for the separation of mercury.
- Carrier has no significant effect on the transport of mercury in the range of experiments conducted. About 91% of mercury is removed without carrier.
- Coconut oil shows better performance as diluent than organic solvents such as dichloroethane and heptane.

Abbreviation

LS	lignosulfonate
LM	liquid membrane
PE	polyethylene
PTFE	polytetrafluroethylene
PVDF	polyvinyldenefluoride
RTIL	room temperature ionic liquid
SLM	supported liquid membrane
TOA	trioctylamine

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CHAPTER-VI

Separation using Emulsion Liquid Membrane

This chapter focuses on the separation of lignosulfonate (LS) using emulsion liquid membrane (ELM). It presents the results and discussion of the experiments carried out to separate LS with the help of ELM. The effects of the pertinent parameters such as surfactant concentration, phase ratio, strip phase concentration, carrier concentration and treat ratio on the transport of LS through the ELM are studied and discussed. It also presents the performance of the developed ELM on extraction of LS from industrial black liquor.

6.1 ELM based separation of LS

From the previous discussion (Chapters-III and IV), it is evident that the BLM and SLM modules containing TOA as carrier and 1,2-dichloroethane as solvent effectively separated LS from its aqueous solution. About 98% of separation is achieved with BLM and 90% with SLM at optimum conditions [1, 2]. From the introductory discussion and review of the literature reported so far (Chapter-I) it has been observed that there are several studies on ELM based separation of mercury but no report is available yet on the ELM (one of the most feasible and industrially applied LM processes) based separation of LS. In this work ELM technique was applied for LS separation to study its feasibility for such separation. The effects of various parameters on the formation of W/O emulsion and on the transport of LS through the ELM are discussed. Experiments were carried out in the ELM set-up as described in Chapter-II, Section 2.6.1.

6.1.1 Choice of surfactant and surfactant concentration

Nature of surfactant and its concentration play an important role in the ELM separation processes. The stability and types of emulsion depend on the nature of the surfactant as well as its concentration. Span 80 (HLB=4.7) is a widely used surfactant for the preparation of W/O type emulsion [3] in various ELM processes. In this study, two nonionic surfactants are considered. One is the most widely used Span 80 and the other a nonconventional surfactant *i.e.* PEG 20,000. PEG acts as a bifunctional surfactant in the extraction of some metal ions such as Zn^{+}, Mo^{+4}, Co^{+2}, Li^{+}, *etc*. [4]. In such separations, PEG functioned as a carrier as well as a surfactant. However, in the separation of LS, PEG acts only as surfactant as discussed later in Section 6.1.4. Figure 6.1 shows the separations achieved with various concentrations of Span 80. The experiments were carried out with feed phase concentration of 100 mgl^{-1} LS and strip phase concentration of 0.1M NaOH. As the separation of LS is found to be maximum at a pH of 2 (Chapter-III, Section 3.1.2.2), the feed phase pH was maintained at 2 by adding required quantity of HCl [1]. From the figure it is observed that about 96% of LS is separated within 5 minutes. However, with time the LS concentration in the feed phase increases and this is more prominent at higher concentration of Span 80. It is known that Span 80 affects solute transport because of its influence on water transport and swelling via osmotic effects [5]. Breaking of emulsion takes place with time due to swelling and hence LS concentration in the feed increases. Moreover, Span 80 is chemically unstable and undergoes hydrolysis reaction in moderate acidic or basic media [3]. Because of these drawbacks of Span 80, another surfactant *viz.*, PEG 20,000 is considered in the present study. Figure 6.2 shows the extraction of LS at various PEG concentrations. From the figure it is observed that the extraction of LS increases with time and it becomes almost constant after 20 minutes of operation. However in case of Span 80 (at higher concentration, Fig. 6.1) the extraction of LS decreases with time. Though at lower concentration of Span 80 the extraction becomes

constant after 5 minutes of experimentation, the emulsion is not stable for longer time. Hence, PEG is selected as the surfactant for this separation. Concentration of the surfactant is of critical importance in ELM separation processes. It ensures stability of the emulsion during the extraction. At the same time, it increases the viscosity of the membrane phase too that leads to increase in mass transfer resistance. With increase of PEG concentration up to 4% (w/v), the extraction of LS increased. The reduction of extraction when PEG concentration was more than 4% (w/v) is due to the increase of viscosity of the membrane phase. However, to ensure the stability of the ELM the subsequent experiments were carried out at a higher PEG concentration of 5% (w/v).

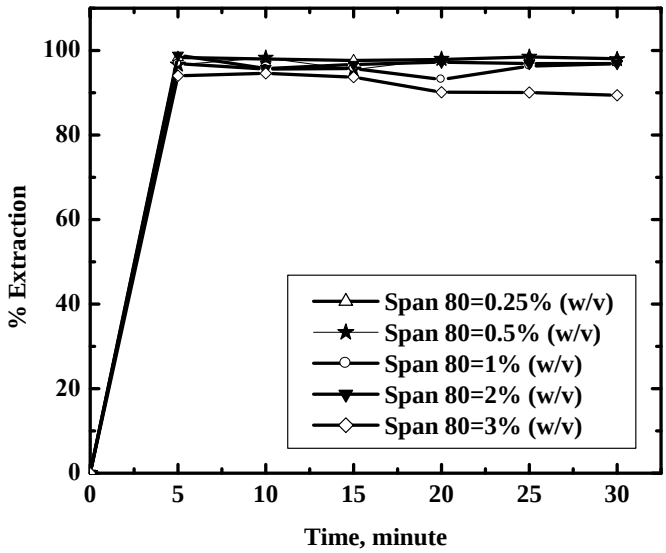

Figure 6.1 Effect of Span 80 concentration on the transport of LS ***(****feed concentration=100 mgl^{-1}, pH=2, feed volume=100 ml, phase ratio=1.5:1, strip concentration=0.1M NaOH, TOA=2%, treat ratio=50).*

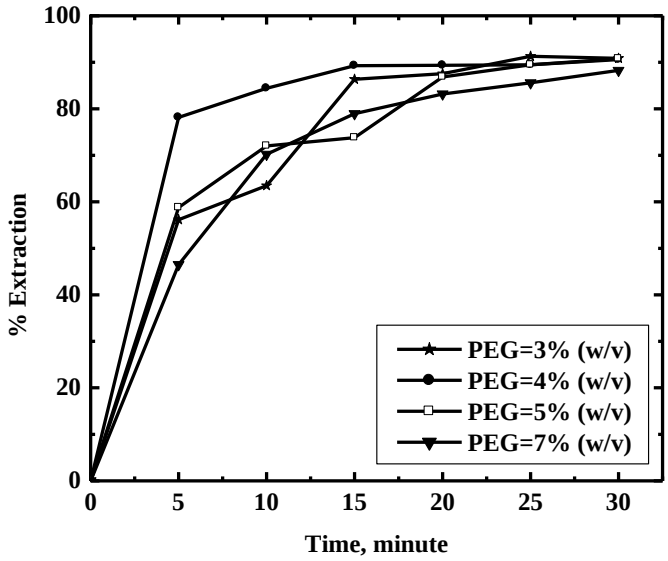

Figure 6.2 Effect of PEG 20,000 concentration on the transport of LS (*feed concentration=100 mgl^{-1}, pH=2, feed volume=100 ml, phase ratio=1.5:1, strip concentration=0.1M NaOH, TOA=2%, treat ratio=50).*

6.1.2 Effect of phase ratio

The volume ratio of membrane phase to strip phase is termed as phase ratio. This ratio should be maintained properly to have a stable and effective emulsion. The effect of the phase ratio on the extraction of LS is shown in Table 6.1. The experiments were carried out with 2% (v/v) TOA and 5% (w/v) PEG in membrane phase and with 0.1M NaOH as strip phase. The ratio of volume of emulsion to feed phase was maintained at 2:100. From the Table it is observed that with increase of phase ratio beyond 1:1 the transport of LS decreases. With the increase of phase ratio the absolute amount of each component in the membrane phase is raised and hence extraction should increase [6]. Although at higher phase ratio capacity of the membrane phase increases, at the same time membrane thickness and viscosity of the emulsion phase also increase. This increases the membrane phase resistance to transport and also hampers the intermixing in the organic membrane phase [7]. This phenomenon becomes more predominant particularly for macromolecules like LS. Hence the merit of incorporation

of relatively more membrane volume could not be extracted at higher phase ratio. It may be seen from the Table 6.1 that with increase of phase ratio, extraction of LS remains more or less same during 20-30 minutes of experiment. However, the subsequent experiments were carried out at a phase ratio of 1.5:1.

Table 6.1 Effect of phase ratio

Experimental conditions	Time, minute	% Extraction of LS		
		$V_{membrane}$:V_{strip} =1:1	$V_{membrane}$:V_{strip} =1.5:1	$V_{membrane}$:V_{strip} =2:1
PEG=5% (w/v), TOA=2%	15	86.2	73.8	71.3
$C_{LS,0}$=100 mgl^{-1}, feed phase pH=2	20	88.6	86.8	84.0
V_{Feed}=100 ml, Treat ratio=50	25	90.3	90.1	89.8
Strip phase concentration=0.1M NaOH	30	93.4	92.2	91.6

6.1.3 Effect of strip phase concentration

The influence of NaOH concentration in the strip phase on the transport of LS was studied in the range of 0.1M NaOH to 0.75M NaOH. The results are represented in Fig. 6.3. With increase of NaOH concentration the transport of LS increases and attains a maximum at a strip phase concentration of 0.4M NaOH. The mechanism of LS transport in presence of carrier TOA, is discussed in chapter-III and IV.

According to Eq(3.3) (Chapter-III, Section 3.1.1), with increase of NaOH concentration in the strip phase the extraction of LS should increase. The decrease of extraction occurs at higher NaOH concentration due to the formation of unstable emulsion [7]. Increase of NaOH concentration in the strip (internal) phase, increases the osmotic pressure difference between the external and internal phases, which eventually causes membrane swelling. Similar effect

of NaOH concentration was also observed in the SLM based separation of LS discussed in Chapter- IV, where recovery of LS was reduced beyond a strip phase concentration of 0.5M NaOH [2]. Further experiments were carried out at a strip phase concentration of 0.2M NaOH, as the extraction of LS in the range of 0.2-0.4M NaOH is almost same after 15 minutes of experiment.

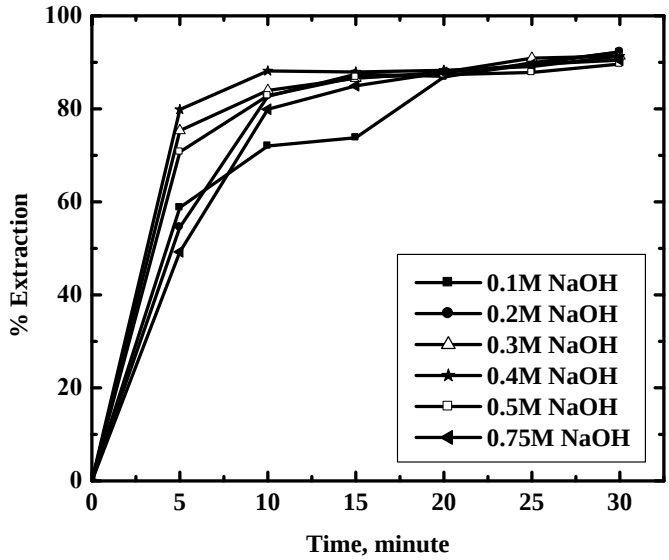

Figure 6.3 Effect of strip phase concentration on extraction of LS (*PEG=5% (w/v), feed concentration=100 mgl^{-1}, pH=2, feed volume=100 ml, Phase ratio=1.5:1, TOA=2%, treat ratio=50).*

6.1.4 Effect of carrier concentration

In a carrier mediated ELM process the carrier plays an important role. The influence of TOA (carrier) concentration on the extraction of LS was studied in the range of 0% to 5% (v/v). The results are reported in Fig. 6.4. The figure reveals that the transport of LS is negligible in the absence of carrier. This indicates the function of PEG only as a surfactant in the present study. With the increase of carrier concentration in the membrane phase the extraction of LS increases. It is in good agreement with Eq (3.2) (Chapter-III, Section 3.1.1). Increase of TOA

should enhance the extraction of LS as more numbers of TOA molecules get associated with the LS and form complex that is diffused through the membrane phase [1]. However beyond 2% (v/v) TOA, the rate of extraction is more or less constant. This is due to the increase of viscosity of the membrane phase at higher TOA concentration [1].

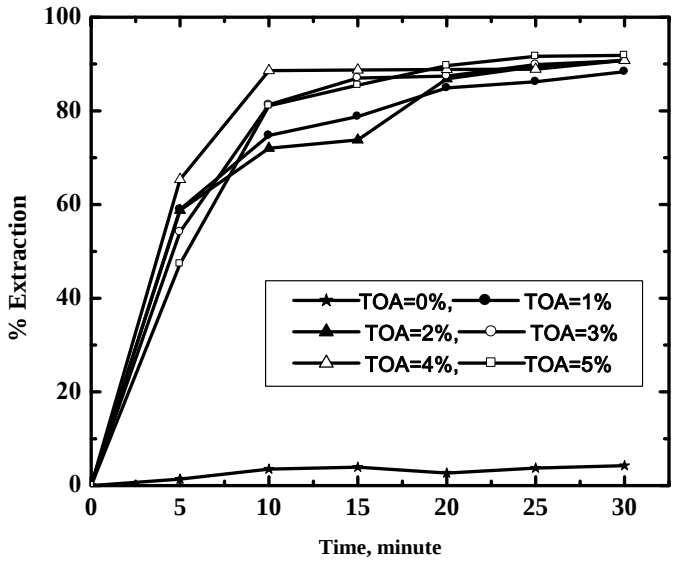

Figure 6.4 Effect of carrier concentration on the extraction of LS (*PEG=5% (w/v), feed concentration=100 mgl^{-1}, pH=2, feed volume=100 ml, Phase ratio=1.5:1, strip concentration=0.2M NaOH, treat ratio=50).*

6.1.5 Effect of initial feed concentration

The influence of initial feed concentration on the extraction of LS through ELM was studied in the concentration range of 117 mgl^{-1} to 1223 mgl^{-1}. The experiments were carried out at a TOA concentration of 4 % (v/v) and treat ratio (feed volume/ emulsion volume) of 100:2. The results are shown in Fig. 6.5. From the figure it is observed that with increase in initial feed concentration up to 378 mgl^{-1}, the transport of LS is not affected much, however for feed concentration above 378 mgl^{-1} the extraction rate decreases. At high initial feed concentration

the membrane gets saturated and hence the extraction rate decreases. A similar finding (Chapter-III, Section 3.1.3.3) was reported in the BLM separation of LS [1].

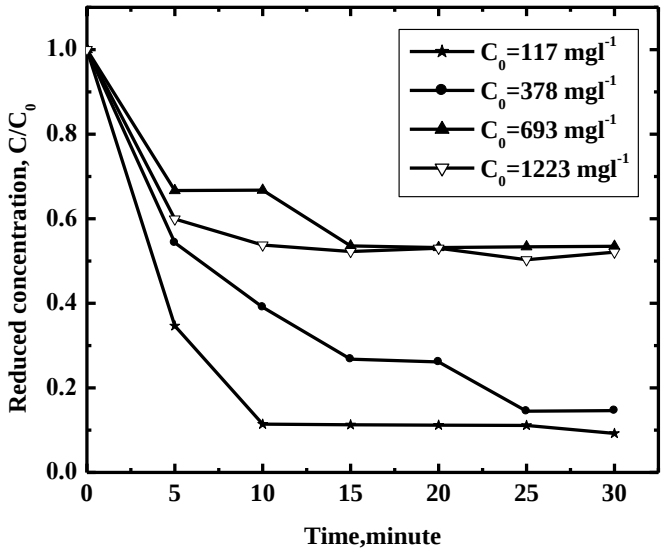

Figure 6.5 Effect of initial feed concentration (*PEG=5% (w/v), feed pH=2, feed volume=100 ml, Phase ratio=1.5:1, strip concentration=0.2M NaOH, TOA=4% (v/v), treat ratio=50).*

6.1.6 Effect of treat ratio

The volume ratio of feed to emulsion is referred as treat ratio. The influence of treat ratio on the transport of LS is shown in Fig. 6.6. From the figure it is observed that the extraction of LS is almost same for the treat ratios 50, 25 and 20 and the extraction decreases when the treat ratios are lowered further *i.e.* 13.33 and 10. This behavior can be explained from the following two opposite phenomena occurring simultaneously.

- Decrease of treat ratio in turn increases the membrane and internal phase amount, amount of total carrier in the membrane phase and membrane phase surface area for transport. This would enhance the permeation and stripping of LS [4, 7].

- Increased coalescence of emulsion globules with increase in emulsion volume reduces the mass transfer area as well as the rate of extraction. In that case, higher extraction time is needed. And with increase in extraction time, emulsion breakage increases [4]. This in turn reduces the permeability and stripping of LS.

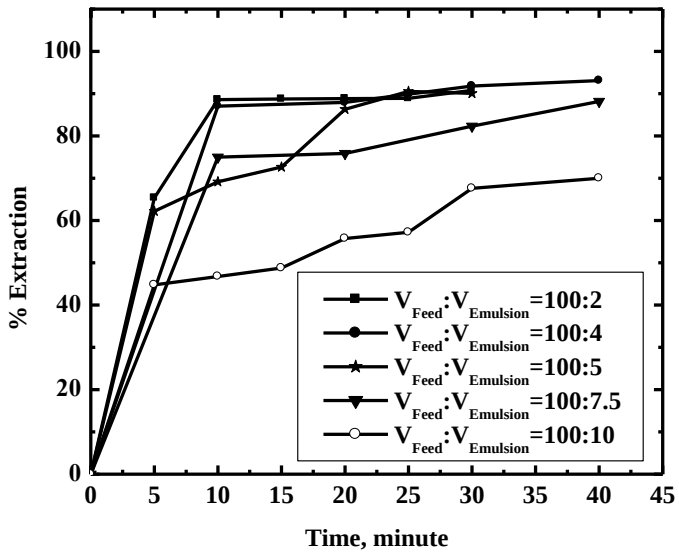

Figure 6.6 Effect of treat ratio on the extraction of LS (*PEG=5% (w/v), feed concentration=100mgl^{-1}, pH=2, feed volume=100 ml, Phase ratio=1.5:1, strip concentration=0.2M NaOH, TOA=4% v/v).*

6.1.7 Extraction of LS from industrial black liquor (a case study)

The above ELM process was applied to industrial black liquor collected from sulphite pulping unit of a pulp and paper plant in order to study the efficiency of the process in the extraction of LS. The experiments were carried out with diluted (500 times of the original liquor) black liquor (pH=10) and the pH was adjusted to 2 by adding HCl. The carrier concentration and strip phase concentration were maintained at 4% (v/v) and 0.2M NaOH, respectively. The experiments were carried out at two treat ratios *viz.* 50 and 20. The results

are reported in Fig. 6.7. From the figure it is observed that about 85-86% of LS is extracted within a period of 30 minutes. Similar to the synthetic LS solution, the separation achieved at the treat ratios 50 and 20 is almost same.

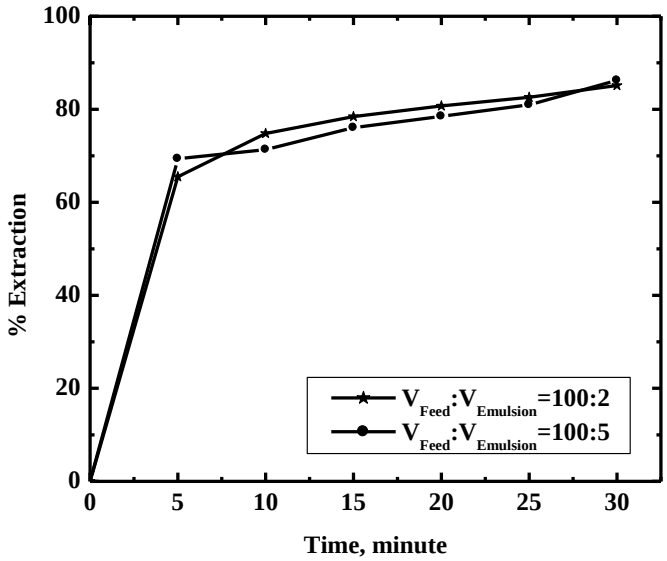

Figure 6.7 Separation of LS from industrial black liquor (*PEG=5% (w/v), feed pH=2, feed volume=100 ml, Phase ratio=1.5:1, strip concentration=0.2M NaOH, TOA=4%)***.**

6.2 Summary of ELM separation of LS

- The ELM containing TOA and dichloroethane as LM and PEG 20,000 as surfactant is efficient in the extraction of LS from aqueous solution as well as from industrial black liquor.

- About 91 % extraction of LS is achieved within a period of 15 minutes and at optimum condition.

- Separation of LS is more with Span 80 (96% in 5 minutes) than PEG 20,000 (91%). Because of the high swelling nature, Span 80 cannot be chosen as a right surfactant in this separation process.

Abbreviation

BLM	bulk liquid membrane
ELM	emulsion liquid membrane
LS	lignosulfonate
LM	liquid membrane
PEG	polyethylene glycol
SLM	supported liquid membrane
Span 80	sorbitrate monoleate
TOA	tricotylamine

Nomenclature

$C_{LS,o}$	initial concentration of LS in the feed, mgl^{-1}
$V_{membrane}$	volume of membrane phase, ml
V_{Feed}	volume of feed phase, ml
V_{Strip}	volume of strip phase, ml
$V_{Emulsion}$	volume of emulsion phase, ml

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CHAPTER-VII

Conclusion and Scope of Further Research

This chapter summarizes the inferences drawn from the present research work and provides recommendations towards future direction.

7.1 Conclusion

In the present work the performances of liquid membrane (LM) based processes in the separation of pollutants having wide differences in their nature and sizes from wastewater were investigated. The pollutants, namely, lignosulfonate (LS) and mercury (II) were separated from aqueous solution using various LM techniques such as bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM). The efficiency of these LM techniques in the separation of the said pollutants was then measured and compared through a series of experiments. The major conclusions are summarized below:

- Selection of LM suitable for the separation of LS as well as mercury was carried out through a series of equilibrium studies. The LM combination "dichloroethane-trioctylamine (TOA)" showed the encouraging result in the separation of both the pollutants. Hence the LM comprising of dichloroethane and TOA was selected as the suitable LM to study the performance of the various LM modules.

- BLM separation study is very important as it helps in understanding the separation feasibility of a LM process for any system of concern. It also provides the useful equilibrium and kinetic parameters necessary for mass transfer studies. Strip phase

concentration, carrier concentration and stirring speed have significant impact on the transport of LS and mercury and it is found to be favoured by acidic pH. The BLM module has been found to be equally effective for high as well as low concentrations of pollutants.

- BLM is in general useful only for lab scale study and its up-gradation to a pilot/commercial scale is ineffective due to much lower value of surface area to volume ratio. Hence, the efficiency of a SLM module in the separation of LS, mercury and their mixture was investigated. Various supports impregnated with the LM, dichloroethane and TOA were examined to design a suitable SLM module. The SLM combination "Nylon 6,6-TOA-dichloroethane" is found to be suitable for this purpose. About 88-90% separation of the pollutants in their pure form was achieved with this module. The extraction efficiency of the mixture was reduced to 50-52% due to increased number of ions against the fixed area of the feed/ membrane interface.

- Due to the strict environmental regulations and instability of SLM, it is important to look for an environment friendly LM for the above separation. The performance of coconut oil with/without carrier (TOA) as LM is investigated for this purpose. The SLM configuration "PVDF-TOA-coconut oil" is found to be efficient in the separation of mercury and is capable of extracting 91% mercury without carrier.

- Stability is an important criterion of SLM for its application to be feasible. The present SLM "Nylon 6,6-TOA-dichloroethane" is found to be reasonably stable up to 10 hours of operation with membrane life time of 48 hours. The SLM "PVDF-TOA-coconutoil" is stable for more than 98 hours.

- Extraction of LS from aqueous as well as from industrial black liquor performed with the ELM module containing PEG 20,000 as surfactant, is quite encouraging.

- Separation of LS is performed using all the three types of LM based processes *i.e* BLM, SLM and ELM. The extraction efficiency of all the three types of LM processes is more or less same. Percentage recovery of LS in BLM is slightly higher (50%) in comparison to SLM (43%). In comparison to BLM and SLM, ELM separation of LS is much faster. However, all these processes have their inherent merits and demerits. BLM process is the simplest of all the three LM based processes. However it can not be applied for large scale applications. SLM are also simple in design and require less volume of organic (LM) phase compared to BLM and ELM and thus provide the advantage of using expensive carrier. However, it suffers from the problem of low stability which makes it difficult to implement in large scale applications. ELM process has high efficiency due to large surface area available for mass transfer, simple configuration, and recyclable membrane phase. Though it posses many potential advantages, it suffers from the drawbacks such as formulation of emulsion, demulsification, separation of surfactants, *etc*. It can be concluded that though SLM and ELM are equally efficient in the separation and preconcentration of LS. Choice of suitable one depends on a techno-economic analysis of both the processes.

7.2 Recommendations towards future direction

- The bulk liquid membrane module developed in the present work gives 98% separation of lignosulfonate. However the recovery achieved is 70%. Further study can be carried out in search of an efficient stripping agent that can give better recovery of LS.

- The effect of temperature on the transport of LS through BLM was studied in the range of 25-45ºC. This may be carried out in a wider range to generate rigorous experimental data so that a kinetic model can be developed which gives many useful data on extraction of LS.

- The emulsion liquid membrane separation of LS focuses only on extraction. Further work needs to be carried out to study the effect of various parameters on recovery of LS with the application of proper demulsifying device. The effect of some major parameters such as size of emulsion droplets, stirring speed, time of emulsification etc., on the transport of LS through ELM is yet to be studied. This work can be extended to incorporate the above effects in future. Based on these experimental data a model can be developed to represent the system.

- The flat sheet SLM module designed in the present work shows encouraging result in the separation and recovery of LS as well as mercury (II) from aqueous solution. A similar study can be carried out in other membrane modules such as hollow fiber, spiral wound and series SLM module and thus the process parameters can be optimized. Further research is needed to improve the stability of the SLM.

- All the experiment in this research work is carried out in batch mode. The efficiency of a continuous mode can be studied in future.

- The efficiency of the SLM module designed in the present work may be examined for real wastewater that contains various components other than LS and mercury. This will help in improving the present module as well as in optimizing the process and thereafter scaling up for large scale applications.

- Further research is necessary to develop an environment friendly liquid membrane based process for the separation of LS.

APPENDIX

Appendix-I

Analysis of LS using UV-vis spectrophotometer

An UV-vis spectrophotometer (Perkin Elmer, Model: Lamda-35) was used to measure the concentration of lignosulfonate (LS) in aqueous solution. The working principle and details of the analysis procedure are discussed in the following sections.

AI.1 Working principle of UV-vis spectrophotometer

The working principle of UV-vis spectrophotometer is based on the **Beer-Lambert's** Law. The instrument operates by passing a beam of light (monochromatic) through a sample and measuring the intensity of the transmitted light by a detector. When light incidents on a sample a portion of the light is absorbed by the sample. The amount of light absorbed can be written in terms of Lambert's law as follows [1]:

If "I_0" is the intensity of the incident light falling on the sample of thickness "*l*", "I" is the intensity of the transmitted light then according to Lambert's law,

$$A = \log \frac{I_0}{I} = Kl \qquad \text{(AI.1)}$$

Where, *A* is the absorbance and *K* is the constant for the wavelength and the absorbing sample.

According to Beer's law,

$$K = ac \qquad \text{(AI.2)}$$

Where "*a*" is the molar absorption coefficient and "*c*" is the concentration of the sample.

Combination of Eqs. (AI.1) and (AI.2) gives the Beer-Lambert's law as

$$A = \log \frac{I_0}{I} = acl \qquad \text{(AI.3)}$$

If wave length of the incident light and thickness of the absorbing medium (i.e. l) is constant, then the Beer-Lambert's law can be written as

$$c \propto \log \frac{I_0}{I} \qquad \text{Or,} \quad c \propto A \qquad \text{(AI.4)}$$

Therefore, by plotting the absorbance A as ordinate and the concentration as abscissa, a straight line passing through origin can be obtained. This straight line is known as calibration curve and the concentration of the unknown sample can be determined from this calibration curve by knowing the absorbance of the sample. The calibration curve is reported in Chapter-II, Section 2.3.1 of the thesis. However, this law is applicable only for dilute solutions. The reproducibility of the UV-vis spectrophotometer (Perkin Elmer, Model: Lamda-35) is ±0.002 at 1 absorbance level [2].

AI.2 Procedure for LS analysis

For determining the concentration of LS in the unknown sample by UV-vis spectrophotometer the following steps were followed:

- The wavelength for LS solution was first determined by scanning. For this, 2-4 samples of known concentration of LS were prepared. Then scanning was performed for each sample (over a wide range of wavelength i.e. 190-900) taking water as the blank. The wavelengths that gave the maximum peak were then determined. It was observed that for each of the sample the maximum peak was obtained at 280 nm wavelength.

- The calibration curve was then prepared by measuring the absorbance of known samples of LS at a constant wavelength of 280 nm. For this, ten samples having various concentrations of LS (10-100 mgl^{-1}) were prepared and their absorbance values were measured taking water as the blank. Those absorbance values were then plotted against the known concentrations and a straight line (slop=0.0171) passing through the origin was obtained. The concentration of the unknown sample was then calculated as follows:

$$c = \frac{A}{0.0171} \tag{AI.5}$$

Where, c is the concentration of the unknown sample and A is the absorbance.

In case of concentrated sample, it was diluted before analysis to reduce the concentration within the range of the calibration curve. The actual concentration was then determined by multiplying with the dilution factor.

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Appendix-II

Sample calculation of viscosity of 1, 2-dichloroethane-trioctylamine solution

The viscosity of the 1, 2-dichloroethane-trioctylamine solution was measured by measuring the efflux time as follows:

$$\mu_{s_i} = \frac{\rho_s t_s}{\rho_w t_w} \mu_w \qquad \text{(AII.1)}$$

Where, μ_s= viscosity of solution, c.p

μ_w= viscosity of water at particular temperature, c.p

ρ_s=density of solution, g/cc

ρ_w=density of water, g/cc

t_s=efflux time of solution, minute and t_w=efflux time of water, minute.

i=concentration of trioctylamine in the solution, % (v/v).

Using Eq. (AII.1) the viscosity of 1, 2-dichloroethane-trioctylamine solution (μ_1) containing 1% (v/v) trioctylamine , was determined as follows:

$$\mu_1 = \frac{\rho_s t_s}{\rho_w t_w} \mu_w = \frac{1.325 \times 3.18}{1.068 \times 4.5} = 0.8767 \text{ cp}$$

Appendix-III

Analysis of mercury (II) concentration using Atomic Absorption Spectrometer (AAS)

Atomic absorption spectrometer (Varian Australia, Model: AA240FS) was used to measure concentration of mercury in aqueous solution. The working principle and procedure are elaborated in the subsequent sections.

AIII.1 Working principle of AAS

The principle of AAS is based on Beer-Lambert's law. The electrons of the atoms of an element can be exited to higher orbitals by absorbing light of a given wavelength. This amount of energy (or wavelength) is specific to a particular electron transition in a particular element. As the quantity of energy put into the flame is known, and the quantity remaining at the other side (at the detector) can be measured, it is possible, from Beer-Lambert law, to calculate how many of these transitions took place [1].

To analyze a sample in AAS, the sample solution is first vaporised and then atomized transforming it to unexcited ground state atoms, which absorbs light at specific wavelengths. A light beam from a hollow cathode lamp whose cathode is made of the element to be detected is passed through these atoms. Radiation is absorbed, transforming the ground state atoms to an excited state. The amount of radiation absorbed depends on the amount of the sample element present [2]. Working principle of AAS can be represented by a block diagram as shown in Fig. AIII.1

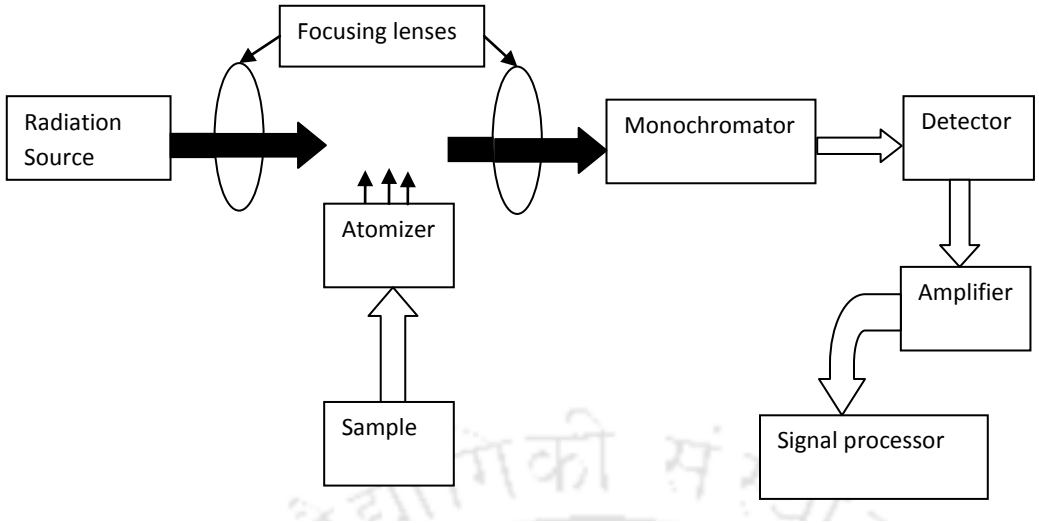

Figure AIII.1 Block diagram showing the working principle of AAS

AIII.2 Procedure for mercury analysis by AAS

Analysis of mercury by AAS is done using the cold vapor mode. The following step by step procedures were followed for its analysis [3]:

- **Preparation of the sample:** Dilute mercury solutions are generally unstable. Hence all the samples were stabilized by adding a solution of nitric acid (5% v/v) and hydrochloric acid (5% v/v) before analysis.

- **Preparation of standards:** Standards were prepared freshly every time an analysis was made. A stock solution of 1 mgl^{-1} of mercury was first prepared from the Varian standard stock solution (1000 mgl^{-1} of mercury). To prepare this, 100 µl of Varian standard stock solution was taken in a 100 ml volumetric flux and then diluted to 100 ml adding Milli-Q de-ionized (DI) water. The standards were then prepared from this stock solution by adding the reagents as per the Table AIII.1 below:

Table AIII.1 Preparation of standards for the analysis of mercury by AAS

Sample	Hg(II), stock solution ($1mgl^{-1}$)	Concentrated HCl	Concentrated HNO_3	Final volume (adding DI water)
Blank	0 ml	5 ml	5 ml	100 ml
10 μgl^{-1}	1ml	5 ml	5 ml	100 ml
20 μgl^{-1}	2 ml	5 ml	5 ml	100 ml
30 μgl^{-1}	3 ml	5 ml	5 ml	100 ml
40 μgl^{-1}	4 ml	5 ml	5 ml	100 ml

- **Preparation of reductant:** Mercury was determined using a 25% w/v stannous chloride ($SnCl_2$) solution in 20% v/v HCl as the reductant. For preparing 100 ml of reductant 25 gm of $SnCl_2$ was taken in a volumetric flux. 20 ml of concentrated HCl was then added to it and the mixture was warmed at 30-40ºC till $SnCl_2$ was completely dissolved. The mixture was then diluted to 100 ml by adding de-ionized water.
- **Preparation of acid:** Milli-Q de-ionized water or distilled water was used in place of acid in the acid container.

A calibration curve was first prepared by injecting the standard samples (as prepared above) into the AAS. In the AAS reaction chamber, acidified sample was reacted with the reductant and vapor of mercury was generated. This mercury vapor was then carried to the spectrometer by argon gas where the concentration of mercury was detected at 253.7 nm wavelength. Unknown samples were injected after the calibration was over. The calibration curve was prepared each time an analysis was made from the fresh standards. Care was taken so that the VGA accessories were free from potassium iodide. Because, traces of potassium iodide will interfere severely with the production of mercury vapor and suppressed the

analytical response completely. The accuracy of the instrument is 1-2% in terms of RSD in μgl^{-1} level [3].

References

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[2] S.J.Haswell, Atomic absorption spectrometry-theory, design and applications, Elsevier, Amsterdam, 1991.

[3] Manual of atomic absorption spectrometer (VGA-77), Varian Australia, Model: AA240FS .

Appendix-IV

Measurement of Interfacial Tension by Kruss Tensiometer

A Tensiometer (Kruss K9, Germany) was used to measure the interfacial tension at the aqueous-organic interface. The working principle and the procedure are described in the subsequent sections.

AIV.1 Working principle

Interfacial tension is the surface tension at the surface separating two immiscible phases. It is somewhat similar to surface tension in that cohesive forces are also involved. However the main forces involved in interfacial tension are adhesive forces (tension) between the two immiscible liquid phases and the interaction occurs at their interfaces [1].

Ring method was used to measure the interfacial tension at the liquid-liquid (aqueous-organic) interface. It consists of a horizontally suspended platinum ring which is immersed in the liquid and then lifted out again. The maximum force which is required to pull the ring through the interface (aqueous-organic) is the required interfacial tension. The interfacial tension is calculated from the following equation [1]:

$$\sigma = \sigma^* \times F = \frac{K}{l_b} \times F \qquad \text{(AIV.1)}$$

Where, σ = true interfacial tension, σ^* = measured interfacial tension, F=correction factor, K=maximum force measured and l_b=wetted length.

The correction factor F (in case where interfacial tension is below 35 mNm^{-1}) is calculated using the Zuidema equation as follows:

$$F = 0.725 + \sqrt{\frac{0.00363 \times \sigma^*}{\pi R^2 \times \Delta\rho}} + 0.04534 - \frac{1.679 \times r}{R} \qquad \text{(AIV.2)}$$

Where, Δρ= density difference between phases (in gcm^{-3}), *R*= mean ring radius= 0.9545 cm (for Kruss standard ring) and *r*= radius of the wire cross section= 0.0185 cm [1].

AIV.2 Procedure [1]

To measure the interfacial tension at the liquid-liquid interface the following steps were followed:

- The ring was first heated to red heat and then hanged from the hook.
- The sample vessel was cleaned properly and filled up with the sample (heavier phase) of about 25 ml and placed on the sample support.
- The sample vessel was then raised until the ring was immersed in the liquid.
- Then the lighter phase (about 25 ml) was pored into the sample vessel slowly and carefully.
- Sample vessel was then lowered carefully and slowly by adjusting the sample support so that the ring lifted upward and a film was formed between the ring and the liquid surface.
- The maximum force (highest value displayed on the display) required to pull the ring just to cross the interface is the interfacial tension of that particular system.
- The measurement was repeated for 2 to 3 times to get a consistent result.

AIV.3 Interfacial tension data for various feed-membrane systems

Interfacial tension between the aqueous and organic phase is an important parameter in liquid membrane processes. Especially in supported liquid membrane processes low interfacial tension causes instability in SLM. Most of the carriers used in facilitated liquid membrane processes show surface activity and thereby reduce interfacial tension. Therefore, interfacial tension between the liquid membrane (dichloroethane and trioctylamine of various concentrations) and the aqueous solution (having various LS concentrations) was determined using tensiometer. The results are reported in the Table AIV.1. It is observed that the interfacial tension marginally increases at higher trioctylamine (TOA) concentration. It reveals that TOA has little surface activity. The increase of interfacial tension in presence of TOA might be due to the absorption of TOA- LS complex at the interface. On the other hand with increase of LS concentration the interfacial tension reduces. It is reported that LS exhibit surface activity but have only a slight tendency to reduce interfacial tension between liquids [2]. Decrease of surface tension at higher LS concentration is due to the surface activity of the LS.

Table AIV.1. Interfacial tension data for LS solution/ dichloroethane- TOA system

Concentration of LS solution, $mgl^{-1.}$	Interfacial tension, mN/m					Density of LS solutions, g/cc
	Volume percentage of TOA					
	0	2	4	6	8	
0 (Water)			21.0			
100 (pH=2.0)	10.35	11.91	11.93	11.96	11.986	0.991
250 (pH=2.0)			11.08			0.991
500 (pH=2.0)			10.61			0.991
1000 (pH=2.0)			10.15			0.992
1500 (pH=2.0)			9.297			0.992

References

[1] Manual of Kruss Tensiometer, Germany, Model: Kruss K9.

[2] Kirk Othmer, Lignin, Encyclopedia of chemical technology, vol.15 (4^{th} edition), (1992) 268-287.

Appendix-V

Leakage test for BLM set-up

The BLM cell as described in Chapter-II was tested for leakage in the following manner.

- ✓ The cell was first filled up with carbon tetrachloride (CCl_4) to few mm above the bottom clearance.
- ✓ Then one compartment of the cell was filled with clear water and the other with a colored (crystal violet) solution.
- ✓ Both the aqueous phases were stirred continuously for 6-7 hours at a stirring speed of 500 rpm.
- ✓ The intensity of color in the aqueous phases was then measured with UV-vis spectrophotometer at a wave length of 584 nm.

The results of the leakage test are furnished in the Table-AIV.1 below:

Table AV.1 Result of leakage test of BLM set-up

Time, hr	Absorbance of clear water	Absorbance of colored water
0	0	0.0176
7	0	0.0171

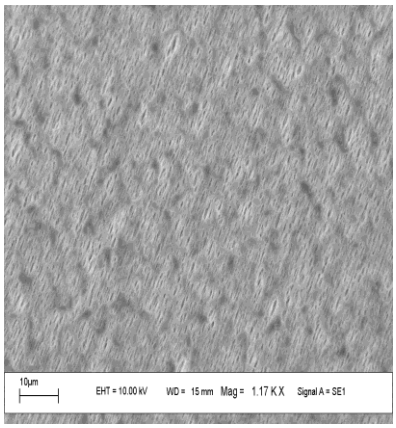
The zero absorbance of the clear water confirmed that there was no lekage in the set-up.

Appendix-VI

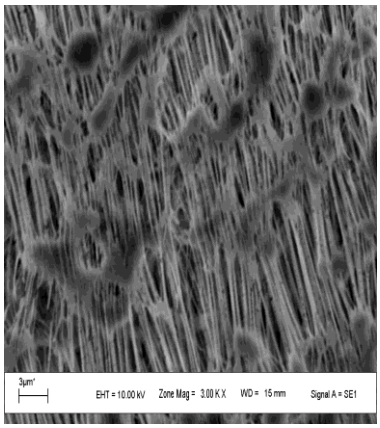
SEM pictures of various support materials

AVI.1 SEM pictures of various support materials used for the calculation of porosity

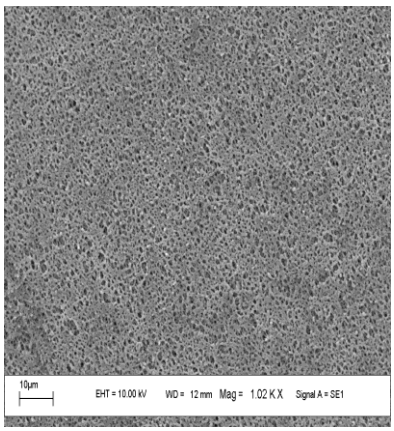
The Fig. AVI.1 below shows the SEM images (top view) of various polymeric membranes used for the present study.



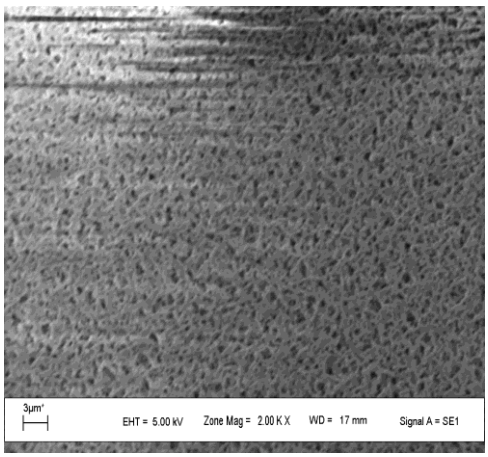
PTFE(0.2µm)



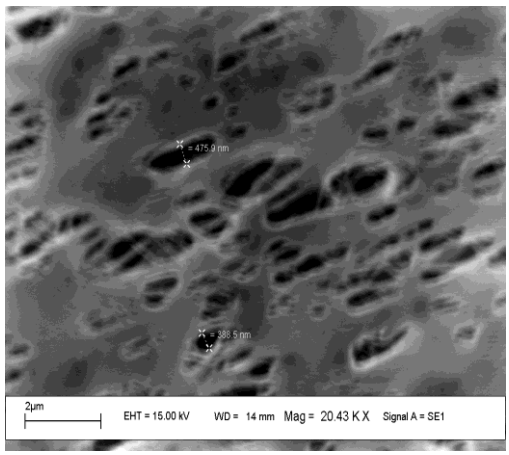
PTFE(0.45 µm)



PE (0.2 µm)



Nylon 6,6 (0.2 µm)



PVDF (0.2 µm)

Figure AVI.1 SEM images (top view) of various polymeric membranes

AVI.2 Sample SEM picture of support material used for the calculation of thickness of the membrane

The cross sectional view (viewed by SEM) of Nylon 6,6 membrane used for the calculation of its thickness is shown in the Fig. AVI.2 below as an example.

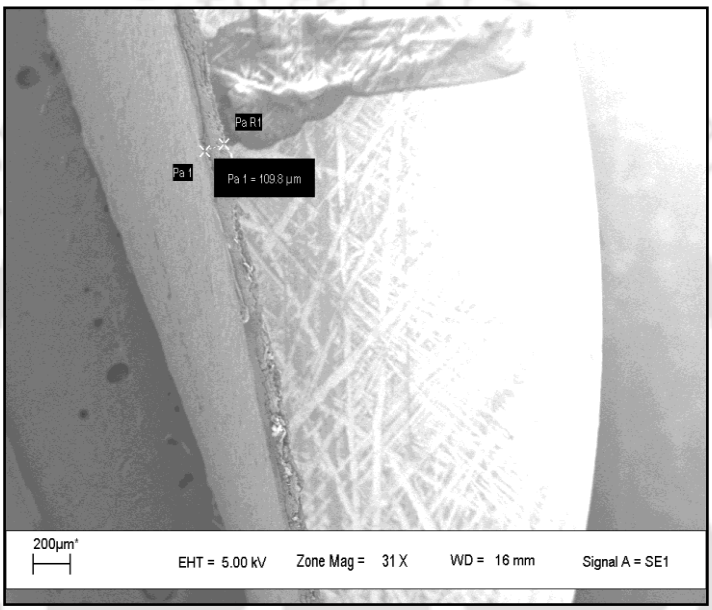


Figure AVI.2 SEM image (cross sectional view) of Nylon 6, 6 membrane

Appendix-VII

Composition of common coconut oil

Coconut oil is basically long and medium chain triglycerides [1]. It contains about 91% saturated fatty acids, 7% monounsaturated fatty acids and 2% omega-6 fatty acids. The fatty acid composition (according to McCane and Widdowson) of coconut oil is tabulated in Table AVII.1

Table AVII.1 Composition of fatty acids in coconut oil [2]

Name of components	Quantity (%)
Caprylic Acid (C8:0)	7.5
Capric Acid (C10:0)	7.1
Lauric Acid (C12:0)	47.7
Myristic Acid (C14:0)	15.8
Palmitic Acid (C16:0)	9.0
Stearic Acid (C18:0)	2.4
Arachidic Acid (C20:0)	1.0
Palmitoleic Acid (C16:1)	0.4
Oleic Acid (C18:1)	6.6
Linoleic Acid (C18:2 n6)	1.8

***[*0- means saturated, 1- means mono saturated, 2- means poly saturated and n6- means Omega-6*]**

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