A STUDY ON THE PERFORMANCE AND STABILITY OF HOLLOW FIBER SUPPORTED LIQUID MEMBRANES USING IONIC LIQUID AS BI-FUNCTIONAL CARRIERS FOR EXTRACTION OF MERCURY

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ABSTRACT

Ionic liquids (ILs) are known as the replacement solvent over volatile organic compounds because of their novel properties. The purpose of this study was to evaluate the performance of Aliquat 336 on mercury (Hg) removal using hollow fiber liquid membrane (HFSLM) system. The system consists of a feed phase , a stripping phase and a membrane phase. In this study, the membrane mixture was prepared by mixing Aliquat 336 with [Emim][NTF$_2$] as co-extractant/carrier. The prepared membrane mixture was used to extract Hg from the feed phase. In the feed phase, Hg solution was prepared in lower concentration which was 50 ppb. In addition, thiourea acted as the stripping agent to strip Hg from the membrane phase . The optimization of the process was carried out through investigation on the parameters: effect of concentration of co-extractants, stripping agent concentration, circulation time of extractants, flow rates of feed and stripping phase and the number or separation cycles. The findings pointed to the introduction of co-extractant was the key factor for Hg removal as it improved membrane stability and provided more Hg-complexes formation. Thus, the performance of HFSLM can be enhanced. An optimization study showed that the maximum Hg removal efficiency was achieved at 99.99% Hg removal with the used of 0.12M Aliquat 336 with 0.18M [EMIM][NTF$_2$] as the extractants, 0.1M thiourea as the stripping agent with the flow rates of feed and stripping solution of 100 ml/min at 3-cycle separation.

ABSTRAK

Cecair ionik (IL$_S$) yang dikenali sebagai pengganti kepada pelarut sebatian organik meruap kerana ciri-ciri novel mereka. Tujuan kajian ini adalah untuk menilai prestasi Aliquat 336 pada kecekapan penyingkiran merkuri (Hg) dengan menggunakan sistem serat berongga membran cecair (HFSLM). Sistem ini terdiri daripada fasa suapan, fasa pelucutan dan fasa membran. Dalam kajian ini, campuran membran telah disediakan dengan mencampurkan Aliquat 336 dengan [Emim] [NTF$_2$] sebagai pelarut ekstraktan. Campuran membran digunakan untuk menanggalkan Hg dari fasa suapan. Di dalam fasa suapan, larutan Hg disediakan pada kepekatan yang rendah iaitu 50 ppb. Di samping itu, thiourea bertindak sebagai ejen pelucutan untuk menanggalkan Hg dari fasa membran. Pengoptimuman proses dijalankan melalui siasatan kepada beberapa parameter: kesan kepekatan pengekstrakkan bersama, kepekatan ejen pelucutan, masa peredaran pengekstrakkan, kadar aliran pada fasa suapan dan fasa pelucutan dan bilangan nombor kitaran pemisahan. Hasil kajian ini menunjukkan bahawa penambahan pelarut ekstraktan merupakan faktor utama dalam penyingkiran Hg dengan meningkatkan kestabilan membran dan menyediakan lebih banyak pembentukkan Hg kompleks. Oleh itu, prestasi HFSLM boleh dipertingkatkan. Pengoptimuman kajian ini menunjukkan bahawa kecekapan penyingkiran maksimum telah dicapai pada pada 99.99% dengan menggunakan ; 0.12M Aliquat 336 dengan 0.18M [EMIM][NTF$_2$] sebagai ekstraktan, 0.1M thiourea sebagai ejen pelucutan pada 3 kitaran pemisahan dengan 100 ml/min kadar aliran pada fasa suapan dan fasa pelucutan.

ACKNOWLEDGEMENT

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LIST OF SYMBOLS AND ABBREVIATIONS

A   Affective area of hollow fiber module (cm^2)

BDD   Box-Behnken design

BLM   bulk liquid membranes

C_i The initial concentration of the feed phase (M)

C_f The final concentration of the feed phase (M)

C_f Concentration of mercury ions at time t (mol/L)

$C_{f,o}$ Concentration of mercury ions at time 0 (mol/L)

CVAAS   Cold vapor atomic absorption spectrometry

ELM   emulsion liquid membranes

Hg   Mercury

HFSLM   hollow fiber liquid membrane

ILs   Ionic Liquids

L   Length of hollow fiber (cm)

N   The number of hollow fiber in the module

P   Permeability coefficient (cm/s)

ppb   Parts per billion

ε Porosity of hollow fiber (%)

Q_f Feed solution volumetric flow rate (cm^3/s)

RSM   Response surface methodology

RTILs   room temperature ionic liquids

SLM   supported liquid membranes

r_i Internal radius of hollow fiber (cm)

WHO   World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Mercury (Hg) is one of the heavy metals that present in industrial effluent originating from urban and industrial discharges, agricultural wastes, mining and combustion activities (Miretzky & Cirelli, 2009). Hg is recognized as highly toxic, persistence, carcinogenic and non-biodegradable in nature (Chakrabarty *et al.*, 2010b). According to the World Health Organization (WHO), Hg may cause toxic effects on digestive and immune systems, the nervous system, lungs, kidneys, skin and eyes. Exposure to small amount of Hg can cause serious health problems such as threat to the development of the child in utero. Hg exists in three forms, which are elemental, inorganic and organic forms (Bose-O'Reilly *et al.*, 2010). Human may be exposed to inorganic and organic form of Hg through their occupation and the consumption of contaminated fish and shellfish (Al-Saleh, 2009), respectively.

According to the Malaysia Environmental Quality (Industrial Effluents) Regulations 2009, the maximum allowable Hg discharge concentration in the effluent is 5 ppb (Hui, 1979). In oil and gas industries, produced water is the largest waste stream generated that contains Hg and other heavy metals. Several treatment methods have been suggested for the effective removal of Hg, e.g. solvent extraction, membrane separation, ion exchange, precipitation, adsorption, filtration, flotation, coagulation, electrochemical technique, biological process, sedimentation and reverse osmosis (Bansal *et al.*, 2005; Chakrabarty *et al.*, 2010b). However, these methods were reported as ineffective at low concentration of Hg and other heavy metals (Inbaraj *et al.*, 2009).

Liquid membrane has been suggested as an effective alternative to separate low concentration of Hg from its aqueous phase (Bansal *et al.*, 2005). In comparison to other

methods which have limitations such as high control costs and development, process limitations, various interferences and maintenance problems (Stojanovic & Keppler, 2012), liquid membrane is the promising alternative to separate Hg. Most of liquid membrane techniques utilise organic solvents which are normally flammable, toxic and volatile and these lead to poor membrane stability and loss of membrane solvent. In contrast, ionic liquids could be the alternative replacement to organic solvents as they have unique properties. In this study , liquid membrane technique is the focus and ionic liquids are used as the extractant in liquid membrane to remove Hg from the aqueous phase.

1.2 Research Objectives

This study embarks on the following objectives:

i.   To evaluate the performance of ionic liquids Aliquat 336 on Hg removal using HFSLM.

ii.   To investigate the effect of various parameters such as concentration of co-extractants, concentration of stripping agent, circulation time of extractants, flow rates of feed and stripping phase and the number or separation cycles .

iii. To optimize the process parameters on Hg removal by varying the effect of co-extractant concentration, stripping concentration, flow rate of feed and stripping phase and the number of separation cycles by using Response Surface Methodology to gain optimum Hg removal.

CHAPTER 2

LITERATURE REVIEW

2.1 Mercury

Hg is one of the heavy metals that are present in the aquatic system. It is highly toxic, carcinogenic and non-biodegradable in nature. Hg is found in various forms, such as elemental Hg, ionic Hg (also known as inorganic Hg, and exists as Hg (II) mercuric compounds) and organic Hg. The toxicity of Hg is strongly dependent on its redox state and the most toxic form is Hg^{2+} which has high tendency to bind with proteins (Gupta *et al.*, 2013).

The major sources of Hg are from various industries such as urban and industrial discharges, agricultural wastes, mining and combustion (Miretzky & Cirelli, 2009). Besides that, Hg is also found to present in waste oil together with other metals and inorganic compounds such as arsenic, cadmium, cobalt and copper. Once Hg is released into the environment, the inorganic Hg is converted to a more toxic methyl Hg by the action of microbial activity under aerobic conditions. This could risk the wildlife and humans as this species may disrupt the blood chain barrier and upsetting the metabolism of nervous systems.

Hg promotes several health hazards such as brain damage, chromosome breakage and dysfunction of liver, kidney, and central nervous system. It also induces cellular toxicity by binding to intracellular sulfhydryl groups even at very low concentration (Ghodbane & Hamdaoui, 2008; Hassan *et al.*, 2008; Inbaraj *et al.*, 2009; Miretzky & Cirelli, 2009). Besides that, Hg is also persistent, bio-accumulative, and has the ability to evaporate from soil and water. This can further cause chronic exposure and acute exposure for human through skin absorption and inhalation. Chronic exposure

of low levels Hg over an extended period may damage the central nervous system. On the other hand, acute exposure to high levels of Hg vapor may cause severe respiratory damage.

2.2 Liquid Membrane

The conventional methods such as precipitation, ion exchange coagulation, electrodialysis , adsorption, solvent extraction, chemical oxidation and reduction and reverse osmosis have been used by researchers and industries for treating Hg contaminated water. However, these methods are ineffective at low Hg concentrations of less than $100 mgL^{-1}$(Inbaraj et al., 2009). In addition, the application of the treatment methods mentioned above is also limited due to various interferences, development and control costs, maintenance problems, and process limitation (Stojanovic & Keppler, 2012). In contrast, liquid membrane emerges as an effective tool for the separation of metal ions from its aqueous phase when the amount of ion in the solution is traces (Bansal et al., 2005).

Liquid membrane technology is well known for its wide application in the separation of organic compounds (Le et al., 2002; Gonzalez-Munoz et al., 2003; Cichy et al., 2005; Chakrabarty et al., 2009) and metal ions (Gasser et al., 2008; G. Muthuraman et al., 2009). Liquid membrane serves as a semi-permeable liquid which forms a barrier between the feed phase and the stripping phase and it allows the targeted components to diffuse across it from one phase to another phase. This method can be treated as a simultaneous multistages extraction and stripping processes which is notable for its combined ability of extraction, diffusion, and stripping of the targeted component. In general, liquid membrane can be defined as a homogenous, non-porous,

thin film of organic liquid interposed between two aqueous phases of different compositions.

The system consists of a feed phase, a liquid membrane phase and a stripping phase. The feed phase is a solution containing the target component. The stripping phase is a solution which extracts the target component from the liquid membrane into it via diffusion and complexation. In contrast, the liquid membrane phase is a layer that is impermeable by these phases and it allows the target compound to pass through it only. In general, there are three types of liquid membranes which are bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM). Among them, BLM is easy to operate but offers lower surface to volume ratio for mass transfer. On the other hand, ELM offers a large surface area to volume ratio but the stability of emulsion remains a major concern in the effective use of ELM especially at larger scale. In contrast to them, SLM shows numerous advantages such as low capital investment and operating cost, low energy consumption, low liquid membrane requirement and simple to operate. SLM gains a broad range of separation applications and it is sustainable for continuous flow operation. It demonstrates promising removal of metal ions such as nickel, uranium, chromium, and copper from the effluent streams (Prakorn & Pancharoen, 2003; Lothongkum *et al.*, 2009; Usapein *et al.*, 2009; U. Pancharoen *et al.*, 2010). The details for each type of liquid membrane are discussed in Section 2.2.

2.3 Types of Liquid Membranes

2.3.1 Emulsion Liquid Membranes

ELM consists of a membrane phase (carrier, surfactant, diluents) and internal stripping phase (Park & Chung, 2003). ELM is renowned due to their extraordinary capability to recover heavy metals (Mortaheb *et al.*, 2009), organic compounds (Chakrabarty *et al.*, 2010a), and pharmaceutical compounds (Sahoo & Dutta, 1998). ELM has very high surface area per unit of volume and has low thickness, which means that the separation process and the mass transfer of solute is fast (Park & Chung, 2003) .This provides several advantages such as the versatility of the extraction and stripping processes , relatively low cost (Rousseau, 1987) and non-dependence on the equilibrium consideration.

ELM comprises of aqueous internal of phase which is surrounded by the only membrane phase. The internal phase resides in the oil phase as fine droplets, which is recognized as poly-dispersed in the oil phase. Nevertheless, the whole system can be inferred as homogeneous water in oil system due to the very small diameters of 1-10μm for the dispersion, which are stabilized by the surfactants. This homogeneous emulsion is further dispersed in another aqueous phase, which is known as feed phase and the system eventually becomes three phase water- oil -water (W/O/W) system. The feed phase is a solution that contains the target solutes that are to be extracted. During the extraction process, a gentle stirring is provided to enhance the distribution of globules mixture. From this, the solute is transferred from the feed phase to the internal phase through the membrane phase. In this case, the membrane phase acts as a barrier which selectively allows the target solute to pass through it. The schematic diagram of ELM is illustrated in Figure 2.1.

However, it is worth noting that ELM has a major drawback, which is the stability issue. The instability can be caused by different mechanism such as repeated coalescence of the internal droplets on the interface, creaming due to density difference, Ostwald Ripening and flocculation (Goyal *et al.*, 2011b). To improve the membrane stability and preventing the disadvantages given by emulsion leakage, the ELM treatment process has to be conducted in several unit operations and this make it less technologically attractive.
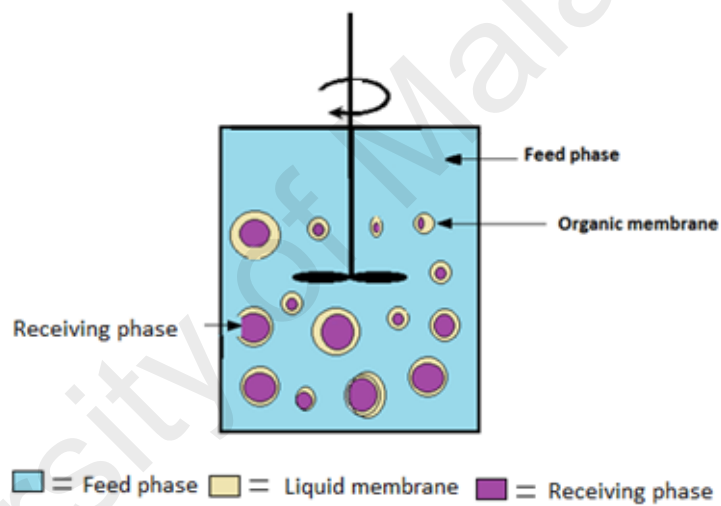
Figure 2.1: Emulsion liquid membrane (Patil & Ghodke, 2015).

2.3.2 Bulk Liquid Membranes

Bulk liquid membrane (BLM) consists of an aqueous feed and stripping phase which is separated by a water – immiscible liquid membrane phase in a U-tube. BLM is known as the simplest liquid membrane and it is often used to study the transport properties of novel carriers/extractant. The schematic diagram of BLM is illustrated in Figure 2.2. BLM emerges as the cheapest liquid membrane separation techniques due to its low capital cost and there is no support for the membrane phase as it separates the feed and stripping phases only by means of its immiscibility.

In comparison to other types of liquid membrane, BLM has less contact surface area. Hence, its permeation rate and separation efficiency are lower than other liquid membranes, such as ELM (Kaminski & Kwapinski, 2000). Thus, BLM is not widely used in the industry.
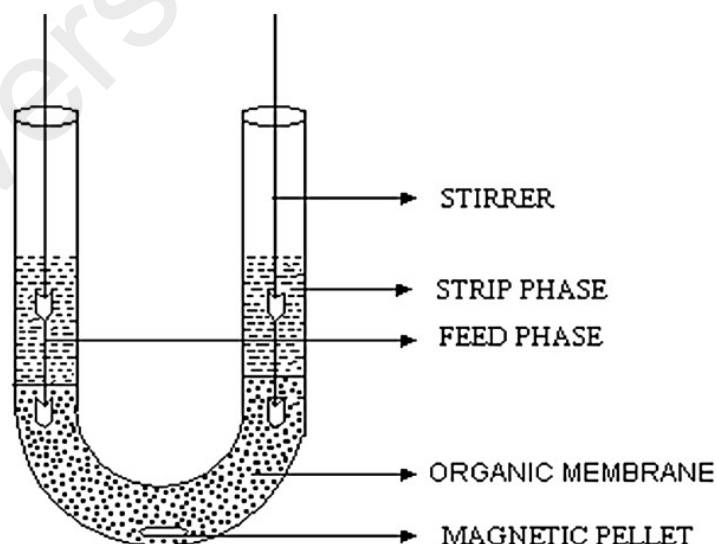
Figure 2.2: Bulk liquid membrane (Govindaraju Muthuraman & Ibrahim, 2013).

2.3.3 Supported Liquid Membrane

The membrane liquid in SLM is embedded in a hydrophobic membrane support by the capillary forces. The hydrophobic membrane support creates an immiscible layer between feed and stripping phases, allowing the targeted components to diffuse through it from one phase to another. The membrane is normally consists of an extractant, a diluent which is an inert organic solvent for adjusting the viscosity and a modifier to avoid third phase formation. In comparison to BLM and ELM, SLM draws more industrial interests due to its high selectivity, low energy consumption and it only requires very little amount of membrane solvent in comparison to other liquid membranes (Matsumoto *et al.*, 2005; Malik *et al.*, 2011).

From the view of membrane support, several configurations are available such as plate and frame, spiral, tubular and hollow fibers (Molinari *et al.*, 1989). Among these types of membrane supports, flat sheet supported liquid membrane (FSSLM) and HFSLM are commonly used. HFSLM is extensively studied by researchers due to its high selectivity and rapid transportation of the desired target components. The transport rate of the target component is driven by the concentration gradient between the feed phase and the stripping phase. The schematic diagram of HFSLM is illustrated in Figure 2.3. Based on this, HFSLM is chosen as the type of membrane support in this study.

SLM system has several advantages over BLM and ELM. Unlike BLM, SLM only requires small amount of liquid membrane to fill in the membranes, therefore the use of expensive carriers is possible. In addition, in comparison to ELM, SLM is a continuous one step operation whilst ELM is a batch process and is energy consuming. Furthermore, SLM is also free from emulsion stability issue which is faced by ELM (Kim, 1984). Thus, SLM is chosen as the liquid membrane configuration in this study.
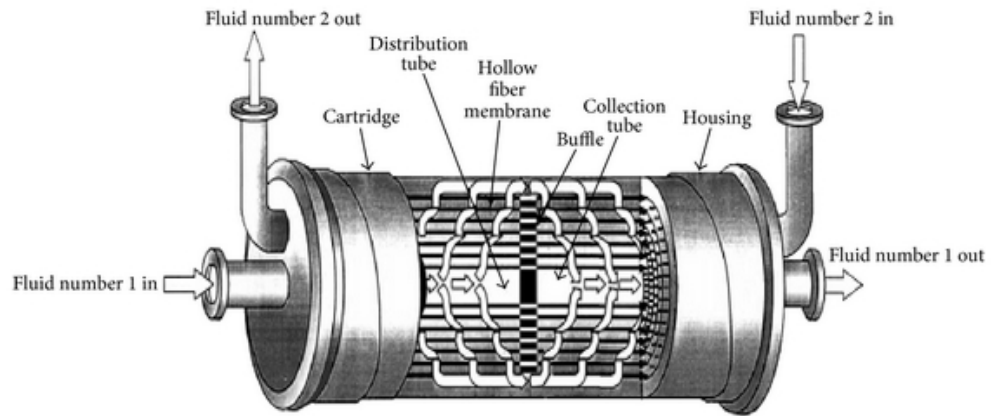
Figure 2.3: Hollow fiber supported liquid membrane (Gabelman & Hwang, 1999)

2.4 Supported Liquid Membrane

2.4.1 Supported liquid membrane preparation

In general, SLM contains two major components which are carrier/extractant and solvent. In this process, the membrane mixture is prepared by mixing these two components using a mechanical stirrer. The types and concentration of the components are highly dependent on the application of SLM. The carrier should react thermodynamically with the target solute to form a complex and the complex should react kinetically with the stripping agent to release the solute into the stripping phase (Bhowal & Datta, 2001). In this study, Aliquat 336 was chosen because it contributed to anion displacement reaction between the target solute and the carrier and this reaction is relatively fast in comparison to other complex formation (Björkegren & Karimi, 2011). Then, the membrane solution was circulated into shell and tube side of the membrane module for the impregnation of the membrane into the pores of membrane support.

2.4.2 Diffusion of solute in Hollow Fiber Supported Liquid Membrane.

HFSLM acts as an immiscible layer with an organic extractant embedded into the micropores of hydrophobic membrane that separates the feed phase and the stripping phase. The target component in the feed phase reacts with the extractant in the membrane phase to form a complex species at the feed-membrane interface. The complex diffuses through the liquid membrane and reacts with the stripping agent at the membrane-stripping interface, and thus the target component is stripped into the stripping solution. The extraction and stripping processes can be accomplished simultaneously in a single step (Lothongkum *et al.*, 2011).

Generally, the mass transfer mechanism through the liquid membranes can be classified into two types which are ; (i) the solution – diffusion mechanism , and (ii) facilitated transport mechanism. The solution – diffusion mechanism describes the transfer of the target species in the absence of chemical reaction or complex formation . On the other hand, the facilitated transport mechanism or carrier – mediated transport takes place when a selective extractant that can form complexes with the target species is used in the liquid membranes system (Bringas *et al.*, 2009). Facilitated transport occurs when the target component reacts reversibly and selectively with the carrier/extractant in the liquid membrane. The facilitated transport can be classified into simple facilitated transport and coupled facilitated transport .The simple facilitated transport is mainly for the transport of neutral species. On the other hand, coupled facilitated transport occurs in the extraction of ionic species whereby the electroneutrality of the system must be maintained (U Pancharoen *et al.*, 2011).

Figure 2.4 illustrates the schematic diagram for facilitated transport. In simple facilitated transport, the feed phase consists of target components (A) and co-ion (B) whereas the organic extractant (C) is embedded in membrane phase. The transport mechanism is observed when organic extractant (C) reacts with target components (A) and complex species ($\overline{AC}$) is formed. The complex ($\overline{AC}$) is decomposed at membrane–stripping interface and the target components (A) is recovered at stripping solution, as shown in Figure 2.4 (a). On the other hand, the coupled facilitated transport can be classified into two types, which are coupled facilitated co-transport and coupled facilitated counter-transport. In coupled facilitated co-transport, the organic extractant (C) reacts with the target component (A) and co-ion (B) to form organic complex ($\overline{ABC}$). Organic complex ($\overline{ABC}$) will diffuse to the membrane–stripping interface. Both ions are released and this regenerates the extractant .This mechanism is common for neutral and basic extraction. In contrast, co-ion (B) is transported from the stripping phase to the feed phase in the coupled facilitated counter-transport. The extractant ($\overline{BC}$) reacts with target components (A) to form organic complex ($\overline{AC}$) and this releases co-ion (B) into the feed phase. The organic complex ($\overline{AC}$) diffuses across liquid membrane to membrane-stripping interphase. The target components (A) is then released into the stripping solution and the organic extractant (C) is regenerated. This mechanism is more common for acidic extraction (Bringas *et al.*, 2009).
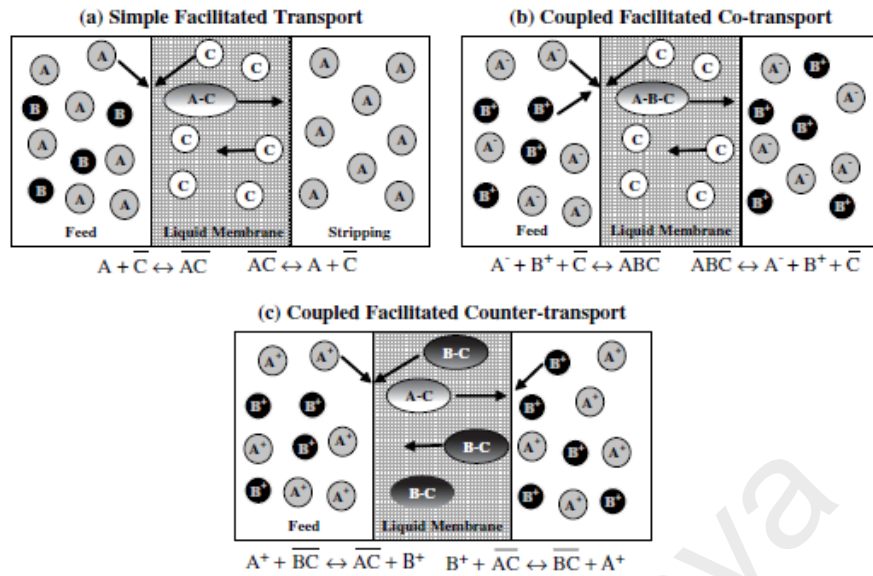
Figure 2.4: Schematic diagram for simple and coupled facilitated transport mechanism.(Bringas *et al.*, 2009)

In the present study, the extraction of Hg fits the coupled facilitated co-transport mechanism. The transport of Hg through the hollow fiber membrane clearly explained in Figure 2.5. The Hg in the feed phase diffuses to the diffusion layer of the feed phase (a). Then , Hg reacts with the extractant at the feed- membrane phase interface (b) to form Hg-complex. The complex diffuses across the membrane to the membrane-stripping interface (c). A reaction between the complex and the stripping agent takes place at the membrane-stripping phase interface (d) where Hg is released into the stripping phase (e). Simultaneously, the extractant is regenerated and is transported back to the membrane phase (f) , for further complex formation.
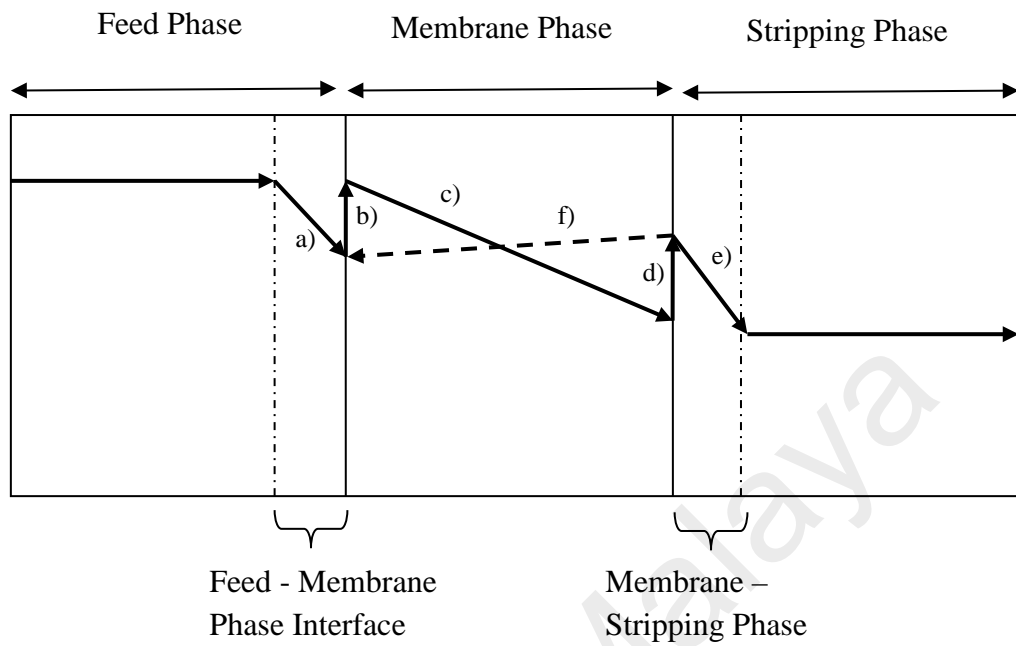
Figure 2.5: Schematic diagram of Hg transport through a hollow fiber membrane.

2.5 SLM Stability

Despite the advantages of SLMs as discussed in Section 2.2.3, SLMs is only used in small scale due to the lack of long-term stability. According to Kemperman *et al.,* (1996) , there are several factors that can lead to membrane instability , such as :

i.   solubility of the liquid membrane in the aqueous feed and stripping phase,

ii. the pressure difference over the membrane,

iii. wetting of pores in polymer support by the aqueous phases,

iv. blocking of membrane pores by carrier precipitation, and

v.   osmotic pressure difference over the membrane.

Dreher and Stevens (1998) considered two major mechanisms in contributing SLM instability, which are emulsification of the liquid membrane and the osmotic pressure difference over the membrane. The other factors which cause membrane instability can be avoided by a properly design and operation of a SLM system. Many attempts have been done to improve SLM stability such as the use of ionic liquid as membrane solvent (Fortunato *et al.*, 2005), re-impregnation of the liquid membrane phase in the support (Tanigaki *et al.*, 1988) and the use of plasma polymerization surface coating (Yang *et al.*, 2000).

2.6 Ionic Liquid

Recently, ILs have gained great attentions in worldwide as the perfect replacement for the conventional volatile organic solvents. ILs are compounds that are composed of either organic or inorganic anions and organic cations .ILs are also known as room temperature ionic liquids (RTILs) due to their characteristic of low melting point whereby they normally have melting points of less than ambient temperature (Goharshadi & Moosavi, 2008). The terms RTILs, non-aqueous ionic liquid, molten salt, liquid organic salt and fused salt have all been used to describe these salts in the liquid state (Welton, 1999).

ILs are known as potential replacement of conventional volatile organic solvents (Welton, 1999; Wasserscheid & Keim, 2000; Seddon, 2003). The outstanding properties of ILs such as negligible vapor pressure, excellent thermal stability, wide interval of hydrophilic-hydrophobic balance, good dissolution properties with many organic and inorganic compounds including polymers or cellulose, and low flammability (Aslanov, 2011) attract great attention to the researchers for nearly two dozens of years. These liquids are generally colorless with relatively high viscosities. Their polarity, hydrophobicity and physical properties can be tailored by selection of anion or cation combination. For example, the water solubility of ILs can be controlled by the length of the alkyl group whereby the increase of the length of alkyl chain improves the hydrophobicity of the ILs (Visser & Rogers, 2003). In addition, the choice of anion such as halide, nitrate, acetate, trifluoroacetate, and tetrafluoroborate also strongly affects the chemical and physical properties of ILs. For example , imidazolium based ILs with the anions halide, nitrate, acetate, trifluoroacetate are totally miscible with water, whereas hexafluorophosphate and bis(trifluromethysulfonyl)imide anions provide water immiscible ILs (Seddon *et al.*, 2000) .

Table 2.1 shows a comparison between ionic liquids with the conventional organic solvents. ILs possess several advantages over conventional organic solvents because of their outstanding properties mentioned above. This makes them environmentally compatible (Seddon, 1996; Welton, 1999; Brennecke & Maginn, 2001; Lagrost *et al.*, 2003; Yang & Dionysiou, 2004; Shariati *et al.*, 2005; Shariati & Peters, 2005). ILs also play important role in separation science such as in gas chromatography, extractions and supported liquid membrane as they have a very high solvent properties in dissolving a wide range of organic and inorganic molecules, including , salts, fats, proteins, amino acids, surfactants, sugar,crude oil, inks, and even DNA (Renner, 2001).

Table 2.1: Comparisons of ionic liquids with the organic solvents (Plechkova & Seddon, 2008)

Properties	Ionic liquids	Organic solvents
Number of solvents	>1,000,000	>1,000
Applicability	Multifunction	Single function
Vapour pressure	Negligible vapour pressure under normal conditions	Obeys the Clausius–Clapeyron equation
Flammability	Usually nonflammable	Usually flammable
Solvation	Strongly solvating	Weakly solvating
Polarity	Polarity concept questionable	Conventional polarity concepts apply
Tuneability	Virtually unlimited range means ''designer solvents''	Limited range of solvents available
Cost	Typically between 2 and 100 times the cost of organic solvents	Normally cheap
Recyclability	Economic imperative	Green imperative
Viscosity, cP	22–40,000	0.2–100
Density, g /cm^3	0.8–3.3	0.6–1.7

2.6.1 Ionic liquid as extracting agents for heavy metals

ILs are known as "designer solvent" due to their ability to be fine tuned for specific properties for particular needs. The selection of negatively charged anions and positively charged cations will design a task specific IL in the extraction of solute from a solution. The IL are normally consisted of an organic cation from imidazolium, quartenary ammonium, pyrrolidinium, pyridinium and tetra alkylphosphonium group as illustrated in Figure 2.6 (a), and a polyatomic, inorganic anion such as chloride, hexafluorophosphate) or an organic anion (e.g. bis[(trifluoromethyl)sulfonyl]imide), trifluoromethylsulfonate) as shown in Figure 2.6 (b) (Brennecke & Maginn, 2001).
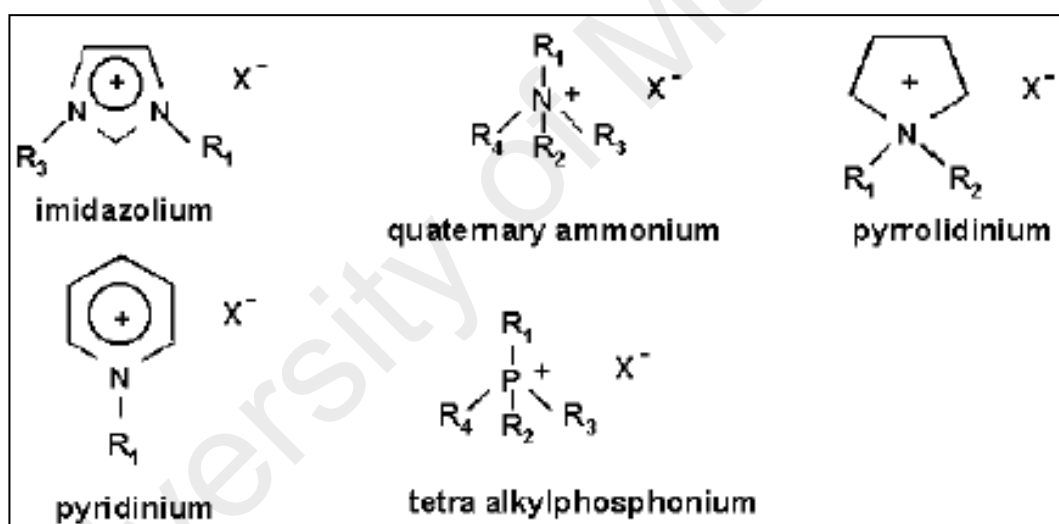
Figure 2.6 (a): Example of cations for ILs.
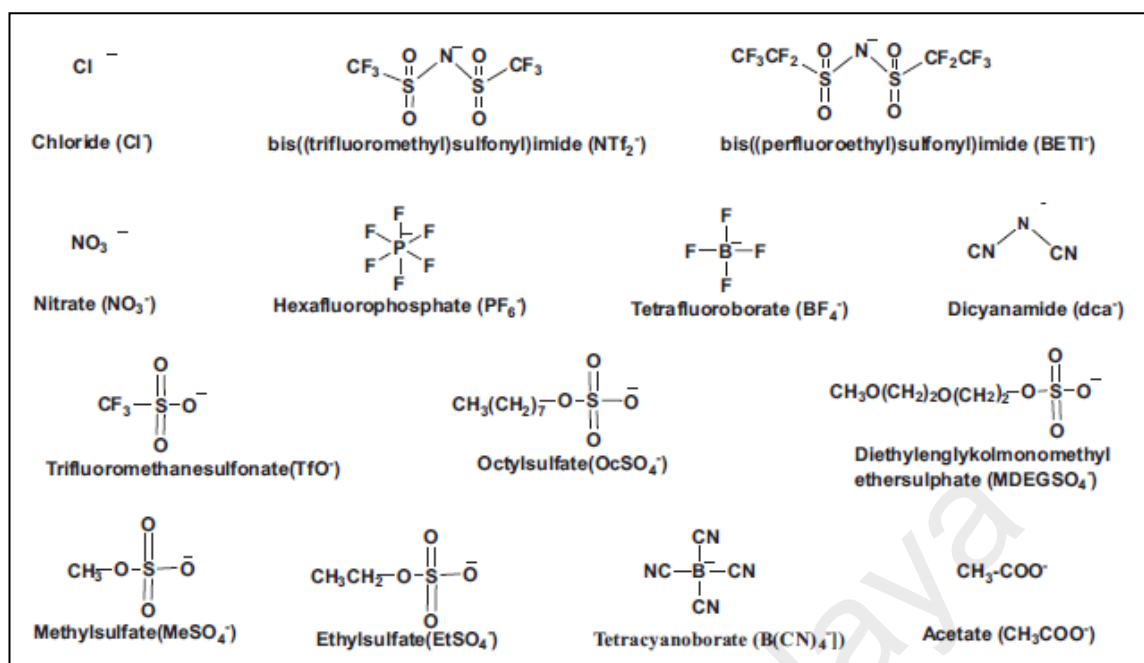
Figure 2.6 (b): Example of anions for ILs.

Di-alkylimidazolium is the most popular cation for ILs due to the ease of synthesis and its attractive physical properties. Several research works have been published and it is reported that classical hydrophobic RTILs based on imidazolium cations show positive behaviour on the extraction of different metals such as alkali metals, Cobalt, Nickel, Zinc and Manganase from aqueous solutions (Kozonoi & Ikeda, 2007; Fujii *et al.*, 2008; Umebayashi *et al.*, 2008; Zuo *et al.*, 2008).

[$C_n$mim][PF_6] ILs have been investigated as an extracting agent at pH of 4.68 for removing Hg from aqueous solutions using acetate buffer (Germani *et al.*, 2007). It is reported that the alkyl chain length strongly affects the hydrophobicity of the ILs and the anion concentration in the aqueous phase. This further affects the performance of the extraction system.

Besides imidazolium based ILs, quartenary ammonium based ILs are also applied as extraction agents for heavy metal removal due to they have improved thermal and chemical stability than pyridinium and imidazolium based ILs. Furthermore, their unique miscibility, solvating properties and higher viscosity also enhance their use in specific applications. In fact, the study on the utilization of quaternary ammonium based

ILs, Aliquat 336 as ion exchanger for the removal of different metal species from acidic solution had been started since 1960s. Nayl (2010) has successfully separated Co(II) and Ni(II) from acidic sulfate solutions using a mixture Aliquat 336-kerosene. Their study showed that the increase in pH and Aliquat 336 concentration increased the extraction efficiency. The performance of Aliquat 336 to extract Hg from acidic solution was also investigated by Fabrega and Mansur (2007). A very fast reaction kinetic was reported whereby Hg was quantitatively extracted within 5 minutes at pH $\geq$ 1. The regeneration test also showed that Hg can be stripped out in a satisfactory performance when thiourea was applied as the stripping agent.

Besides acting as single extractant, the ability of Aliquat 336 as co-extractant together with Bromo-PADAP, Cyanex923 and Cyanex471 in the extraction of arsenic and Hg from natural gas co-produced water from Gulf of Thailand has also been investigated by Lothongkum *et al.* (2011).The combination of two or more extractants can produce a synergistic effect in the extraction of metal ions. Among the extractants, 0.22M Aliquat 336 with 0.06M Cyanex 471 were identified as the best combination in the study as they showed the highest extraction efficiency with the synergistic coefficient of 2.8.

Moreover, the design of task specific ionic liquids (TSIL) in the removal of cadmium and Hg from contaminated water was investigated by Visser *et al.* (2002). Different TSILs cations were produced by appending alkyl groups namely thiourea, urea and thioether into the immidazolium cations. This synthesized TSILs were combined with [PF$_6$] anions and their extraction performance were tested. The results of the study indicated that the TSILs had lower thermal stability and better extraction performance than [C$_n$mim][PF$_6$].

2.6.2 Ionic liquid in supported liquid membrane

The application of ionic liquid as liquid membrane in SLM has been studied due to the nature of SLM which is more stable than ELM and BLM. The work of Zeng *et al.,* (2012) which utilized RTIL in hollow fibre liquid phase microextraction for cadmium removal showed that 1-butyl-3- methylimidazolium hexafluorophosphate $[C_4mim][PF_6]$ can be immobilized in the pores of hollow fiber and acted as acceptor solvent for cadmium absorption. Other than heavy metals removal, ILs has also been utilised for organic compounds extraction. This was observed in the work of Zhang *et al.* (2014) for the separation of toluene and cyclohexane using hollow fiber supported ionic liquid membrane. Two types of ionic liquids were used in this study, namely N-Butylpyridinium tetrafluoroborate ($[Bpy][BF_4]$) and 1-Butyl-3-methylimidazoliumte trafluoroborate ($[Bmim][BF_4]$). It was reported that the interaction between ($[Bpy][BF_4]$) with toluene was stronger in comparison to cyclohexane. In addition, supported ionic liquid membrane also showed good long term stability due to the high viscosity of the ILs.

This is also supported by Nosrati *et al.* (2011) who investigated the use of ILs based on 1-n-alkyl-3-methylimidazolium cation, $[C_nMIM]^+[X]^-$ for the removal of phenol from wastewater. By the aid of polytetrafluoroethylene hydrophobic membrane filter in the SLM, the use of 1-Butyl-3-methylimidazolium hydrogensulfate, $[BMIM][HSO_4]$ can achieve 85% phenol removal with a membrane stability of more than 24 hours.

Other than imidazolium based ionic liquids, quarternary ammonium based ionic liquid has also been investigated as liquid membrane. The use of Aliquat 336 as phase transfer catalyst in reducing chloride content in brackish water using HFSLM was investigated by (Hofmeister *et al.*, 2013). A positive result was obtained whereby the process was mainly due to the ion exchange between the phases through the membrane.

The study showed that the transport mechanism was mainly governed by two criteria, which were the concentration of Aliquat 336 and the viscosity of the liquid membrane. The increase of Aliquat 336 was reported to improve chloride removal. However, it was worth noting that an excessive high Aliquat 336 concentration could lead to high viscosity of the liquid membrane, which was not favoured for mass transfer.

In the present study, the role of hydrophobic ionic liquid Aliquat 336 as extractant or carrier was evaluated extensively. Aliquat 336 contains an electron deficient nitrogen group and mobile chloride counter ion. Thus, it can behave as a bridge for an active reaction, as known as anion displacement reaction, which occurs between the extractant and the metal ion.

CHAPTER 3

METHODOLOGY

3.1 Chemicals

Mercuric chloride ($HgCl_2$) and hydrochloric acid (HCl) which were used as the feed solution, were supplied by R&M chemicals. The ILs , 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl imide [Bmim][NTF$_2$], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl imide [Emim][NTF$_2$], and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl imide [Hmim][NTF$_2$] were supplied by Merck Sdn Bhd whilst tri-octyl methyl ammonium chloride (Aliquat 336) was purchased from Sigma Aldrich. Thiourea, which was applied as the stripping agents in this study was supplied by R&M chemicals. Stannous chloride 99.99% ($SnCl_2$) and sulfuric acid 98 % (H_2SO_4) were used for Hg analysis and they were purchased from Sigma Aldrich and J.T Baker, respectively. De-ionized water was used in the preparation of solutions in this study.

3.2 Apparatus

3.2.1 Hollow fiber supported liquid membrane system

The HFSLM system used in this study was fabricated by Lotus Scientific (M) Sdn Bhd. The system consisted of two gear pumps, two flow rate controllers, four pressure gauge and four reservoirs were used. The schematic diagram of the system is as shown in Figure 3.1.The membrane module used in this study consists of several numbers of fibers , as shown in Figure 3.2. The membrane module was prepared by arranging the fibers into a bundle and the ends of the fibers were embedded into two glass tubes that

were made of polyurethane potting material. Then , the plug was sliced at the glass tube end when the potting material was hardened to allow the passage of the aqueous through the lumen of the fibers. Following that, the fibers were inserted into the outer shell of the module. Finally, the potted fibers was fixed in the shell with O- ring screw caps .
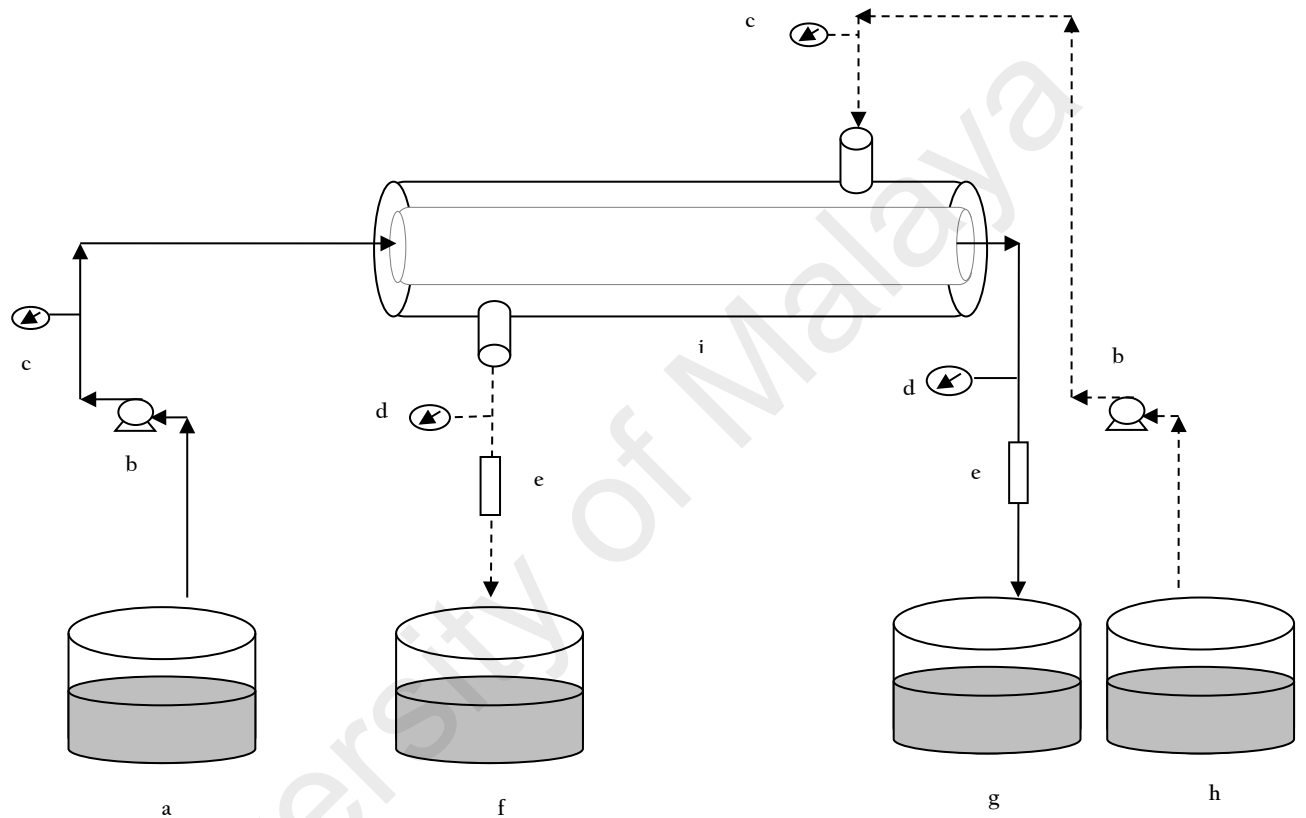
Figure 3.1: Schematic counter-current flow diagram for one-through-mode operation separation by HFSLM.(a) feed reservoir, (b) gear pumps, (c) inlet pressure gauges, (d) outlet pressure gauges , (e) flow meters, (f) outlet stripping reservoir,(g) outlet feed reservoir ,(h) inlet stripping reservoir and (i) HFSLM module.
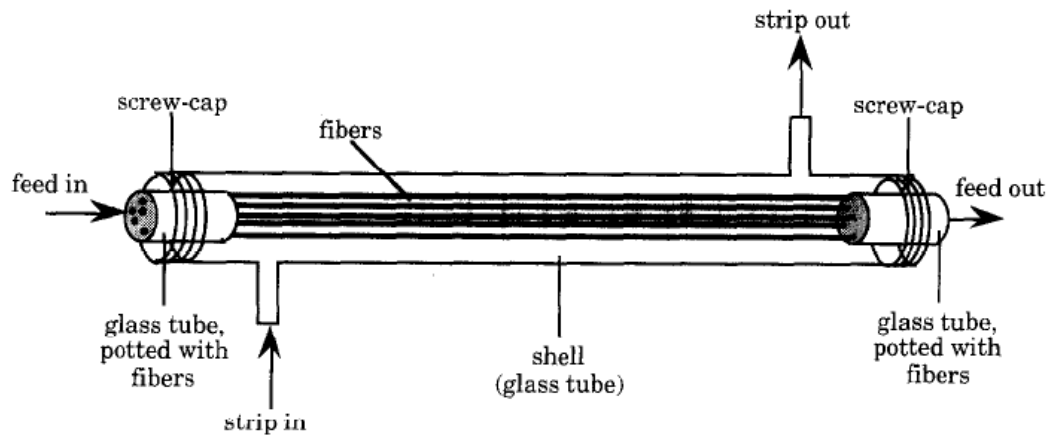
Figure 3.2: Schematic diagram of the hollow fiber supported liquid membrane module(A. J. Kemperman *et al.*, 1997).

3.2.2 Membrane

The HFSLM module was supplied by Liqui-Cel® Laboratory Liquid .The membrane support was made of Celgard® microporous polypropylene. The properties of membrane are shown in Table 3.1.

Table 3.1 Properties of hollow fiber supported liquid membrane module

Membrane characteristic	Properties
Membrane material	Polypropylene
Membrane surface area	1.4 m^2
Effective length	15 cm
Inner diameter of hollow fiber	220 µm
Outside diameter of hollow fiber	300 µm
Number of fibers	10,800
Membrane porosity	40%
Membrane pore size	0.04 µm
Membrane tortuosity	2.6

3.3 Analytical Instruments

3.3.1 Cold Vapor Atomic Absorption Spectrometry (CVAAS)

CVAAS was used for Hg analysis as the limit of detection of CVAAS are in ppb. The model of CVAAS used in this study was (RA-3, NIC), and was purchased from Kromtek Sdn Bhd. Hg analysis was conducted by reducing Hg^{2+} into Hg using $SnCl_2$ solution. Then, CVAAS was used to convert the Hg in the aqueous sample into gaseous stream. The optical absorbance at a wavelength of 253.7 nm was measured when the gaseous stream passed through the cell.

3.4 Experimental Procedures

3.4.1 Preparation of hollow fiber supported liquid membrane

The HFSLM consists of three phases. They are feed phase, stripping phase and membrane phase. For liquid membrane phase, the ILs functioned as the extractants. The ILs used in this study were tri-octyl methyl ammonium chloride (Aliquat336) (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl imide [Bmim][NTF_2], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl imide [Emim][NTF_2], and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl imide [Hmim][NTF_2] .The membrane phase was prepared by dissolving appropriate amount of ILs into toluene. This was prepared in a 1000 mL unbaffled beaker. The mixture was homogenized using a motor driven homogenizer (IKA, model : T25 digital ultra Turrax) for 5 minutes. Then, the mixture was circulated into the shell and tubes sides for 20 minutes to embed the liquid membrane into the pores of the membrane support.

3.4.2 Mercury extraction

The feed phase was prepared by dissolving $HgCl_2$ into deionized water for producing 50 ppb Hg solution . The pH of the solution was adjusted by HCl to below 1.0 in order to maintain the pH difference between the feed and stripping phase, which was the driving force for Hg diffusion through the membrane during the experiments. The mixture was stirred gently for 10 minutes.

The stripping solution was prepared by dissolving a theoretical amount of thiourea in HCl solution. Then, the mixture was stirred gently for 10 minutes. After conducting liquid membrane impregnation as discussed in Section 3.4.1, the feed and stripping solutions were placed in the feed and stripping reservoirs, respectively. These two solutions were pumped into the shell and tube side for 40 minutes at a flow rate of 100mL/min. Then, a 20 ml sample was collected from the feed and stripping reservoir after 40 minutes of the experiment. The extraction of Hg was determined through the changes of solute concentration in the feed phase.

3.5 Analytical Methods

3.5.1 Preparation of Standard and Calibration Curves

A series of standard Hg solution of 0, 2, 4, 8, and 10 ppb were prepared using $HgCl_2$ and the deionized water. The standard solution for stannous chloride, H_2SO_4 and Hg standard were prepared and then were scanned through CVAAS at the absorbance of 253.7 nm. A linear plot of absorbance versus Hg concentration was obtained. These tests were triplicate to determine the accuracy of the calibration curve.

3.5.2 Dilution of samples

The samples taken from the feed phase were diluted before analysis due to the limitation of the maximum detection by CVAAS. The final concentration of Hg detected by CVAAS was multiplied by the dilution factor to obtain the actual Hg concentration in the sample.

3.5.3 Mercury concentration analysis

The removal efficiency and recovery efficiency of Hg using HFSLM process was calculated using Equation (3.1) and (3.2) where C_i , C_f and C_s were the initial Hg concentration of the feed phase, final Hg concentration of the feed phase and final Hg concentration of the stripping phase, respectively.

$$\text{Removal efficiency}: \frac{C_i - C_f}{C_i} \ x \ 100 \tag{3.1}$$

$$\text{Recovery efficiency}, \% = \frac{C_s}{C_i} x \ 100 \tag{3.2}$$

3.6 Precautionary Steps for Chemicals Handling

The precautionary steps on the handling of chemicals are as follows:

i. Full face respirator with Hg vapor filter and nitrile glove were worn during the preparation of ILs, HCl, thiourea solutions and also during the whole experiments.

ii. The preparations of liquid membrane, feed and stripping solutions were conducted in a fume cupboard.

iii. The chemicals were stored in a dark place to prevent any degradation of chemicals by exposure to light.

iv. After completing each experiment, the used glassware were cleaned by soaking in the detergent and rinsed using the distilled water. The glassware were dried in the dryer before being reused.

3.7 Error Minimization

The experiments were repeated to verify the accuracy of the experimental data. The instruments were calibrated before using so that the systematic error could be minimized. The readings were triplicated during the analysis in order to reduce the measurement error. Furthermore, the sequence of the experiment was assigned randomly using Microsoft Excel on order to average out the unknown nuisance factor.

CHAPTER 4

RESULTS AND DATA ANALYSIS

4.1 Introduction

This chapter covers six sections; which are i) identification of the role of ionic liquid Aliquat 336 in HFSLM, ii) the removal of Hg by HFSLM using Aliquat 336 as the extractant and imidazolium based ionic liquids as co- extractant, (iii) the mechanism on the Hg extraction by mixture of ionic liquid Aliquat 336 and [Emim][NTF$_2$] , (iv) parameter optimization for the extraction process using Aliquat 336 and [Emim][NTF$_2$] stabilized supported liquid membrane, (v) permeability coefficient and (vi) design of experiment using Response Surface methodology.

4.2 Identification of the role of single ionic liquid Aliquat 336 in hollow fiber supported liquid membrane

Aliquat 336 was chosen in this study due to its higher melting point and outstanding properties such as solvating properties and miscibility behavior. In comparison to imidazolium and pyridinium based ILs, quaternary ammonium cation has improved thermal stability and is chemically stable. The physical and chemical properties of Aliquat 336 are as shown in Table 4.1.

Table 4.1: Physical and chemical properties of Aliquat 336

Properties	Value
Density (at 25 °C) (g /ml)	0.880
Viscosity (at 30 °C) (mPa)	1450
Solubility in water (at 20 °C) (g/L)	10
Boiling point (°C)	225
pH (at 100 g/L water (25 °C))	3.5

4.2.1 Identification of the role of Aliquat 336 in hollow fiber supported liquid membrane without imidazolium cations

In the first stage of this study, the role of single extractant was investigated using Aliquat 336. The results and discussion was as shown in the sub-sections.

4.2.1.1 Consideration of Aliquat 336 as a extractant

In order to identify the role of Aliquat 336 as the extractant, the membrane solution was prepared by dissolving Aliquat 336 into toluene. The role of extractant in this study is to facilitate the transport of targeted metal through the membrane.

Aliquat 336 has been applied in supported liquid membrane for the transport of phenylalanine (Campbell *et al.*, 1994) , amino acids (Adarkar *et al.*, 1997) and tantalum and niobium (Buachuang *et al.*, 2011). According to (Hofmeister *et al.*, 2013), Aliquat 336 is the best choice for single transfer due to several reasons :

i. Reasonable price.

ii. Easy to handle as Aliquat 336 is not highly volatile in comparison to other conventional solvents and is chemically and thermally stable.

iii. The salts produced from Aliquat 336 reaction are insoluble and thus the precipitates may be filtered out easily.

iv. Aliquat 336 is a stronger extractant in comparison to tertiary and secondary amines in the trend of $R4N^+ > R3NH^+ > R2NH^{2+} > RNH3^+$

In this study, the concentrations of Aliquat 336 in a range of 0.05 M to 0.20 M was used. Figure 4.1 shows that the removal of Hg is increased when Aliquat 336 concentration is increased from 0.05 M to 0.12 M. The removal efficiency was found to decrease when Aliquat 336 concentration was exceed 0.12M. This suggested that Aliquat 336 was less efficient in the formation of metal-complexes when an excessively high Aliquat 336 concentration was applied due to higher viscosity of the extractant which hindered the extraction process. The decrease in extraction efficiency can be explained by the increase of mass transfer resistance as a result of high Aliquat 336 concentration.

Moreover, an excessive high extractant concentration also caused higher operating cost without significant improvement in the system performance. According to Lv *et al.*, (2007), the facilitated transport mechanisms involved in liquid membrane was less affected by the extractant concentration.
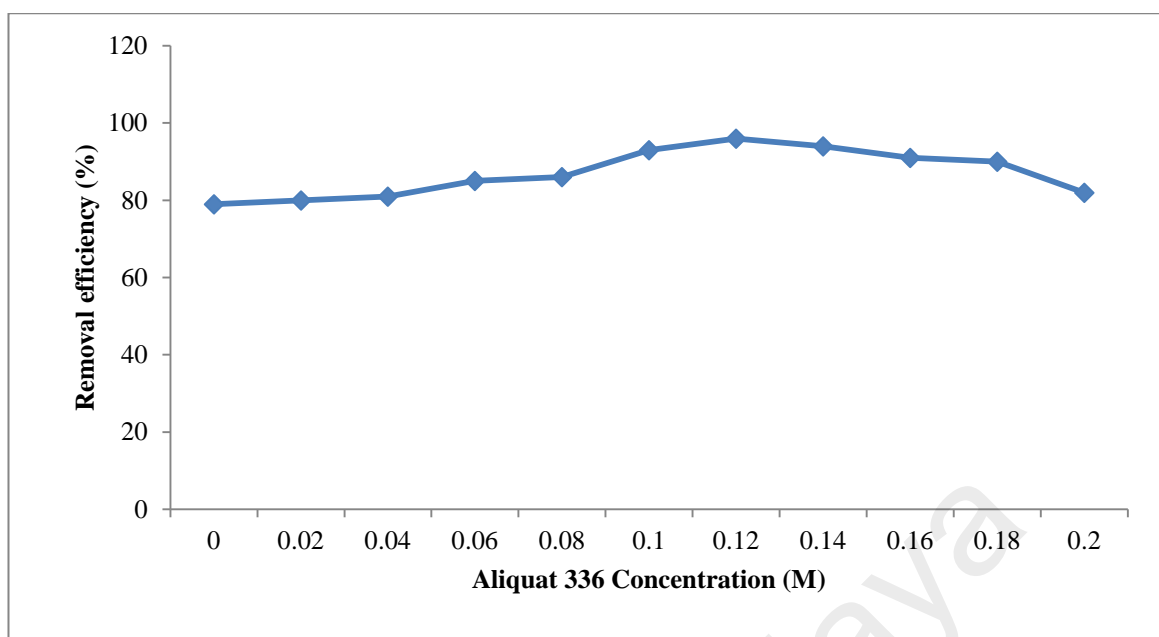
Figure 4.1: The removal efficiency of Hg using Aliquat 336 as the extractant. (Stripping phase: 0.1M thiourea , flow rate for feed and stripping phase :100 mL/min).

4.2.2 Consideration of Aliquat 336 as the extractant and imidazolium cations as co-extractant

Section 4.2.1 shows that Aliquat 336 is a good extractant for Hg removal. This was in line with the work of Nayl (2010) which showed successful separation of Co(II) and Ni(II) from acidic sulfate solutions using a mixture of Aliquat 336 and kerosene. The extraction mechanism is based on anion exchange and the reaction is very fast compared to other complex formation due to the strong electrostatic interactions between electrons (Björkegren & Karimi, 2011). Moreover, mercury exhibits a strong tendency to form complexes with ligands containing nitrogen, sulphur or phosphorus as donor atoms rather than with oxygen containing electron donors (Fabrega & Mansur, 2007).

The observation as shown in Figure 4.2 (a) shows that membrane solution is stable up to five hours when ionic liquid 0.1 M [Bmim][NTF$_2$] is added into the solution mixture. On the other hand, the membrane solution only stable up to three hours when [Bmim][NTF$_2$] is absent. The increase of membrane stability by [Bmim][NTF$_2$] can be explained by the Coulumbic interactions of the charged ions between Aliquat 336 and [Bmim][NTF$_2$] (Goyal *et al.*, 2011a).

Based on this observation, it was suggested that the introduction of ionic liquid [Bmim][NTF$_2$] prolonged the membrane stability. Thus, the performance of HFSLM can be enhanced.

(a)	(b)
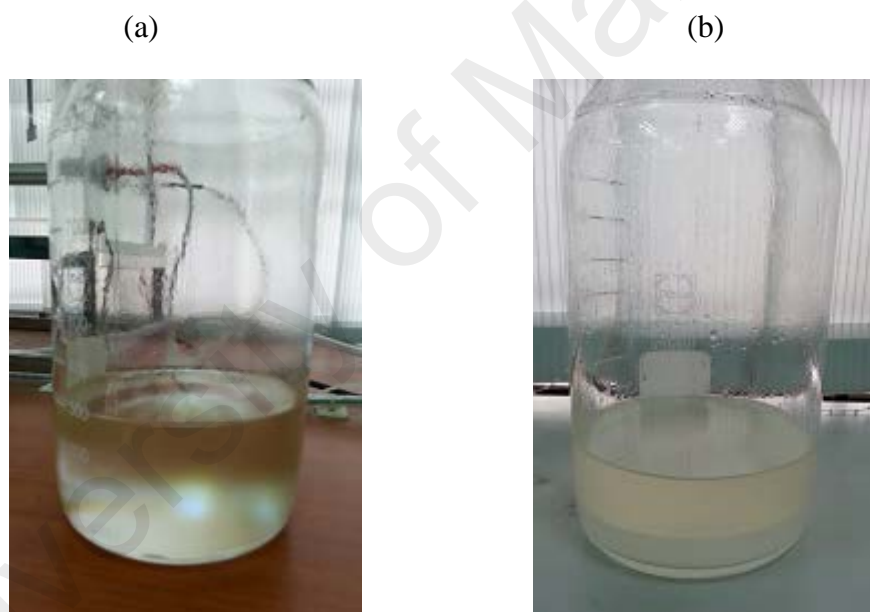
Figure 4.2: Membrane solution prepared with (a) 0.12 M Aliquat 336 and 0.10 M [Bmim][NTF$_2$] (b) 0.12 M Aliquat 336 only.

The miscibility of these ionic liquids was also studied by mixing 2 mL of Aliquat 336 with 2 mL of imidazolium based ionic liquids and 1 mL of HCl. Table 4.2 shows that all the ionic liquids tested resulting on homogenous liquid phase. This suggested that Aliquat 336 tends to form a good interaction with imidazolium based ionic liquids where the clear phase was formed . Hence, the study of Hg extraction efficiency by the mixture of ionic liquid- Aliquat 336 was conducted for [Emim][NTF$_2$], [Bmim][NTF$_2$] and [Hmim][NTF$_2$].

Table 4.2: Miscibility of Aliquat 336 with imidazolium based ionic liquids

Extractant	Co - extractant	Observation
Aliquat 336	[Emim][NTF$_2$]	Miscible, a very clear phase was formed
	[Bmim][NTF$_2$]	Miscible, a clear yellowish phase was formed
	[Hmim][NTF$_2$]	Miscible, a clear yellowish phase was formed

4. 3 The removal of mercury by hollow fiber supported liquid membrane using Aliquat 336 as the extractant and imidazolium based ionic liquids as the co-extractant.

Section 4.2.2 revealed that, the addition of [Bmim][NTF$_2$] improves the stability of membrane solution. Thus, the imidazolium based ionic liquids were introduced as co-extractant in the membrane solution. Three types of imidazolium based ionic liquids were used, namely [Emim][NTF$_2$], [Bmim][NTF$_2$] and [Hmim][NTF$_2$]. The concentration of ionic liquids was kept at 0.10 M.

The mixture of Aliquat 336 - [Emim][NTF$_2$] , Aliquat 336 - [Bmim][NTF$_2$] and Aliquat 336 - [Hmim][NTF2] were utilized as the membrane solution for Hg removal. Figure 4.3 shows that the order of extraction efficiency follows a trend of Aliquat 336 - [Hmim][NTF$_2$] < Aliquat 336 - [Bmim][NTF$_2$] < Aliquat 336 - [Emim][NTF$_2$]. Aliquat 336 - [Emim][NTF$_2$] gave the highest Hg removal efficiency at 95% in comparison to single ionic liquid Aliquat 336. Even though the work of de Ios Rios et al. (2008) claimed that the performance of ionic liquid can be improved by enlarging the length of alkyl chain in the cation, the present study showed that the alky chain of the cation had little effect on the extraction efficiency enhancement. Instead, the increase of alkyl chain length on imidazolium based ionic liquids increases the viscosity of the ionic liquids lowering the removal efficiency.
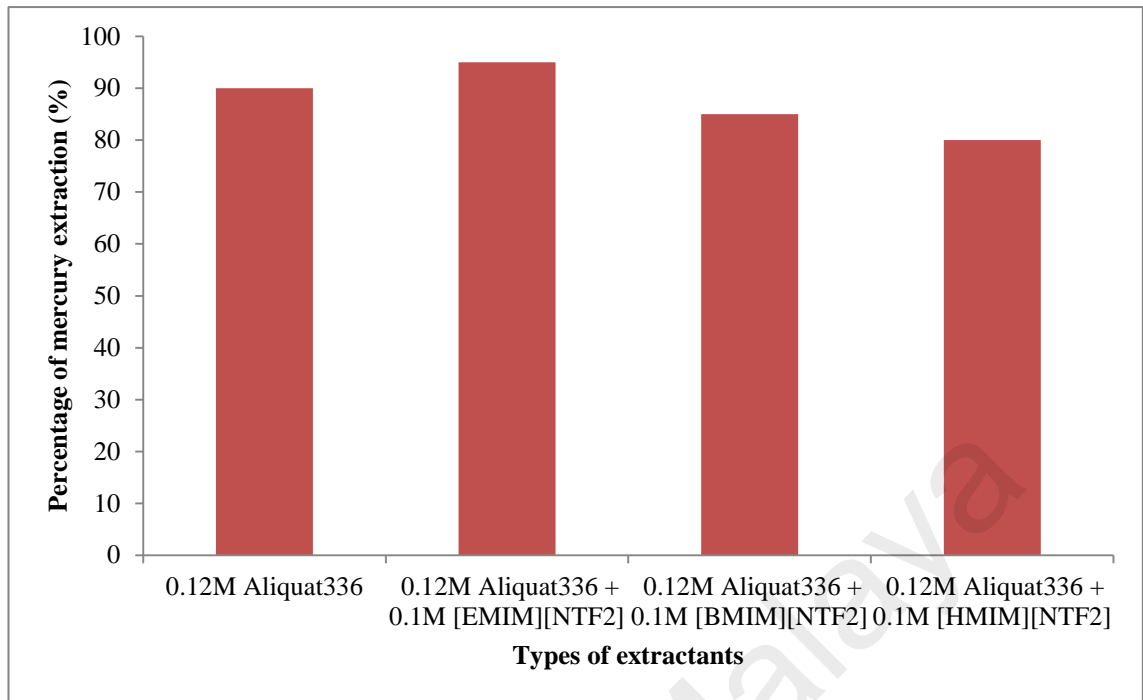
Figure 4.3: The effect of co – extractant on the removal efficiency of H. (Stripping phase : 0.1M thiourea , flow rate for feed and stripping phase :100 mL/min).

4.4 The mechanism for mercury extraction using the mixture of ionic liquid Aliquat 336 and [Emim][NTF₂]

In HFSLM process, the extraction and stripping occur simultaneously in single step through the transport of Hg across the liquid membrane via the extractant in the membrane pores. The transport of Hg from feed phase to stripping phase is driven by the concentration gradient between the two phases, which is proportional to the pH difference between the phases.

The feed phase was prepared by dissolving the theoretical amount of $HgCl_2$ in the HCl solutions. Hg ion existed in various form in aqueous phase such as Hg^{2+}, $HgCl^+$, $HgCI_2$, $HgCl_3^-$ and $HgCl_4^{2-}$ (Sato & Nakamura, 1980). In the presence of Cl^-, $HgCl_2$ was converted to $HgCl_4^{2-}$, especially when the concentration of Hg in the feed phase was <5 ppb . The deprotonation of Hg by HCl in the feed phase is as shown in Equation (4.2).

$$HgCl_2 + 2HCl \rightarrow HgCl_4^{2-} + 2H^+ + 2Cl^- \qquad (4.2)$$

In the membrane phase, two types of ionic liquid extractants was present , namely Aliquat 336 and [Emim][NTF₂] . The reaction between $HgCl_4^{2-}$ with Aliquat 336 and [Emim][NTF₂] took place at the membrane interface. The extraction of $HgCl_4^{2-}$ with the mixture of extractants Aliquat 336 $[(CH_3R_3N^+)Cl^-]$ and [Emim][NTF₂] yielded Hg complex, as show in Equation (4.3):

$$HgCl_4^{2-} + 2[(CH_3R_3N^+)Cl^- + m[Emim]^+[NTF_2]^- \longleftrightarrow \overline{[(CH_3R_3N^+).HgCl_4^{2-}.(EMIMNTF_2)_m}} \quad (4.3)$$
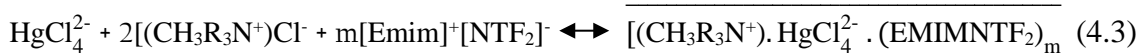
where m represents the stoichiometric coefficients.

The complex formed diffused across the membrane phase to membrane - stripping interface. This complex reacted with thiourea, the stripping agent. The Hg ion was stripped by thiourea at membrane stripping interphase as $HgCl_4^{2-}$ ion and the ionic liquid extractant was regenerated , as shown in Equation (4.4). The schematic mechanisms of the extraction and stripping of $HgCl_4^{2-}$ are shown in Figure 4.4.

$$\overline{[(CH_3R_3N^+).HgCl_4^{2-}.(EMIMNTF2)_m} + y(NH_2CSNH_2) \longleftrightarrow$$

$$2(CH_3R_3N^+)Cl^- + \overline{HgCl_2(NH_2CSNH_2)y} + m(EMIMNTF_2) \qquad (4.4)$$
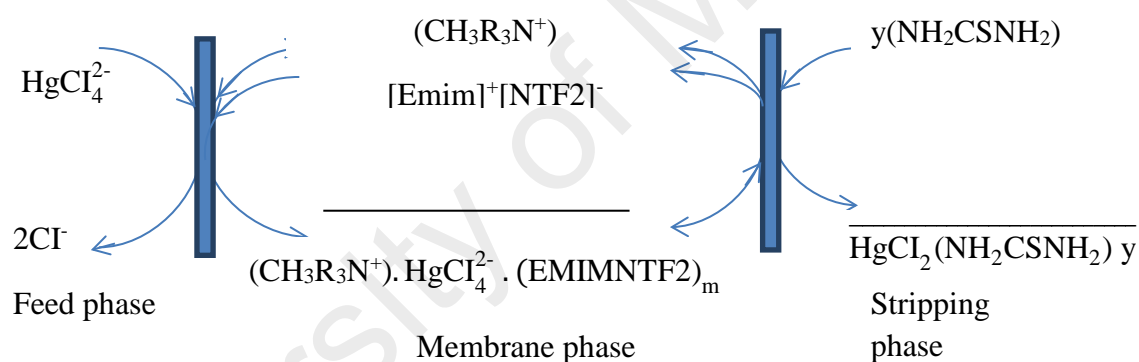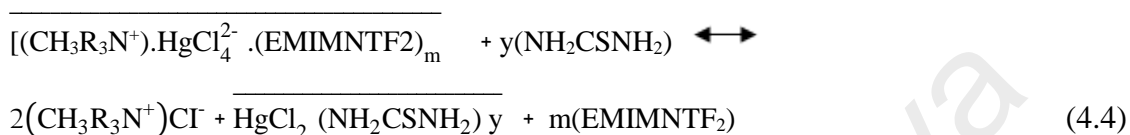
Figure 4.4: The schematic mechanisms of the extraction and stripping of $HgCl_4^{2-}$ by a mixture of ionic liquid Aliquat 336 and [Emim][NTF$_2$] with thiourea as stripping agent.

4.5 Parameter optimization for mixture of Aliquat 336 and [Emim][NTF$_2$] stabilized supported liquid membrane extraction process

The performance of HFSLM technology is dependent on several factors such as the types of extractant, co–extractant and stripping agent, circulation time for the extractant, the flow rates of feed and stripping phases and the number or separation cycles. Other important process parameters are the pHs of the feed and the stripping phases which are the main driving force in Hg migration. The effects of process parameters to Hg removal were investigated in this study. The concentration of Aliquat 336 was kept constant at 0.12 M , which was the optimum concentration, in all experiments. The results are presented in the following sub-sections.

4.5.1 Effect of co- extractant concentration on HFSLM performance

The effect of co-extractant was investigated using [Emim][NTF$_2$] at a range of 0.1M-0.26M. In this study, Aliquat 336 was kept constant at 0.12M. Figure 4.5 shows that the removal efficiency for Hg increases with the increase of co – extractant concentration up 0.18M due to enhanced stability of the membrane. When [Emim][NTF$_2$] concentration was increased, more Hg-complex formation took place . However, this also resulted in the increase of high viscosity of HFSLM and thus the mass transfer resistance . This eventually caused the reduction in Hg removal when the co-extraction concentration was > 0.18M.

Chakrabarty *et al.*, (2010b) also reported that the increase in liquid membrane viscosity resulted in the reduction of Hg recovery. This phenomenon also explained by the physical observation during the experiment whereby the changes in liquid membrane turbidity was observed when high concentration of co–extractant was applied. According to Ghosh *et al*.,(1995), the extraction of cephalosporin C through

Aliquat 336 based SLM showed a similar extraction efficiency trend as in this study. The extraction efficiency increased with the increase of extractant concentration. However, beyond the optimum concentration, the transport of cephalosporin C decreased due to the increase in Aliquat 336 which reduced the diffusion process in the membrane phase (Ghosh *et al.*, 1995) .Nevertheless, Figure 4.5 illustrates the optimum Hg extraction and recovery efficiencies that are achieved at 0.18M [Emim][NTF$_2$] concentration..
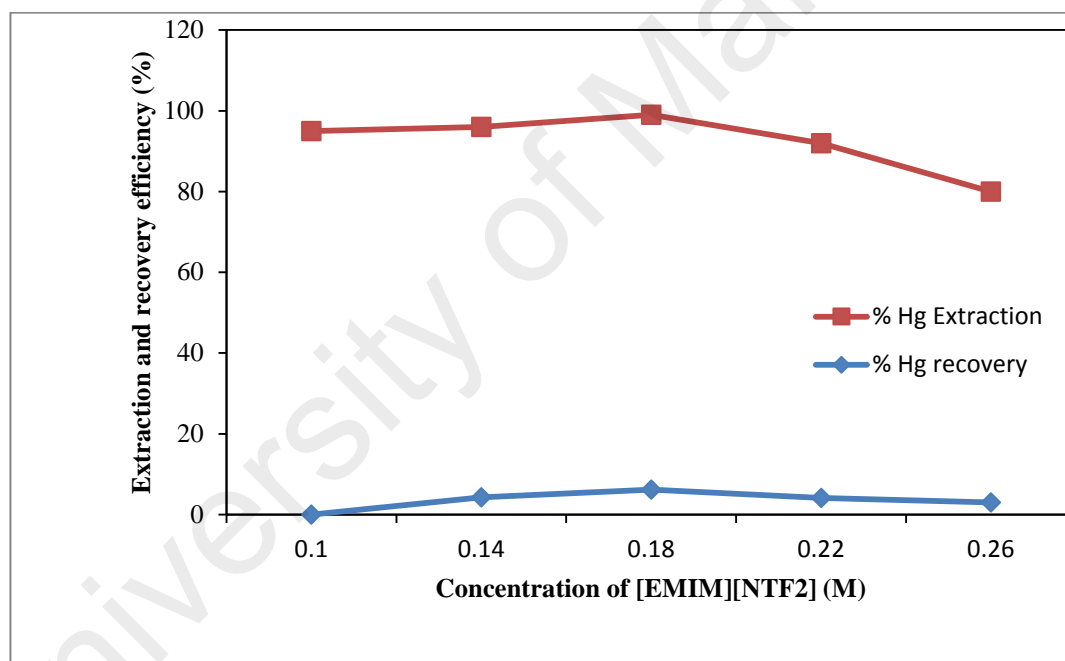
Figure 4.5: The effect of co – extractant concentration on the extraction and recovery efficiency for Hg. (Aliquat concentration 336 : 0.12 M , stripping phase : 0.1M thiourea, feed and stripping flow rate = 100 mL/min.)

4.5.2 Effect of stripping agent concentration on HFSLM performance

Thiourea was selected as the stripping agent in this study due to the structure of Aliquat 336. The quaternary ammonium cation was difficult to be stripped compared to the other amines. Hence, the stripping agent chosen must be strongly attracted to the quaternary ammonium cation rather than the anion (Fabrega & Mansur, 2007). Thiourea was chosen as stripping agent as there is no formation of precipitate in the stripping solution. This can further reduce the membrane fouling which can cause the decrease in stripping efficiency (Fabrega & Mansur, 2007; Chakrabarty *et al.*, 2010b; Lothongkum *et al.*, 2011).

Thiourea was used as the stripping agent to strip Hg ions from Hg–complex as shown in Equation (4.4). The Hg species formed in the stripping phase was impermeable to the membrane phase. In this study, thiourea concentration in a range of 0.05 M - 0.25 M was used in order to investigate the effect of stripping agent concentration on the stripping efficiency in HFSLM system. Figure 4.6 shows that Hg stripping efficiency is increased from 31% to 35% when thiourea concentration is increased from 0.05M to 0.1M. However, it is worth noting that when thiourea concentration is > 0.1M, a lower stripping efficiency of 10- 25% is observed, as shown in Figure 4.6. Thus, an optimum thiourea concentration of 0.1M was taken for further investigation.
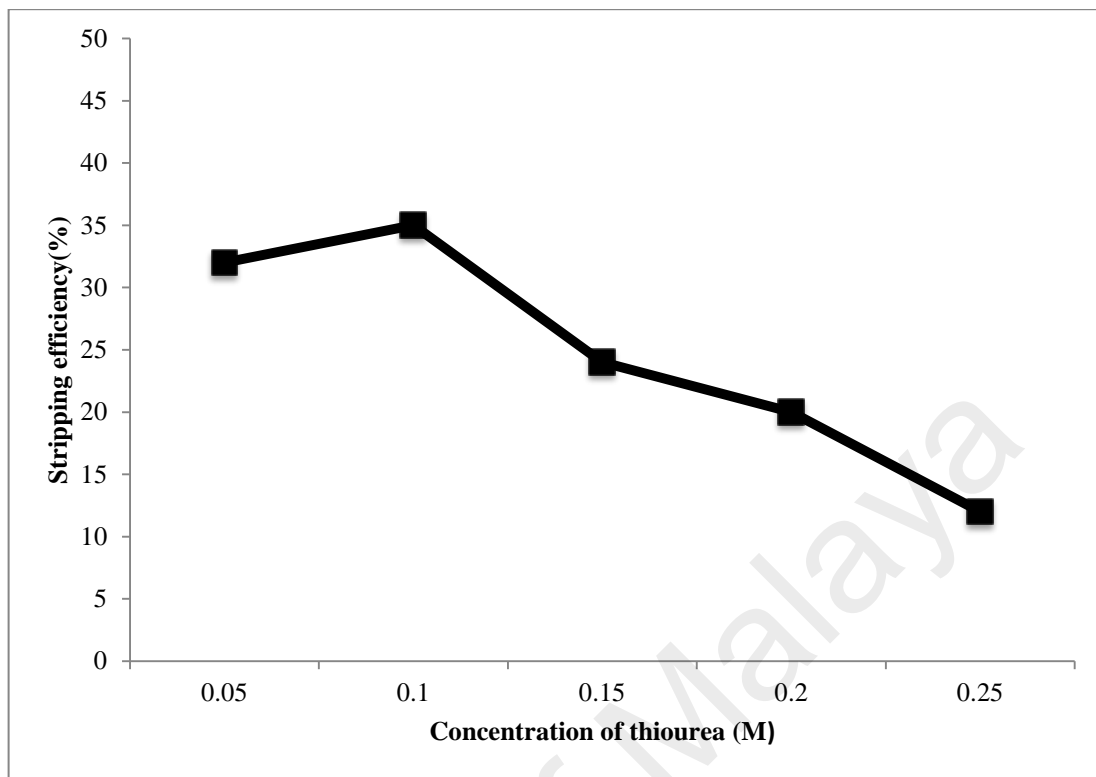
Figure.4.6: The effect of stripping agent concentration on stripping efficiency . (Aliquat 336 concentration : 0.12M ; Emim][NTF$_2$] concentration : 0.18M, feed and stripping flow rate : 100 mL/min.)

4.5.3 Effect of circulation time of extractants on HFSLM performance

The circulation time of extractants is also another important parameter that influences Hg removal efficiency. In this study, the effect of circulation time on the stability of HFSLM was investigated from the view of liquid membrane loss from the membrane module. The range of the circulation time investigated was 20-80 minutes.

Figure 4.7(a) depicts that the membrane solution is stable after 20 minutes of circulation. In contrast, milky solution is observed when the membrane solution is circulated for 40, 60, and 80 minutes, as shown in Figure 4.7(b). This suggested that poor membrane stability was observed for the tests of 40, 60 and 80 minutes circulation time. This is supported by the experimental results that the extraction efficiency for Hg is negligible in these tests (Figure 4.8), indicates that the failure of liquid membrane.

(b)

Figure 4.7: Membrane solution prepared with 0.12M Aliquat 336 and 0.18 M [Emim][NTF$_2$] : (a) 20 minutes of circulation time ; (b) 40- 80 minutes of circulation time.

When ionic liquid/membrane solution was circulated for 20 minutes, a stable solution with yellowish layer was formed, indicated that the membrane phase remained stable. This can be explained by the appearance of excess ionic liquid on the membrane surface that needed to be removed. The immobilized ionic liquid remained inside the tube and shell sides of the membrane module. On the other hand, a prolonged used of membrane circulation of > 20 minutes resulted in the diminish of membrane stability and this further deteriorated the membrane efficiency. This could be due to several reasons, such as chemical degradation, loss of membrane solution at prolonged circulation time and formation of emulsion (Zha *et al.*, 1995). In this study, the best circulation time, for membrane solution to achieve maximum of 99.99 % Hg removal efficiency was 20 minutes.
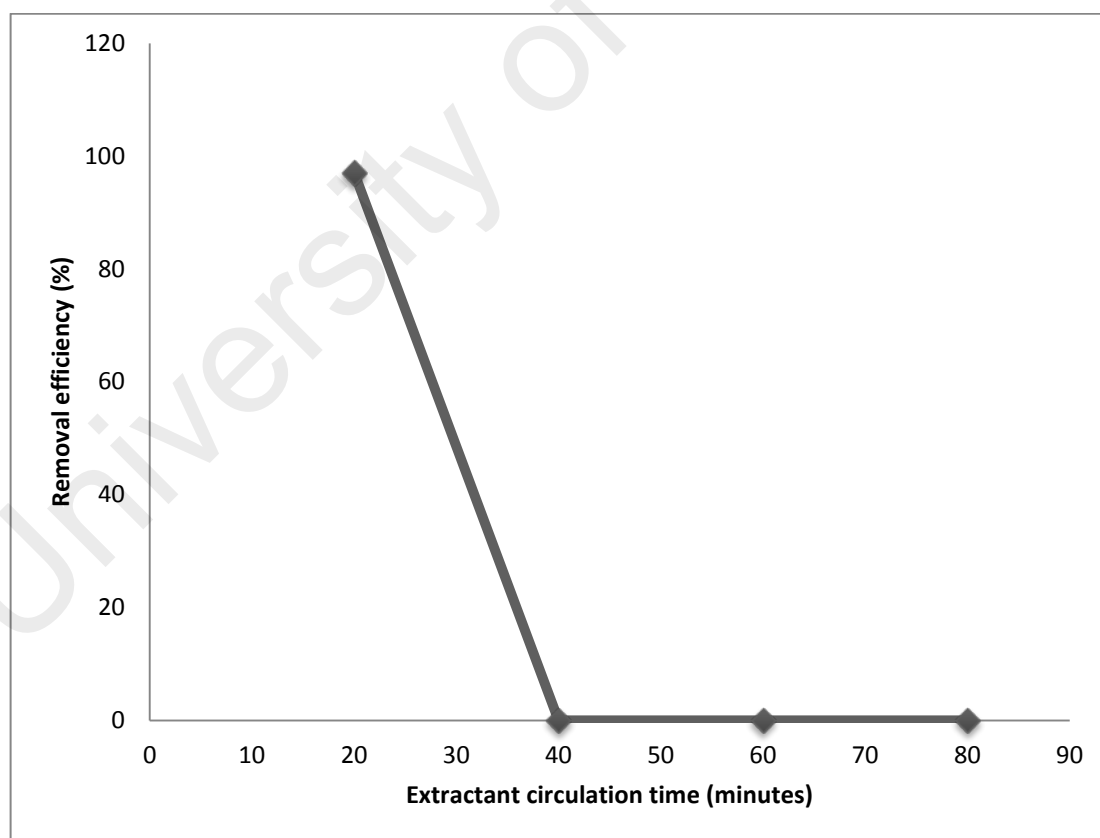
Figure 4.8 : The effect of circulation time for membrane solution on Hg removal efficiency. (Aliquat 336 concentration : 0.12 M; [Emim][NTF$_2$] concentration : 0.18 M; flow rate for feed and stripping phases : 100 mL/min ; stripping phase : 0.1 M thiourea).

4.5.4 Effect of flow rates of feed and stripping phase on HFSLM performance

The effect of feed and stripping flow rates on Hg removal efficiency was evaluated in a range of 50 mL/min – 250 mL/min. Figure 4.9 illustrates that the increase in feed and stripping flow rates from 50 mL/min to 250 mL/min increases the removal efficiency. This was mainly due to the formation of internal droplet in the process. When the speed of the homogenizer was increased, droplets with smaller size were produced. This resulted in higher contact surface area and thus increased the mass transfer rate (Hanna & Larson, 1985).

In addition, the increase in flow rates also resulted in the reduction of boundary layer thickness between the feed-membrane-stripping phases (Gabelman & Hwang, 1999). This reduced mass transfer resistance and induced higher mass transfer flux for the solute, in this case, Hg across the membrane (Shen *et al.*, 2009; Zidi *et al.*, 2010).

However, it is worth noting that as the flow rate of feed and stripping phases increase from 100 mL/min to 150 mL/min, a sudden decrease in removal efficiency is observed, as shown in Figure 4.9. This was plausibly to be caused by the reduction in residence time for mass transfer, as a result of high flow velocity. Low residence time resulted in less contact time between Hg and the membrane, and this lead to lower diffusion rate and removal efficiency. From this study, the best flow rates for the feed and stripping phases were 100 mL/min.
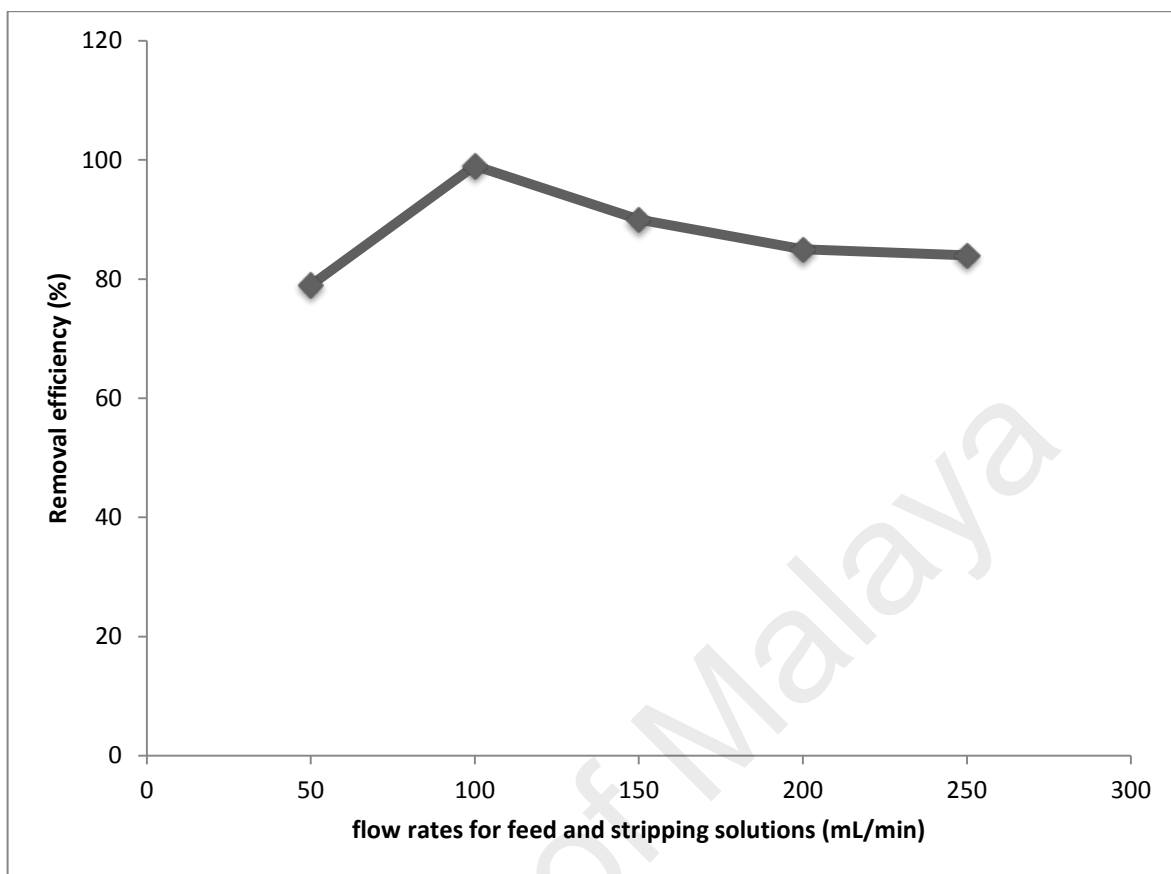
Figure 4.9: The effect of feed and stripping flow rates on Hg removal efficiency. (Aliquat 336 concentration : 0.12 M; [Emim][NTF$_2$] concentration :   0.18 M; stripping phase : 0.1 M thiourea)

4.5.5 Effect of the number or separation cycles on HFSLM performance

Previous experiments were conducted in 1 cycle (40 minutes) operation. In order to further evaluate long term application of ionic liquid membrane in HFSLM, a study on the investigation of multiple number of separation cycles was carried out in order to obtain the optimum removal efficiency.

Figure 4.10 depicts that a slight increment in removal efficiency from 97% to 99.99% is observed when the separation cycle is increased from 1 to 3. However, the removal efficiency is found to reduce when the number of separation cycle was exceed 3. This was mainly due to the loss of membrane stability via pore fouling at prolonged operation (120 minutes). Hence, in order to maintain the removal efficiency and to minimize ionic liquid loss from the membrane pores, the operation was suggested not to exceed 120 minutes.
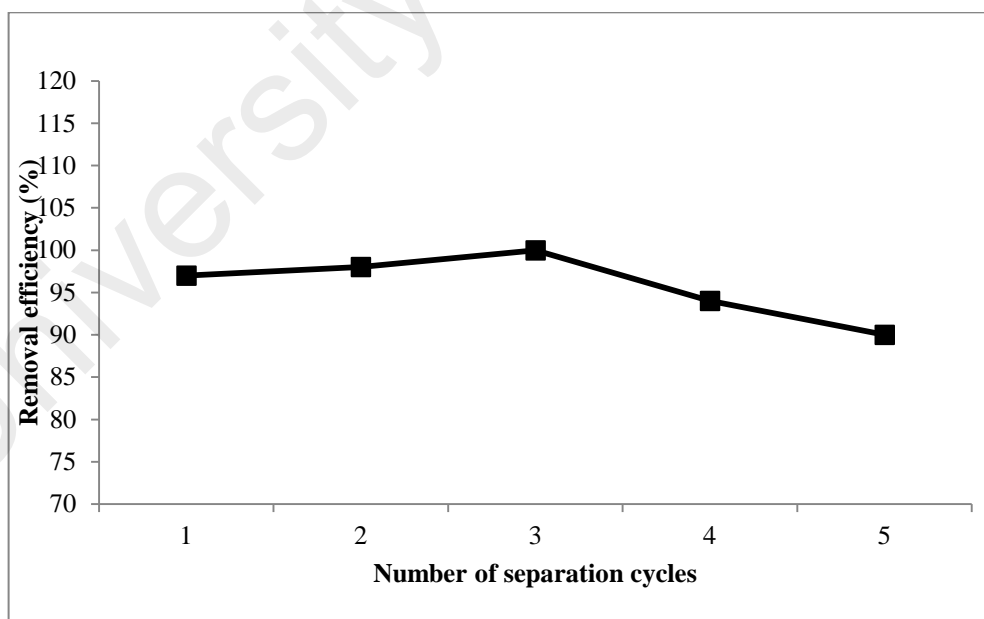
Figure 4.10: The effect of separation cycles on Hg removal . (Aliquat 336 concentration : 0.12 M; [Emim][NTF$_2$] concentration : 0.18 M; flow rate for feed and stripping phases : 100 mL/min ; stripping phase : 0.1 M thiourea)

4.6 Permeability coefficient

The permeability of ionic liquid membrane was determined from the mass transfer rate equation, as shown in Equation (4.5) (Danesi, 1984):

$$-V_f \ln\left(\frac{C_f}{C_{f,o}}\right) = AP\frac{\beta}{\beta+1}t \qquad (4.5)$$

where, $\beta = \frac{Q_f}{PL\varepsilon\pi r_i}$

V_f : volume of feed (cm^3)

C_f : concentration of mercury ions at time t (mol/L)

$C_{f,o}$: concentration of mercury ions at time 0 (mol/L)

A : affective area of hollow fiber module (cm^2)

P : permeability coefficient (cm/s)

Q_f : feed solution volumetric flow rate (cm^3/s)

L : length of hollow fiber (cm)

ε : porosity of hollow fiber (%)

N : the number of hollow fiber in the module

r_i : internal radius of hollow fiber (cm)

The permeability coefficient of Hg was determined from the gradient of the plot of $-V_f\ln\left(\frac{C_f}{C_{f,o}}\right)$ versus t. The value of P (cm/s) at different extractant concentrations are as shown in Table 4.3. The permeability coefficient of Hg was increased from 0.327×10^{-2}cm/s to 2.056×10^{-2}cm/s when the concentration of [Emim][NTF$_2$] was increased from 0.1M to 0.18M. However, a further increase of [Emim][NTF$_2$] concentration reduced the permeability coefficient. This could be due to the high viscosity of the extractants which resulted in low mass transport.

Table 4.3: The permeability coefficient of Hg at 0.1-0.26 M [Emim][NTF$_2$] .(Aliquat 336 concentration : 0.12 M ; stripping phase 0.1 M thiourea ; feed and stripping flowrate = 100 mL/min)

[Emim][NTF$_2$]	Permeability coefficient of mercury (x10^{-2} cm/s)
0.1	0.327
0.14	0.339
0.18	2.056
0.22	0.451
0.26	0.287

4.7 Design of experiment

Design of experiment provides statistical models that help in understanding the interaction between the operating parameters and subsequently analysing the results. Response surface methodology (RSM) is one of the techniques that are commonly applied in many fields. RSM is a collection of statistical and mathematical approaches that help researchers to model, analyse the response of interest and optimize the responses (Montgomery, 1997). RSM not only explores the optimum level for each process parameter but also connects the interaction between the parameters and provides the impacts on the measured responses. In comparison to normal factorial experiment design, this methodology offers some advantages such as it requires fewer numbers of experiments without affecting the interactions between the parameters.

The purpose of this study was to evaluate the interaction effect between co-extractant concentration, stripping concentration, flow rates of feed and stripping phases and the number of separation cycles on Hg removal efficiency.

The study was conducted using Box-Behnken design (BDD) through the aid of Design-Expert 6.0.8 software. The design consisted of 29 experiments including five replicates for centre point experiments. BDD was used to estimate the coefficients of response function which denoted as second order polynomial as given by Equation (4.6), where Y is the predicted response, β_i, β_j and β_{ij} are the coefficients estimated from the regression, X is the value of the parameters investigated, i is the linear coefficient, j is the quadratic coefficient, k is the number factors and e is the random error.

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_j X_i^2 + \sum_{i<j}^{k} \sum_j^{k} \beta_{ij} X_i X_j + \ldots + e \qquad (4.6)$$

The range of the parameters investigated and the sequence of the experiments are as shown in Table 4.4 and Table 4.5, respectively.

Table 4.4: The operating parameters and their levels in response surface methodology study.

Parameters	Levels		
	-1	0	1
Co- extractant concentration (Molar)(X_1)	0.1	0.18	0.26
Stripping agent concentration (Molar)(X_2)	0.05	0.15	0.25
Flowrate feed and stripping phase (mL/min)(X_3)	50	175	300
Number of separation cycles (cycles)(X_4)	1	3	5

Table 4.5: Box-Behnken design matrix

Experiment	X_1	X_2	X_3	X_4	Hg removal efficiency
1	0.10	0.15	175	5.0	96
2	0.18	0.15	50	1.0	97
3	0.26	0.15	50	3.0	92
4	0.18	0.25	175	5.0	83
5	0.18	0.05	50	3.0	93
6	0.18	0.15	175	3.0	94
7	0.10	0.25	175	3.0	90
8	0.18	0.05	175	1.0	78
9	0.18	0.15	175	3.0	92
10	0.18	0.15	175	3.0	88
11	0.18	0.25	50	3.0	87
12	0.18	0.05	175	5.0	79
13	0.18	0.25	175	1.0	83
14	0.18	0.15	300	1.0	79
15	0.18	0.25	300	3.0	78
16	0.18	0.05	300	3.0	70
17	0.26	0.15	175	1.0	90
18	0.26	0.15	175	5.0	90
19	0.26	0.05	175	3.0	90
20	0.18	0.15	300	5.0	88
21	0.18	0.15	50	5.0	90
22	0.10	0.15	300	3.0	90
23	0.10	0.15	175	1.0	85
24	0.26	0.25	175	3.0	98
25	0.18	0.15	175	3.0	99
26	0.10	0.15	50	3.0	96
27	0.26	0.15	300	3.0	94
28	0.18	0.15	175	3.0	99
29	0.10	0.05	175	3.0	78

4.7.1 Interactions and optimization of the parameters

In the design of experiment (DoE), Hg removal efficiency was the predicted response. The experiments were conducted in the same sequence as provided in Table 4.5. All of the experiments conducted followed the matrix given while keeping constant value of 20 minutes circulation time of the extractants. The methodology of the experiments followed the same procedure as described in Chapter 3. The optimum values of selected parameters were obtained from the model by solving the regression equation and analyzing the response surface contour plots (Krishna *et al.*, 2013).

Based on the experimental results, quadratic model was suggested by the ANOVA analysis. The summary of ANOVA is illustrated in Table 4.6. The table shows that the Model F-value of 4.47 implies the model is significant whereby there is only a 0.29% chance that a Model F-Value this large could occur due to noise. For the model terms analysis, values of Prob > F of less than 0.05 indicate that the model terms are significant. In this case, C, B^2 and D^2 are significant model terms. Besides that, the Lack of Fit F-value of 1.13 also implies that the Lack of Fit is not significant in relative to the pure error, which is desired for the model.

In addition, the Predicted R^2 of 0.3586 is in reasonable agreement with the Adjusted R^2 of 0.5536. The Predicted R^2 is the prediction of a response value estimated by the model. To maintain the adequacy of the model, the difference between Adjusted R^2 and Predicted R^2 should be less than 0.20. In this model, the difference of 0.195 implies that the model is adequate. Furthermore, an adequate precision of 7.774, which is greater then 4 also indicates that the model is adequate and is suitable to be used to navigate the design space. This is further supported by the diagnostic of the model whereby the predicted value

fits the experimental values in a deviation of ±5%, as illustrated in Figure 4.11. Based on

the ANOVA, the coded statistical model was obtained, as shown in Equation (4.5), where:

$$Y = 72.9 - 74.4X_1 + 286.8\ X_2 - 0.02X_3 + 5.02X_4 + 261.7\ X_1{}^2 - 857.5X_2{}^2 - 1.7\text{x}10^{-4}X_3{}^2 - 1.17X_4{}^2 - 1.25X_2X_4 + 0.016X_3X_4 \tag{4.5}$$

Table 4.6: ANOVA analysis for Hg removal efficiency

Source	Sum of Squares	DF	Mean Square	F value	Prob > F	
Model	1100.37	14	110.04	4.47	0.029	significant
A	30.08	1	30.08	1.22	0.2834	
B	80.08	1	80.08	3.25	0.0880	
C	261.33	1	261.33	10.62	0.0044	
D	16.33	1	16.33	0.66	0.4259	
A^2	18.20	1	18.20	0.74	0.4011	
B^2	476.96	1	476.96	19.39	0.0003	
C^2	47.29	1	47.29	1.92	0.1826	
D^2	143.29	1	143.29	5.82	0.0267	
BD	0.25	1	0.25	0.010	0.9208	
CD	64.00	1	64.00	2.60	0.1242	
Residual	442.87	18	24.60			
Lack of Fit	89.20	14	25.26	1.13	0.5008	not significant
Pure Error	89.20	4	22.30			
Cor Total	1543.24	28				
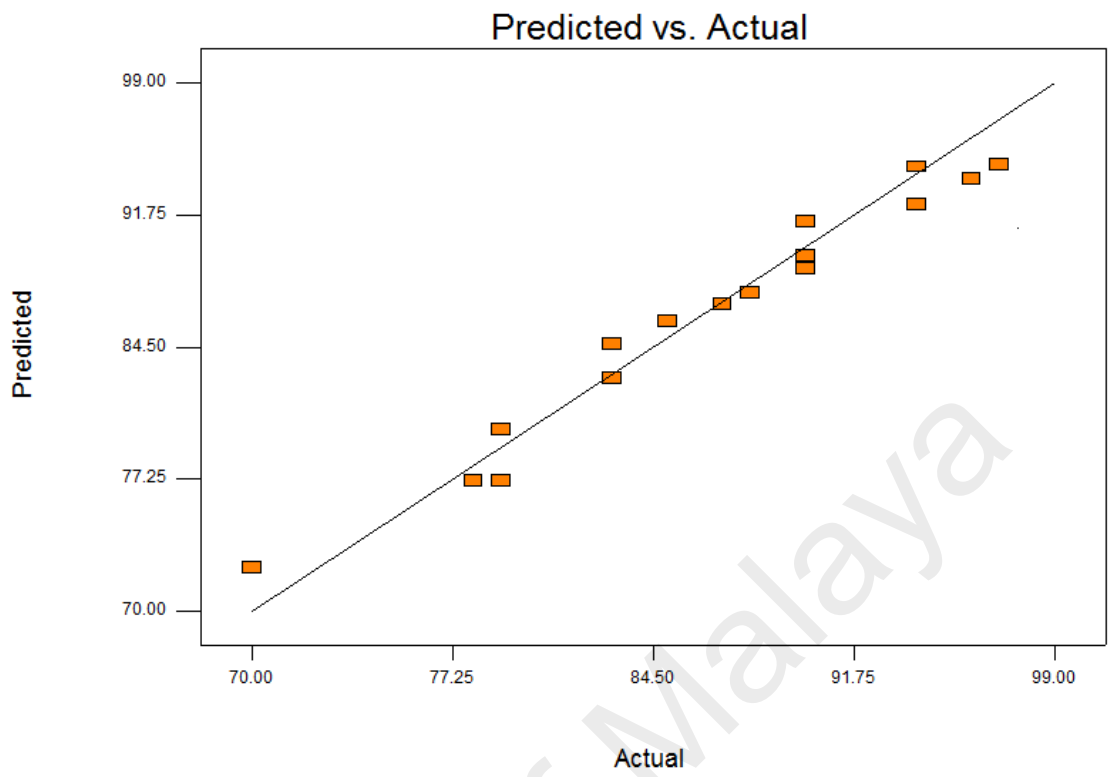
Figure 4.11: Predicted results versus experimental result for Hg removal efficiency.

4.7.2 Response surface (Contour plots)

Figure 4.12 illustrates the effects of separation cycle and stripping concentration on Hg removal efficiency. The removal efficiency was increased when the separation cycles and stripping agent concentration were increased up to the optimum values of 3 cycles and 0.12M, respectively. Beyond the optimum values , the removal efficiency is found to decrease. This was mainly due to the instability of HFSLM when membrane fouling took place at prolonged operation. Furthermore, the increase of stripping concentration beyond the optimum conecentration retarded the stripping process, as the reaction was shifted to the left hand side (Equation 4.4) , as suggested in Le Chatelier's principle.
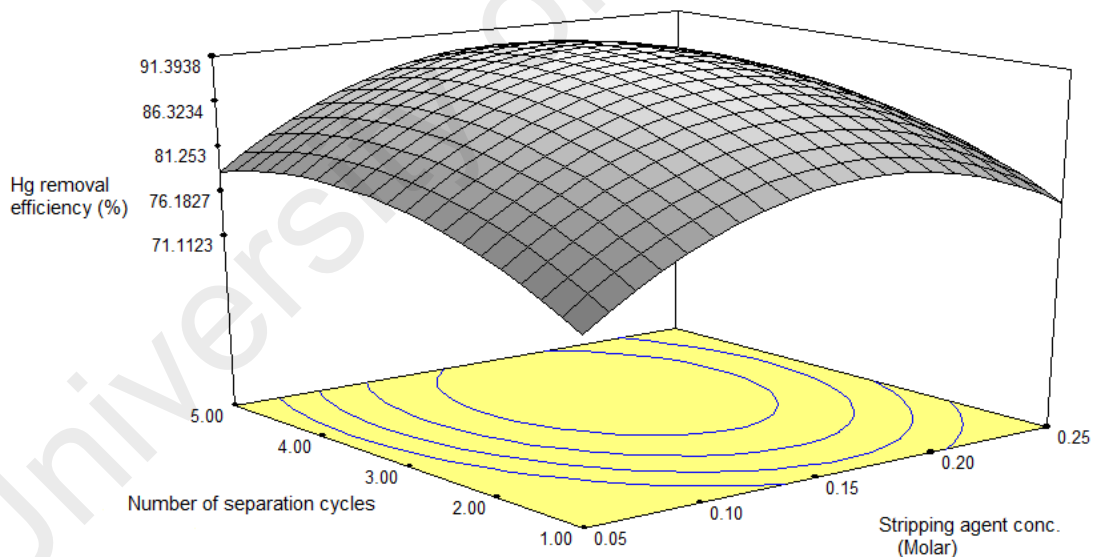
Figure 4.12: The effect of separation cycles and stripping concentration on Hg removal efficiency.

The interaction effect of separation cycles and the flowrates of feed and stripping phases on Hg removal efficiency is as illustrated in Figure 4.13. The removal efficiency decreased when the feed and stripping flow rates were increased. On the other hand, the increase of separation cycle up to three gave the optimum Hg removal at 98%. However, there was a reduction in the removal efficiency when the number of cycle was further increased. This was mainly due to the instability of HFSLM when membrane fouling took place at prolonged operation. Nevertheless, it was worth noting that the interaction between these parameters was small.
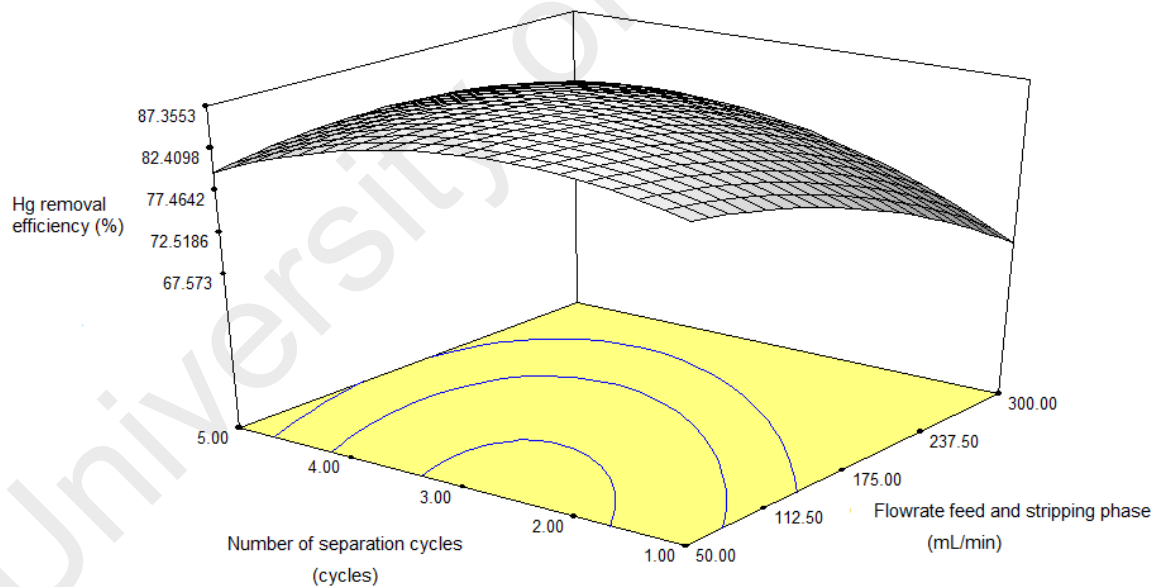
Figure 4.13: The effect of separation cycles and flowrate feed and stripping phase on Hg removal efficiency.

4.7.3 Optimization study

An optimization study was conducted using Design-Expert 6.0.8 based on the four parameters studied in Section 4.7. The optimum Hg removal efficiency could be achieved at 98% under 0.17M co-extractant concentration, 0.12M thiourea concentration, feed and stripping phases flow rates of 110 mL/min and three separation cycles. This combination was validated through an experimental study. The values of optimized parameters were found in good agreement with the experimental data, as shown in Table 4.7. This suggested that the model fits the experimental results and is statistically valid.

Table 4.7: Optimized value for the experimental result versus predicted result

Parameters	Experimental result	Predicted result
co-extractant concentration (M)	0.18	0.17
stripping concentration (M)	0.10	0.12
flowrate feed and stripping phase (mL/min)	100	110
number of separation cycles (cycle)	3	3
Removal efficiency (%)	99.99	95.00

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The investigation on the ability of Aliquat 336 and imidazolium based ionic liquids as extractant and co-extractant in liquid membrane was carried out. The addition of [Emim][NTF$_2$] as co-extractant was found to enhance the stability of HFSLM and Hg removal efficiency, as a result of strong dipolar and ionic interaction between Aliquat 336 and [Emim][NTF$_2$]. In contrast, [Bmim][NTF$_2$] and [Hmim][NTF$_2$] showed relatively lower enhancement in comparison to [Emim][NTF$_2$].

A further study was conducted for evaluating the effect of various operating parameters on Hg removal efficiency. They were : co-extractant concentration, stripping concentration , number of separation cycle and the flow rates for feed and stripping phase. The co-extractant concentration was the key factor for Hg removal as it improved membrane stability and provided more Hg-complexes formation. However, an excessive high concentration for co-extractant led to low mass transfer rate. Statistical study on these parameters using Box-Behnken based Response surface methodology revealed than the use of optimum conditions of 0.12M Aliquat 336 with 0.18M [EMIM][NTF$_2$] as the extractants, 0.1M thiourea as the stripping agent with the flow rates of feed and stripping solution of 100 ml/min at 3-cycle separation achieve 99.99% Hg removal. As a conclusion, HFSLM using ionic liquid is an efficient method in Hg separation in which the concentration of Hg is low.

As the future work, the use of task-specific ionic liquids (TSILs), where the anion and cation of the ionic liquid are tailored specifically for Hg removal should be studied. The role of anionic and cationic part of the ionic liquid can be explored in further study

using the different types of anions (FAP, PF_6) and cations. Besides that, the effect of temperature in the extraction of Hg should also be further studied.

From the view of equipment, the use of double membrane module in enhancing the stability of membrane is proposed to be further studied. Single membrane module was used to extract the Hg ion from the feed phase. The addition of extra module can provide higher surface area and thus providing higher contact surface between the Hg ions with the membrane for better removal efficiency.

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