DEVELOPMENT AND OPTIMIZATION OF NOVEL EMULSION LIQUID MEMBRANES STABILIZED BY NON-NEWTONIAN CONVERSION IN TAYLOR-COUETTE FLOW FOR EXTRACTION OF SELECTED ORGANIC AND METALLIC CONTAMINANTS

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To my family (both real and academic)
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SUMMARY

Extraction processes employing emulsion liquid membranes (ELMs), water-in-oil emulsions dispersed in aqueous phase, have been shown to be highly efficient in removing a variety of organic and inorganic contaminants from industrial wastewaters. As a result, they have been considered as alternative technologies to other more common separation processes such as pressure-driven membrane processes. Unfortunately, a widespread use of the ELM process has been limited due to the instability of emulsion globules against fluid shear. Breakup of emulsions and subsequent release of the internal receptor phase to the external donor phase would nullify the extraction process. Numerous studies have been, therefore, made in the past to enhance the stability of ELMs. Examples include adding more surfactants into the membrane phase and increasing the membrane viscosity. However, increased stability has been unfortunately accompanied by loss in extraction efficiency and rate in most reported attempts.

The primary objective of this research is to apply the ELMs in a unique contacting device, a Taylor-Couette column, which provides a relatively low and uniform fluid shear that helps maintaining the stability of emulsion without compromising the extraction efficiency of a target compound. The ELM used in this study is made of membrane phase converted into non-Newtonian fluid by polymer addition, which provides additional uncommon remedy for the problem. This innovative ELM process was optimized to treat various types of simulated industrial wastewaters containing selected phenolic compounds and heavy metals. Experiments performed in this study suggested that the newly developed ELM process achieved exceptionally high overall removal efficiencies for the removal of these target compounds in relatively short contact time. Mechanistic predictive models were further developed and verified with the experimental data. Combined with the experimental data and novel mathematical predictive models, this study is expected to have a high impact on immediate practices of emulsion liquid membrane technologies in relevant industries.
CHAPTER 1

INTRODUCTION

1.1. STATEMENT OF THE PROBLEM

Emulsion liquid membranes (ELMs), also called surfactant liquid membranes or liquid surfactant membranes, are basically double emulsions formed by emulsifying two immiscible phase (e.g. water droplets in an oil phase and vice versa) and dispersing the resulting emulsion in another external feed (or donor) phase containing solutes to be removed. Therefore, there are two different configurations for the ELM: (1) oil-in-water-in-oil (O/W/O) system and (2) water-in-oil-in-water (W/O/W) system. The latter ELM configuration is the target of the present study in which solutes are present in aqueous phase.

The ELM process is very unique and promising in the separation of mixtures (e.g. industrial wastewater containing toxic organic or inorganic substances). The ELM separation process has several attractive characteristics: 1) relatively low energy consumption especially compared to other separation processes such as thermal evaporation, electrodialysis and pressure-driven membrane processes (Naim and Monir, 2003), 2) rapid extraction with relatively high efficiency due to large surface area available for mass transfer (Frankenfeld and Li, 1987), 3) potential for removing various
toxic substances down to very low levels (Frankenfeld and Li, 1987; Skelland and Meng, 1999), 4) high selectivity especially when carrier agents are used in the membrane phase that bind exclusively with target compounds (Frankenfeld and Li, 1987), and 5) easy regeneration of the spent emulsions by a demulsification process (Li and Calo, 1992).

As a result, since the ELM technology was first introduced by Li in 1968, the ELMs have been intensively investigated and demonstrated as an effective alternative technology for diverse separation and purification processes including metal extraction (Draxler and Marr, 1986; Mikucki and Osseoasare, 1986; Reis and Carvalho, 1993; Urtiaga et al., 2000), separation of organic acids and bases (Halwachs et al., 1980; Terry et al., 1982; Yan et al., 1985; Baird et al., 1987; Wang and Bunge, 1990), and pharmaceutical separations (Frankenfeld and Li, 1987; Thien et al., 1988; Itoh et al., 1990). The ELMs have also received special interest for the treatment of industrial wastewaters containing a wide range of toxic contaminants such as phenolic compounds (Teramoto et al., 1983; Zhang et al., 1988; Gadekar et al., 1992; Devulapalli and Jones, 1999; Correia and de Carvalho, 2000) and heavy metals (Draxler et al., 1988; Ruppert et al., 1988; Marr et al., 1990; Raghuraman et al., 1994).

Unfortunately, the widespread use of the ELM process has been limited due to the instability of emulsion globules against fluid shear. Breakup of emulsions and subsequent release of the internal receptor phase to the external donor phase would nullify the extraction process (Nakashio et al., 1988; Skelland and Meng, 1996; Wan and Zhang, 2002). As a result, several attempts to enhance the stability of ELMs have been
made in the past decades, such as adding more surfactants in the membrane phase and increasing the membrane viscosity. However, it has been found to be extremely challenging to simultaneously maintain the advantages of this process (e.g. high membrane permeability and consequent high solute extraction rate) and to enhance the emulsion stability.

1.2. RESEARCH OBJECTIVES

The primary objective of this research is to apply the ELMs in a unique contacting device, a Taylor-Couette column, which provides relatively low and uniform fluid shear and help maintaining the stability of emulsion without compromising the extraction efficiency of a target compound. The ELMs used in this study is made of membrane phase converted into non-Newtonian fluid by polymer addition, which is, combined with the use of Taylor-Couette flow, also unique to this study. The combination of both measures is original in the literature and expected to provide very high extraction efficiency as a result of both stabilization mechanisms. The optimized ELM system is further employed to treat various types of simulated industrial wastewaters containing toxic substances (e.g. phenolic compounds and heavy metals) and to extract metallic ions from concentrated phosphoric acid solutions (as a case study for industrial application). Mathematical models are also developed to predict the performance of the ELM systems in the above processes. In particular, the proposed mechanistic model includes the effect of water chemistry in external phase that plays a critical role in extraction process but has not been well characterized in past studies.
More specific objectives of this study include:

*Chapter 3* – the extraction of a weak acid (benzoic acid as a model compound) using Type I ELM is studied. Optimum operating conditions are determined in terms of surfactant concentration, internal phase volume and polymer concentration. The effect of mixing intensity on both extraction rate and the leakage rate are also measured. The experimental results are used to elucidate the rate limiting step for mass transfer and the mechanism for the leakage of emulsion globules. A mathematical model is developed to simulate the performance of ELMs in this system and both analytical and numerical solutions are developed depending on the situation. Finally, comparisons are made between the Taylor-Couette column and stirred tank geometries as a function of equal power per unit volume.

*Chapter 4* – the applicability of the newly developed Type I ELM process is further evaluated for the removal of phenol and selected substituted phenols. Of particular interest in this study is elucidating the factors affecting the extraction efficiencies of various compounds including octanol-water partitioning coefficient of target compounds, pH of external phase, and the amount of surfactant used as an emulsifier. Key operational conditions such as volume fraction of internal phase, agitation speed, and dosage of a non-Newtonian additive are also determined.

*Chapter 5* – the Type II ELM process is applied and optimized for the extraction of metallic cations from synthetic phosphoric acid solutions. The study is specifically
focused on selecting appropriate carriers and stripping agents as well as on optimizing operating conditions for the effective extraction of the metallic cations by the ELM process. Several key parameters in this particular ELM system, such as concentration of carriers, metallic cations and phosphoric acid are also intensively investigated. Solvent extraction experiments are performed in parallel to screen the candidate carrier agents.

Chapter 6 – The applicability of the Type II ELM process is further evaluated for removal of common heavy metals such as cadmium, lead, nickel, and zinc from the simulated industrial wastewater. The effect of membrane composition (e.g. type of carrier agent) and operating conditions (e.g. the external feed phase and the agitation speed of Taylor-vortex column) on the metal extraction rate are also examined. A mathematical model is developed to predict the removal rates of metal ions from unbuffered solutions. In particular, the model incorporates the effect of change in external phase pH, which is found to be critical to determine the extraction efficiency of metal species.
REFERENCES


CHAPTER 2

BACKGROUND

2.1. GENERAL DESCRIPTION OF EMULSION LIQUID MEMBRANES (ELMS)

Emulsion liquid membranes (ELMs) consist of an aqueous phase (or internal stripping (or receptor) phase) stabilized by oil soluble surfactants and dispersed as very fine droplets (1 – 10 µm) inside an oil phase (liquid membrane phase). The resulting liquid membrane, or W/O emulsion, is further dispersed as emulsion globules (0.1 – 2 mm) in another aqueous solution (external feed (or donor) phase). The schematic of an ELM system is shown in Figure 2-1. Target solutes in the external feed phase (e.g. contaminants in industrial wastewater) are transferred across the membrane phase into the internal stripping phase during an extraction process. In this W/O/W ELM (i.e. in contrast to an O/W/O type ELM), the oil phase functions as a selective barrier, or membrane. The solute mass transfer is driven by the concentration difference between the external feed phase and the internal stripping phase. Activity of target solutes in the internal phase is typically kept at near zero by using a trapping agent in order to maintain the concentration gradient, although it gradually decreases, until most of target solutes are extracted from the external phase.
Figure 2-1. Schematic of an emulsion liquid membrane system.
2.2. EXTRACTION MECHANISMS AND DRIVING FORCES

ELMs have two categorized systems called Type I and II depending on whether a carrier agent (or an extractant) is present or not in the liquid membrane phase. In both ELM systems, the driving force of the solute transfer (or transport) through the membrane is the difference of the chemical potentials between the external feed phase and the internal stripping phase (Ho and Sirkar, 1992).

2.2.1. Type I ELM System

For the Type I ELM system, a solute should be soluble in all the three phases: external feed phase, oil membrane phase, and internal stripping phase. Therefore, a solute can diffuse across the membrane phase to the internal stripping phase. Then a stripping agent typically reacts with the transferred solute to convert it insoluble in the membrane phase, which makes a reaction product incapable of diffusing back through the membrane phase. Consequently, the solute concentration in the internal stripping phase is also maintained at zero by the reaction.

A benzoic acid extraction from an aqueous phase by ELMs is a representative example of the Type I system as shown in Figure 2-2. Benzoic acid in the external feed phase dissolves in the membrane phase. Then, it diffuses across the membrane phase and reacts with a stripping agent, NaOH in the internal stripping agent. Because of the high pH of the internal stripping phase resulted from the high concentration of NaOH, the
Figure 2-2. Schematic of benzoic acid extraction by ELMs.
transferred benzoic acid is converted into benzoate which is not soluble in the membrane phase. Thereby, it is trapped in the internal stripping phase. The zero concentration of benzoic acid in the internal stripping phase gives high concentration gradient across the membrane phase until they are completely extracted. In addition, the capacity of the internal phase can be increased by employing a sufficient amount of NaOH as a stripping agent.

2.2.2. Type II ELM System

A Type II ELM system involves the facilitated transport of a solute across the membrane phase by incorporating a carrier agent (or extractant). In this system, a solute is not soluble in the membrane phase, so it needs a carrier agent to transport the solute from the external feed phase to the internal stripping phase. Two reactions involved with a carrier agent take place at the external interface between the external and membrane phases and at the internal interface between the membrane and internal phases.

The zinc extraction from an aqueous phase by ELMs is an example of the Type II system as shown in Figure 2-3. A carrier agent dissolved in the membrane phase first reacts with zinc ion at the external interface to form a zinc-carrier complex. The complex is soluble in the membrane phase, so it can diffuse across the membrane phase to the internal stripping phase. Then, the transported zinc is stripped from the complex by a stripping agent. At the both reactions, protons are exchanged for the zinc ions. The extracting and stripping reactions take place as follow:
Figure 2-3. Schematic of zinc extraction by ELMs.
\[ \text{<Extraction Reaction> } \]
\[
Zn^{2+} + 2HR \rightarrow ZnR_2 + 2H^+ \\
\text{ (external phase)} \quad \text{ (membrane phase)} \quad \text{ (membrane phase)} \quad \text{ (external phase)}
\] (2-1)

\[ \text{<Stripping Reaction> } \]
\[
ZnR_2 + 2H^+ \rightarrow Zn^{2+} + 2HR \\
\text{ (membrane phase)} \quad \text{ (internal phase)} \quad \text{ (internal phase)} \quad \text{ (membrane phase)}
\] (2-2)

where \( Zn^{2+} \) = zinc ion; \( HR \) = a carrier agent; \( ZnR_2 \) = a zinc-carrier complex; \( H^+ \) = proton.

The concentrated acid drives the stripping reaction as shown in Equation (2-2) and maintains very low concentration of the zinc-carrier complex at the interface between the membrane phase and the internal stripping phase, which gives high driving force in terms of a concentration gradient of the zinc-carrier complex. Besides, the concentration gradient of the proton across the membrane phase also facilitates the transport of zinc.

**2.3. EMULSION LIQUID MEMBRANE PROCESS**

ELM process largely consists of three steps, which are emulsion preparation, solute extraction/emulsion separation, and demulsification. The schematic flow sheet of the process is shown in Figure 2-4. The configuration and key components of ELMs can vary depending on their application and the types of target solutes and the external feed phase treated. Choosing a suitable formulation of ELMs and optimizing the process are often pretty complicated.
Figure 2-4. A schematic flow sheet of an emulsion liquid membrane process.
Prior to the first step of emulsion preparation, it is required to prepare a membrane phase containing surfactant, extractant (or carrier agent for a Type II system), and the other additives such as polymer. The membrane phase is mainly composed of a solvent such as aliphatic and aromatic diluents. It is very critical to employ an appropriate solvent as membrane phase for an efficient ELM process. There are several considerations in choosing a suitable solvent (Ho and Sirkar, 1992): (1) low solubility in the external feed phase and the internal stripping phase in order not to lose the solvent during emulsion preparation and solute extraction, (2) compatibility with surfactant and extractant dissolved, (3) moderate viscosity balancing the membrane stability and permeability, (4) enough density difference from the aqueous phase for the fast process of emulsion separation, (4) low cost of its production, and (5) low toxicity because of environmental concern. Considering the above criteria of the membrane phase, aliphatic solvents are preferred, such as Soltrol 220 (an isoparaffinic oil, Chevron Philips Chemical, Spring, TX) used in this study. The physical properties of Soltrol 220 are below:

- Boiling point, °F = 450 – 550
- Specific gravity (at 60/60°F) = 0.809
- Molecular weight (Avg.) = NA
- Viscosity, cp = 3.7 (at 100°F)

A surfactant is also one of key components of the membrane phase for the establishment of an effective ELM process. The surfactant composed of a polar head group and a non-polar tail is an emulsifying agent which not only determines the stability of emulsion but also affects several other parameters such as osmosis, water solubility,
and mass transfer resistance (Draxler and Marr, 1986). The emulsifying agents form an interfacial film around the dispersed internal droplets and this film prevents or retards the droplet coagulation and flocculation (Cavallo and Chang, 1990). An appropriate surfactant should have the following properties. First, it should be soluble in the membrane phase only, neither the internal stripping phase nor the external feed phase in order not to lose any surfactant during operation. It should not react with the extractant in the membrane phase. If any, it would facilitate the decomposition of the extractant and subsequently affect the efficiency of the ELM process. In addition, it must have a low resistance to mass transfer and is stable against acids, bases, and bacterial activity. Last, demulsification must not be hindered by the surfactant.

In this study, Span 80 (sorbitan monooleate with a molecular weight of 428) was used as an emulsifying agent for the following reasons: it provides relatively stable and easily demulsified emulsions and it shows less resistance to mass transfer than other surfactants like Span 20 (sorbitan monolaurate), Span 40 (sorbitan monopalmitate), Span 60 (sorbitan monostearate), Span 65 (sorbitan tristearate), and ECA 4360 (a nonionic polyamine) (Draxler and Marr, 1986; Draxler et al., 1988; Nakashio et al., 1988; Strzelbicki and Schlosser, 1989; Lee and Chan, 1990). The molecular structure of Span 80 is presented in Figure 2-5.

For the Type II system, an extractant in the membrane phase selectively shuttles insoluble solutes across the liquid membrane. Accordingly, the selection of a suitable carrier is vital for the high performance of the system. The selection of a suitable
Figure 2-5. Schematic structure of sorbitan monoooleate (Span 80) (Nakashio et al., 1988).
extractant is generally based on the thermodynamic and kinetic considerations. That is, the selected extractant should thermodynamically favor to form a complex with a solute from the external feed phase and it should react kinetically fast for solute extraction. Therefore, the extractant with higher stability of the complex is more appropriate for the fast solute extraction from the external feed phase. However, it needs to be noted that the stability of the solute-extractant complex should be moderate for the ease of stripping process in the internal stripping phase.

2.3.1 Emulsion Preparation

For the preparation of stable emulsion, the size of internal droplets should be very tiny as small as 1 – 3 μm in diameter. It can be accomplished by high input of energy density to W/O emulsion during emulsification. For the small ELM system, high-speed agitators with stirring rates up 20,000 rpm and/or ultrasonic emulsifiers are used to prepare emulsion. Commercial devices such as colloidal mills are often used for a large ELM system (Zhang et al., 1988). During emulsification, an internal aqueous phase containing a stripping agent is introduced. Like the extraction process with an extractant in the membrane phase, the selected stripping agent should be also thermodynamically favorable for the stripping process and exhibit a fast reaction with a solute-extractant complex. Interestingly, however, owing to the very large interfacial area of internal droplets provided, even the stripping process with very low reaction kinetics can be employed in an ELM system.
2.3.2. Solute Extraction and Emulsion Separation (Settling)

The solute extraction step of an ELM process is initiated by dispersing the previously tailored emulsion into the external feed phase in a mixing contactor. During the dispersion operation with agitation in the external feed phase, emulsion is dispersed to form numerous small globules with a typical size of 0.1 – 2 mm in diameter. The consequent large interfacial area of emulsion globules is able to provide fast reaction in solute extraction process. Generally, higher agitation is desired for smaller emulsion globules, larger interfacial area, and resulting fast mass transfer. However, increasing the agitation speed increase shear rate and shear stress and thus, reduce the stability of emulsion, which causes breakage (or rupture) of emulsion liquid membranes. Hence, there is an optimal agitation speed in an ELM process. After the solute extraction, the emulsion separation from the treated external feed phase is completed by density difference in a settler.

2.3.3. Demulsification

Demulsification (i.e. the breaking of the loaded emulsion) is one of the critical steps in ELM process. After the solute extraction by ELMs, the spent membrane phase should be reused repeatedly and the enriched internal stripping phase is recovered or discarded. Hence, the separation of two immiscible liquids of oil membrane phase containing surfactant and extractant and internal aqueous phase containing highly concentrated solute is generally inevitable (Dines, 1982; Sun et al., 1998).
Demulsification has largely two major approaches: (1) chemical treatment and (2) physical treatment (Ho and Sirkar, 1992). Chemical treatment is adding a demulsifier to the loaded W/O emulsion and this method seems to be very effective in terms of the membrane recovery ratio. However, the added chemicals will change the properties of the membrane phase and thus, the recovered membrane phase cannot be reused. Besides, the additional cost for the demulsifiers and their recovery are another flaws. Therefore, this method is not usually used in demulsification process. Physical treatment includes heating, centrifugation, ultrasonics, solvent dissolution, high shear, microwave radiation, porous glass or fiber membrane and the use of high-voltage electrostatic fields. It is reported that the loaded W/O emulsion can be effectively broken by those methods (Ho and Sirkar, 1992; Li and Calo, 1992; Larson et al., 1994; Sun et al., 1998; Chan and Chen, 2002; Juang and Lin, 2004). In particular, electrostatic demulsification appears to be the most efficient and economic way for breaking the loaded W/O emulsion (Martin and Davies, 1977; Hsu and Li, 1985; Draxler et al., 1988; Kataoka and Nishiki, 1990). The mechanism of electrostatic demulsification is that the electrical field applied can polarize and elongate the internal droplets. With the induced charge from the electrical field, the adjacent water droplets will attract each other and coalesce to a big internal droplet (Hsu and Li, 1985). The effects of applied voltage, frequency, wave form, etc. are key parameters for the successful demulsification process (Draxler et al., 1988; Kataoka and Nishiki, 1990).
2.4. INSTABILITY OF LIQUID MEMBRANE AND SWELLING OF EMULSION

Despite of the fascinating features of ELMs, this technology is not widespread because of the two main hindrances: (1) the instability of the liquid membrane and (2) the swelling of emulsion. It has been stated that “the emulsion stability is the ‘Achilles heel’ of the ELM process” (Abou-Nemeh and van Peteghem, 1992) and “the unsolved difficulties with emulsion stability have diminished the direction of enlarging the process scale” (Szpakowska, 1996).

The stability of the emulsion is generally understood how resistant the liquid membrane is to leakage (or rupture) under high shear stress during the operation of solute extraction in ELM process. Accordingly, unstable liquid membrane is subject to be broken apart and release the internal stripping phase and the extracted solutes to the external feed phase, which nullify some of the solute separation already achieved (Park et al., 2004).

Swelling is the incorporation of some external feed phase into the emulsion, which increases the volume of the internal stripping phase and subsequently induces several related problems in ELM process. From a process point of view, the swelling is harmful for three reasons: (1) it decreases the driving force for solute extraction and dilutes the final concentration of the solute (Wan and Zhang, 2002); (2) it reduces the membrane thickness, which leads to breakage (Wan and Zhang, 2002; Park et al., 2004);
(3) it impacts on the viscosity of the ELM system and the dispersion of the emulsion in the external donor phase (Kulkarni et al., 2002; Park et al., 2004).

There are two main types of emulsion swelling: entrainment swelling and osmotic swelling (Ho and Sirkar, 1992). Entrainment swelling is caused by the entrainment of the external feed phase into the internal stripping phase due to the repeated coalescence and redispersion of emulsion globules during the dispersion operation (Wan and Zhang, 2002). Osmotic swelling is driven by differences in the osmotic pressure between the external feed phase and internal stripping phase. There are two possible mechanisms of swelling of emulsion induced by osmotic pressure (Ho and Sirkar, 1992). First, a surfactant molecule in the membrane phase can form a complex with a water molecule in the external feed phase. The hydrophilic polar head of the surfactant is hydrated at the interface between the membrane phase and the external feed phase. Then, the hydrated surfactant diffuses across the membrane phase and dehydrates at the interface between the membrane phase and the internal stripping phase. The other mechanism is transporting of a water molecule by reversed micelles. The reversed micelles are surfactant aggregates that stabilize water in the oil membrane phase. The hydrophilic heads of surfactants hold water inside the micelles while the hydrophobic tails of surfactants face toward the non-polar liquid membrane. Similar to the first mechanism, the micelles form at the interface between the membrane phase and the external feed phase and then, transport the water molecules into the internal stripping phase.
2.5. CONVENTIONAL REMEDIES FOR THE MEMBRANE INSTABILITY

Conventional solutions to the current problems in ELM process, particularly the liquid membrane instability, have taken two approaches: (1) increasing the concentration of surfactants in the membrane phase and (2) increasing the viscosity of the membrane phase.

2.5.1. Increase of Surfactant Concentration

Most of surfactant added during emulsification adsorbs at the interface between the oil membrane phase and the internal stripping phase. Therefore, an increase of the surfactant concentration in the membrane phase enhances the strength of the adsorption layer (Kulkarni et al., 2002). The increasing surfactant also decreases the interfacial tension between the membrane phase and the internal stripping phase. The interfacial tension is a surface free energy which exists between two immiscible liquid phases such as oil and water. The energy barrier produced by the interfacial tension prevents forming an emulsion. Hence, the interfacial tension should be lowered by adding an emulsifier (e.g. surfactant) for the emulsification. Because of the lowered interfacial tension by surfactant, the size of the internal droplets can be decreased, which consequently enhances the emulsion stability (Hsu and Li, 1985). There is a critical surfactant concentration beyond which the emulsion stability is improved no more (Kakoi et al., 1993).
However, this remedy is associated with a couple of critical problems in ELM process. First, high surfactant level causes swelling of emulsion, which is explained by one of the swelling mechanisms mentioned above: entrainment of the external feed phase by excessive surfactant in the membrane phase (Kinugasa et al., 1989) and by reversed micelles of surfactant (Itoh et al., 1990). In addition, high surfactant levels can hinder mass transfer of the solute by increasing the interfacial resistance (Nakashio et al., 1988) and interfere with the carrier reaction at the interface (Nakashio et al., 1988).

2.5.2. Increase of Membrane Viscosity

The volume fraction of the internal stripping phase and the viscosity of the membrane phase determine the viscosity of the W/O emulsion. The viscosity of emulsion is directly proportional to the stability of emulsion (Terry et al., 1982; Kinugasa et al., 1989). Therefore, employing highly viscous oil as a membrane phase is able to provide more stable emulsions. However, it has been found that the increased viscosity of the membrane significantly decreases the diffusivity for Newtonian fluids (Terry et al., 1982; Skelland and Meng, 1999). Thus this remedy reduces a solute diffusivity, and consequential decrease in extraction rate has been identified as problematic in ELM process (Terry et al., 1982; Wang and Bunge, 1990; Park et al., 2004).
2.6. PROPOSED NOVEL REMEDIES FOR THE MEMBRANE INSTABILITY

A couple of novel solutions to this decades-old emulsion instability problem were recently proposed by researchers at Georgia Institute of Technology. The first solution involves a conversion of the membrane phase into a suitable non-Newtonian form (i.e. pseudo-plastic) by dissolving high molecular weight polymers such as polyisobutylene. The second solution is utilizing a number of advantages of Taylor-Couette flow for the ELM process.

2.6.1. Non-Newtonian Conversion of the Membrane Phase

Non-Newtonian fluids are all the fluids for which the flow curve (shear stress vs. shear rate) is not linear through the origin at a given temperature and pressure (Skelland, 1967) and the flow curves of various Newtonian and non-Newtonian fluids are shown in Figure 2-6. Interestingly, it has been reported that the diffusivity of the solute is almost independent of the viscosity of many non-Newtonian fluids (e.g. dilute polymer solutions) unlike Newtonian fluids (Hopper, 1964; Skelland, 1967). This fascinating characteristic of the non-Newtonian fluid was first employed to a liquid membrane system by Skelland (1993) and its effectiveness was well demonstrated (Skelland, 1993). An appropriate non-Newtonian membrane phase was prepared by dissolving a proper amount of polymer into a Newtonian fluid. The viscosity of the liquid membrane can be increased by dissolving more polymers into the membrane so as to enhance the membrane stability. However, the diffusivity of the solute in the membrane is not much
Figure 2-6. Flow curves of various types of Newtonian and non-Newtonian fluids.
affected by increasing the polymer concentration up to its critical concentration at which the polymer entanglements begin to hinder the solute diffusion (Skelland and Meng, 1996). Furthermore, the abnormal facilitation of diffusion of the solute by an internal structure was sometimes observed, and that was resulted from the dissolved polymer in the membrane phase (Osmers and Metzner, 1972).

Further detailed benefits of appropriate non-Newtonian conversion of the membrane to the ELM process were as follows (Skelland and Meng, 1996):

1. The apparent viscosity of the non-Newtonian form of the liquid membrane is low because of the high shear rate used in the emulsification process. Therefore, the smaller size of the internal droplets can be obtained at the low apparent viscosity. These smaller internal droplets enhance the emulsion stability and provide much larger interfacial surface area for mass transfer (Lissant, 1974; Hsu and Li, 1985). Consequently, the extraction rate of the solute can be significantly enhanced due to the non-Newtonian membrane. However, the apparent viscosity of the emulsion is high because of the relatively low shear rate during the subsequent solute extraction process. Hence, very stable emulsion globules can be formed when the emulsion is dispersed in the external feed phase. Furthermore, the effect of an increase in polymer concentration (near or below its critical value) on the membrane permeability as well as on the mass transfer rate is negligible.

2. Owing to the stabilized emulsion by the non-Newtonian conversion, it is possible to reduce the surfactant concentration in the membrane maintaining the high stability.
As a result, mass transfer resistance at the adsorbed layer of surfactant can be alleviated and the possible interference of surfactant with chemical reactions can also be decreased (Nakashio et al., 1988). Additionally, reduced surfactant is known to facilitate the following electrostatic demulsification (Hsu and Li, 1985).

3. The high apparent viscosity of the membrane during the solute extraction can also diminish the swelling problem resulted from the entrainment of the external feed phase in the emulsion globules (Kinugasa et al., 1989). And the osmotic swelling in the emulsion liquid membrane can be alleviated by the reduced concentration of surfactant used as well (Itoh et al., 1990).

4. The enhanced strength of the membrane allows an increase in the volume fraction of the internal stripping phase and high agitation speed during extraction. Hence, the former will increase the total interfacial area, reduce the membrane thickness, and increase the capacity of the internal stripping phase for the transferred solute. The latter will increase the mass transfer rate through the external feed phase (Skelland and Moeti, 1990) and total interfacial area of emulsion globules by reducing their size (Hong and Lee, 1985).

2.6.2. Taylor-Couette Flow

Conventional stirred tanks have been frequently used as a mixing contactor in ELM process; however they possess several problems in liquid-liquid extraction. Most of energy dissipated per unit volume of the tank occurs in a small volume defined by the rotation of the impeller tip. In such flows the impeller surface is subject to form drag and
a large shear creating intense turbulence leading to the dominated inertial breakage of the emulsion globule (Groeneweg et al., 1994). The scale-up of stirred tanks with constant power per volume will increase maximum shear rate, which is a serious limitation (Forney et al., 2002). In addition, much of energy is required for the complete mixing of the immiscible phases (e.g. emulsion and external feed phase in the ELM process) (Forney et al., 2002).

Recent work of Forney et al. (2002) demonstrated a number of advantages for liquid-liquid extraction in a Taylor-Couette flow pattern provided by Taylor-vortex column shown in Figure 2-7. With equal power input per unit volume and roughly equal rotor and tank stirrer diameters, Taylor-Couette flow reduces the maximum shear stress by one to two orders of magnitude compared to a stirred tank, depending on the impeller design. The reduced shear stress is the result of an increase by one to two orders of magnitude in the area subjected to the constant maximum shear defined by friction drag on the large cylinder surfaces on the boundaries of Taylor-Couette flow. In addition, scale-up is much simpler for the Taylor-vortex column and is limited to one dimensionless group called Taylor number, $Ta$ (Forney et al., 2002). $Ta$ is defined as follows:

$$
Ta = \frac{2\pi R N d_g}{\nu} \sqrt{\frac{d_g}{R}}
$$

(1)

where $R =$ radius of the rotor [L]; $N =$ rotational speed [T$^{-1}$]; $d_g =$ annular gap width [L]; $\nu =$ kinematic viscosity.
Figure 2-7. Schematic of Taylor-Couette flow (Schlichting, 1979). ($R =$ rotor radius; $U =$ rotor velocity; $d =$ annular gap width)
REFERENCES


CHAPTER 3

OPTIMUM EMULSION LIQUID MEMBRANES STABILIZED BY NON-NEWTONIAN CONVERSION IN TAYLOR-COUETTE FLOW

ABSTRACT

The use of Taylor-Couette flow for extraction by emulsion liquid membranes (ELMs) has been characterized. In particular, the rate limiting step for the extraction of a weak acid (benzoic) in an aqueous continuous phase to a strong base (NaOH) in the encapsulated internal phase has been attributed to a surfactant resistance. Numerical and analytical solutions are developed to characterize the mass transfer in ELMs. It is demonstrated for fixed droplet composition that a single curve exists for all $N$ for the extent of extraction by stretching the time coordinate by a function of the rotation rate $\propto N^{1.2}$ that is proportional to the globule external area per unit total volume. Moreover, the leakage rate is shown to increase as $t^{0.6}$ and to be proportional to $N^{0.75}$, the Kolmogoroff eddy velocity. Comparison with stirred tank data demonstrates that greater droplet stability exists for Taylor-Couette flow.

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3.1. INTRODUCTION

Surfactant-stabilized emulsion liquid membrane processes constitute a separation technology that is effective in such areas as metal extraction (Mikucki and Osseoasare, 1986), food processes (Etuk and Murray, 1990), separation of organic acids and bases from water (Baird et al., 1987; Wang and Bunge, 1990) and pharmaceutical applications (Thien et al., 1988; Itoh et al., 1990). A review of the technology includes that of Araki and Tsukube (Araki and Tsukube, 1990) or Frankenfield and Li (Frankenfeld and Li, 1987).

Despite the promise of emulsion liquid membranes for the removal of toxic substances to very low levels, a serious problem exists in the form of drop or globule breakup thereby permitting leakage of the internal phase. Attempts to eliminate drop breakup, also called leakage or breakage, include the addition of more surfactant (Li, 1971), use of viscous membranes, Newtonian additives to increase the viscosity (Terry et al., 1982; Wang and Bunge, 1990), conversion of the membrane to suitable non-Newtonian form by addition of small amounts of polymers (Skelland and Meng, 1996, 1999), or use of a hollow-fiber contactor containing an internal emulsion liquid membrane (Nanoti et al., 1997; Breembroek et al., 1998; Hu and Wiencek, 1998). Other factors affecting stability include the emulsifying techniques, internal phase volume fraction and the agitation speed (Pfeiffer et al., 1992). Despite those attempts to increase the membrane stability, there are tradeoffs in most remedies. For example, superfluous surfactant and Newtonian additives may reduce the solute permeability through the
membrane. Moreover, a hollow-fiber contactor is subject to both fouling in long term operations and low extraction rates due to a relatively small contacting area.

The motivation for the present study was the observation from earlier work of a cloudy residue in the form of droplet filamentary threads undoubtedly due to inertial stress on the droplet near the impellor region of a stirred tank. Although tank mixing is the common method of contacting the emulsion and external solvent, most of the energy dissipated per unit volume of the tank occurs in a small volume defined by the rotation of the impeller tip. In such flows the impeller surfaces are subjected to form drag and a large shear creating intense turbulence leading to the inertial dominated breakup of the emulsion globule (Groeneweg et al., 1994). These large inertial forces on the order of $\rho v^2$ where $v'$ is the rms turbulent fluctuating velocity will contribute to a small globule size but also to unstable globules at long contact times.

Recent work of Forney et al. (Forney et al., 2002) demonstrated a number of advantages for liquid/liquid extraction in a Taylor-Couette flow pattern of the type shown in Figure 2-7. With equal power input per unit volume and roughly equal rotor and tank stirrer diameters, Taylor-Couette flow reduces the maximum shear stress by one to two orders of magnitude compared to a stirred tank, depending on the impeller design. The reduced shear stress is the result of an increase by one to two orders of magnitude in the area subjected to the constant maximum shear defined by friction drag on the large cylinder surfaces on the boundaries of Taylor-Couette flow.
The objective of the present study is to explore the extraction of a weak acid (benzoic) by an encapsulated strong base (NaOH) for a batch system in Taylor-Couette flow. Optimum operating conditions are determined for surfactant levels, internal phase volume and polymer concentration. Moreover, the effects of rotation rate on both the time scale of extraction and the leakage rate are determined. These results are shown to suggest both a rate limiting step for mass transfer and a mechanism for the leakage of the internal phase by drop breakup that are introduced into both numerical and analytical models. Finally, comparisons are made between the Taylor-Couette and stirred tank geometries with equal power per unit volume.

3.2. EXPERIMENTAL PROCEDURE

Following the previous work of Skelland and Meng (Skelland and Meng, 1996), an aqueous phase (0.5 N NaOH) is dispersed as shown in Figure 3-1 by an ultrasonicator into an aliphatic membrane phase (Soltrol 220) containing a non-ionic surfactant (sorbitan mono-oleate; Span 80) and a non-Newtonian conversion additive, polyisobutylene (PIB, Avg. M.W. = 1,250,000 g/mol). The emulsifying procedure was constant for all experiments with 5 min of emulsification (3-sec-on and 2-sec-off) so that changes in the emulsion temperature were not significant. Details are described in Skelland and Meng (Skelland and Meng, 1996).

The Taylor-Couette flow of external aqueous phase was contained within a Taylor column consisting of a 1.9 cm diameter inner cylinder made of polyacrylate within an
outer glass cylinder of 2.55 cm inside diameter which are both 7.1 cm in length. As indicated in Figure 3-1, 10 ml of emulsion membrane volume was injected into 68 mL of 500-ppm benzoic acid solution. The rpm of the inner cylinder was controlled with a variable speed motor (Cole-Parmer, model 5003-20) providing a range of rotation rates from 50 to 900 rpm. A water bath with refrigerated circulation (Fisher Scientific, model 910) was used to provide a constant temperature for a range of values from 291 to 301 K for the continuous phase. The total conductance of the continuous phase was measured with an electrical conductivity cell (Yellow Spring, model 32) and the digital signal was stored on file. A schematic of the single emulsion globule is shown in Figure 3-1.

3.3. RESULTS AND DISCUSSION

3.3.1. Mass Transfer

A typical plot of total conductance versus time measured in Taylor-Couette flow is shown in Figure 3-2 where the initial concentration of solute (i.e. benzoic acid) decreases with time as reflected by the decrease in total conductance. The rate of extraction decreases with time until the total conductance reaches a minimum. After the minimum the rate of leakage of the internal phase exceeds the falling extraction rate as the concentration driving force decreases. Several of these conductance plots were generated for a range of rpm from 600 to 900. It was apparent that the time to reach the minimum in the total conductance decreased with a total increased globule surface area.
Figure 3-1. Schematic of experimental apparatus.

1. EMULSION PREPARATION
- Ultrasonicator
- Internal Phase (0.5 N NaOH)
- Membrane Phase (Soltrol 220)
- Surfactant (Span 80)

2. SOLUTE EXTRACTION
- Taylor-vortex Column
- External Donor Phase
- A Single Emulsion Globule

Emulsion
- Magnetic Stirrer
- Internal Phase (0.5 N NaOH)
- Membrane Phase (Soltrol 220)
Figure 3-2. External phase conductance versus time for optimum conditions.
due to smaller globule diameters at larger shear or rotation rates. Similar trends were observed for the stirred tank data.

Examination of the conductance versus time plots for various rotation rates revealed that

\[ N^{1.2}t_m = \text{constant} \]  

in the present experiment where \( t_m \) is the time at which the conductance reached a minimum and \( N \) is the rotational speed. The conclusion was the same for both the Taylor-Couette and stirred tank geometries as shown in Figure 3-3. Those data at low rpm for Taylor-Couette flow are deviations caused by buoyancy of the globules. The significance of Equation (3-1) is apparent from the expression for “\( a \)”, the globule surface area per unit volume of total fluid, in the form (Treybal, 1980)

\[ a = \frac{6\phi}{d} \]  

where \( \phi \) is the volume of emulsion per unit volume of total fluid and \( d \) is the mean globule diameter. One concludes that the mass transfer is rate limited by the external surface area of the globule since the globule diameter \( d \propto N^{-1.2} \) (Vermeulen et al., 1955; Chen and Middleman, 1967).

Other possible mass transfer limitations that can be eliminated based on the present data are due to either internal droplet diffusion such that \( t_m \propto d^2 \) \( (N^{2.4}t_m = \text{constant}) \) as suggested by Chan and Lee (Chen and Lee, 1987) or turbulent convection in the external phase where \( k_mat = \text{constant} \). In the latter case the interfacial mass transfer
Figure 3-3. Effects of RPM on extraction time. The first two data points for the stirred tank are affected by incomplete dispersion. Same conditions as Figure 3-2.
coefficient in a stirred tank is \( k_m \propto N^{0.75} \) or \( N^{0.95} t_m = \text{constant} \) as described by Davies (Davies, 1972).

### 3.3.2. Numerical Simulation

Since only total electrical conductance was measured in the present experiments, a model was developed to predict the component concentrations. It should be emphasized, however, that experimental conditions that reduce the total electrical conductance always reduce component solute levels such as benzoic acid in the continuous phase and this fact is used to make comparisons in the discussions below.

For well mixed systems, we will assume uniform or average conditions in both the continuous and internal phases. This greatly simplifies the calculation of internal phase concentrations. For constant internal drop size and membrane composition, the conservation of species in the external phase for a weak acid becomes

\[
\frac{dc}{dt} = -k_i a \frac{V}{V_e} ([HA]_e - m[HA]_m) + k_i a \frac{V}{V_e} [A^-],
\]

where \( c = [HA]_e + [A^-]_e; [HA], [A^-] = \text{concentration of benzoic acid and benzoate, respectively}; \) subscripts e, i denote external and internal phase, respectively; \( V_t, V_e \) are the total emulsion and external phase volumes, respectively; and \( m = ([HA]_e/[HA]_m)_{eq.} \) is an equilibrium partition coefficient.

The overall mass transfer coefficient \( k_t \) that appears in Equation (3-3) between the external and membrane phases can be written in the form \( 1/k_t = m/k_m + 1/k_e \) where \( k_m \) is
the interfacial resistance and $k_e$ is the external convective mass transfer coefficient. Since the data in the present suggest that $k_m << k_e$, one assumes $I/k_i \approx m/k_m$ in the discussion that follows. We also assume in Equation (3-3) that $m[HA]_m << 1$ since $m << 1$ for large surfactant concentration (Wang and Bunge, 1990). Moreover, if there is negligible resistance to transfer across the membrane, the internal phase solute concentration $[HA]_m \approx [HA]_i = 0$ for the large pH > 11 that exists with excess NaOH in the internal encapsulated aqueous phase.

For simplicity in the following discussion, we define the coefficient

$$K = \left( \frac{k_m}{m} \right) \cdot \left( \frac{aV_i}{V_e} \right) \cdot \left( \frac{k_m}{m} \right) \cdot \phi N^{1.2} \quad (3-4)$$

where $K$ is assumed proportional to the globule area per unit total volume $a \sim \phi N^{1.2}$. Also the leakage coefficient for the last term of Equation (3-3) is assumed proportional to the globule surface area or $\Phi = k_\ell aV_i/V_e \sim \phi_\ell N^{1.2}$ where the leakage coefficient is defined by separate experiments discussed below for the loss of encapsulated base in the absence of extraction. Thus, Equation (3-3) can be rewritten in the form

$$\frac{dc}{dt} = -K[HA]_e + \Phi[A^-]_i \quad (3-5)$$

A similar expression exists for the solute anion within the internal phase for negligible holdup of solute in the membrane of the form

$$\frac{d[A^-]_i}{dt} = K[HA]_e \quad (3-6)$$

To complete the numerical description, a charge balance in the external phase is in the form
\[ \left[ B^+ \right]_e + \left[ H^+ \right]_e = \left[ OH^- \right]_e + \left[ A^- \right]_e \tag{3-7} \]

where \( [B^+] = [Na^+] \), \( [OH^-] = K_w/[H^+] \) and \( [A^-] = K_a c/([H^+] + K_a) \); \( K_w \) \( K_a \) are the dissociation constants for water and benzoic acid, respectively. A similar expression for electroneutrality in the internal phase is

\[ \left[ B^+ \right]_i + \left[ H^+ \right]_i = \left[ OH^- \right]_i + \left[ A^- \right]_i \tag{3-8} \]

where \( [B^+]_i = [OH^-]_i \) is assumed to be constant.

Numerical solutions for Equations (3-3) to (3-7) provide concentration profiles for the four ionic species in the external phase. These latter results were combined to compare with the measurements of the total conductance computed from the expression

Total conductance = \( \lambda_1 [H^+] + \lambda_2 [OH^-] + \lambda_3 [Na^+] + \lambda_4 [C_e H_2 CO_2^-] \) \tag{3-9} \]

where the values for the ion conductance coefficient \( \lambda \) for each species at 293 K are listed in Table 3-1. Comparison of measured and predicted total conductance are shown in Figure 3-4 for several rotation rates. Predicted numerical concentration profiles of the total benzoic acid plus anion concentration \( c_t/c_o \) (i.e. \( c_t = [HA] + [A^-] \)) derived from Figure 3-4 are plotted in Figure 3-5 for the indicated rotation rates. This procedure is used in subsequent discussions below to convert measured total conductance into concentration of target solutes which is likely to be a better indicator of extraction efficiency.
<table>
<thead>
<tr>
<th>Species</th>
<th>$\lambda$</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[{\text{H}}^+]$</td>
<td>$\lambda_1$</td>
<td>1864.8</td>
</tr>
<tr>
<td>$[{\text{OH}}^-]$</td>
<td>$\lambda_2$</td>
<td>992.0</td>
</tr>
<tr>
<td>$[{\text{Na}}^+]$</td>
<td>$\lambda_3$</td>
<td>264.5</td>
</tr>
<tr>
<td>$[{\text{C}_6\text{H}_5\text{CO}}_2^-]$</td>
<td>$\lambda_4$</td>
<td>171.1</td>
</tr>
</tbody>
</table>
Figure 3-4. Comparison of numerical predictions for total conductance. Same conditions as Figure 3-2.
Figure 3-5. Numerical predictions of benzoic acid concentration versus time. Same conditions as Figure 3-2.
3.3.3. Optimum Conditions

A number of experiments were performed to determine the optimum operating conditions in terms of surfactant and polymer concentrations, internal phase volume and temperature. In this study, the non-ionic surfactant Span 80 was used to stabilize the membrane phase. The surfactant Span 80 has been used often in emulsion liquid membrane studies because it provides a relatively stable and easily demulsified emulsion (Skelland and Meng, 1996). Figure 3-6 shows the minimum in both the total measured conductance and predicted benzoic acid/benzoate concentration versus surfactant concentration (w/v). The minimum in both curves is related to increased droplet stability. Below a Span 80 level of 5% the leakage rate decreases with increasing surfactant concentration because of the reduction in interfacial tension which provides smaller internal droplets and globule diameters and thus more stability. As surfactant levels increase from approximately 5% to 10%, however, stability decreased, that is, the leakage rate increased. In this case swelling due to both the entrainment and increased permeation of the membrane by the water-carrying Span 80 via hydration reduced stability (Frankenfeld and Li, 1987; Itoh et al., 1990; Skelland and Meng, 1996).

A similar minimum in total extraction was obtained by a change in the aqueous internal phase volume as shown in Figure 3-7. Addition of the internal aqueous phase increases the viscosity of the globule (Treybal, 1980) leading to increased stability. A minimum, however, occurs at a volume fraction of ~ 20%. Larger fractions of the aqueous phase decrease the organic membrane thickness leading to a decrease in stability.
Figure 3-6. Effect of Span 80 on minimum benzoic acid concentration. Solid symbols, numerical; open symbols, experiment. Same conditions as Figure 3-2.
Figure 3-7. Effect of internal phase volume on minimum benzoic acid concentration. Solid symbols, numerical; open symbols, experiment.
The effects of increased temperature controlled with a water bath during the extraction process decreased the membrane viscosity and stability as shown in Figure 3-8 which indicates a lower overall extraction efficiency at elevated temperatures.

The final parameter considered is the concentration of the additive for non-Newtonian conversion. The results of the present study in Figure 3-9 suggest that there is a modest reduction in the minimum benzoic acid concentration (or total conductance) around 1.5% (w/v) of polyisobutylene (PIB). The viscosity of the membrane (Soltrol 220) increases at zero shear rate from 4.2 to 43 cp with the addition of 1.5% PIB. The increase in stability occurs, of course, with no sacrifice in solute permeability through the membrane. The details of the use of non-Newtonian additives are described by Skelland and Meng (1996, 1999). The advantages of introducing non-Newtonian additives into membranes used in Taylor-Couette flow, however, appear to be somewhat smaller in comparison to that demonstrated in stirred tanks, at least at power inputs equivalent to 500 rpm. Major advantages for the non-Newtonian conversion are the substantial reduction in the swelling and the leakage of the globules at longer contact times. It is probable that the much lower maximum shear rates in Taylor-Couette flow would lead to larger globule diameters because of an increase in the apparent viscosity with the addition of the polymer. Future experiments should be conducted at much higher rotation rates to investigate the effects of reduced globule diameters.
Figure 3-8. Effect of temperature on minimum benzoic acid concentration. Solid symbols, numerical; open symbols, experiment.
Figure 3-9. Effect of polyisobutylene on minimum benzoic acid concentration. Solid symbols, numerical; open symbols, experiment.
3.3.4. Leakage

A series of experiments were performed to determine the leakage rate for both the Taylor-Couette and stirred tank geometries. Figure 3-10a shows the conductance increase due to the release of the internal phase of 0.5 N NaOH in the absence of benzoic acid for several rotation rates. The conductance data were converted to concentration of \([Na^+]\) leaked from Taylor-Couette flow by the numerical procedure described earlier. The rate of leakage is therefore defined by the slope to each \([Na^+]\) plot in the form

\[
\Phi = \frac{1}{[Na^+]} \frac{d[Na^+]}{dt}
\]  

(3-10)

Average values for \(\Phi\) were determined for each rotation rate for both the Taylor-Couette and stirred tank geometries and the results are plotted in Figure 3-10b versus power per unit volume.

It is apparent from Figure 3-10b that the lower maximum shear rates within the Taylor-Couette flow have a stabilizing influence on the emulsion globule. A least-squares curve fit to the data provided a leakage rate of the form \(\Phi \propto \Phi_o N^n\) where \(n \sim 1.2\).

3.3.5. Extraction Results

Numerical model

Numerical solutions of Equations (3-5) to (3-8) were computed for benzoic acid (including the dissociated component) in the external phase at the optimum operating
Figure 3-10. (a) Measurement of NaOH leakage in Taylor-Couette flow for fixed rpm. (b) Comparison of normalized leakage rates versus power per unit volume with stirred tank data.
conditions and for several rotation rates \( N \). The time scale was stretched by a quantity proportional to \( N^{1.2} \) corresponding to the external area of the emulsion globule. The results shown in Figure 3-11 indicate a common extraction curve with a maximum extraction of greater than 95% at a normalized time of \( T = 6 \). The latter result suggests that the time to a minimum of benzoic acid is

\[
t_m = \frac{1}{\phi N^{1.2} k_m}
\]  

(3-11)

where \( k_m \) is the mass transfer coefficient due to interfacial resistance in units of cm/s.

**Analytical model**

Analytical solutions were sought for the total normalized benzoic solute \( C = (1/[HA])_o([HA]+[A^-]) \) in the external or continuous phase where \( A^- \) represents the benzoate ion \( C_6H_5CO_2^- \). The numerical results suggest that the rate of extraction follows a first order process to the minimum in solute concentration and that this is followed by time dependent leakage with an increase in the total benzoic solute \( C \).

Analytical solutions were sought for a normalized rate expression in a form suggested by the solution to Equations (3-5) to (3-8), namely

\[
\frac{dC}{dT} = -C(1 - \alpha) + \varepsilon T^{0.6}
\]  

(3-12)

where \( 1 - \alpha \) represents the fraction of the benzoic species that was undissociated and soluble in the membrane and \( T = Kt \) where \( K \) is defined by Equation (3-4). The first term on the right of Equation (3-12) represents the rate of extraction limited by the surfactant resistance and the second term is the proposed time dependent leakage rate where \( \varepsilon \) is
Figure 3-11. Comparison of numerical predictions of benzoic acid concentration versus normalized time with analytical model. Same conditions as Figure 3-2.
a dimensionless constant. Equilibrium chemistry at the beginning of the extraction process suggests that the correction fraction $\alpha$ in Equation (3-12) is of the form

$$\alpha \equiv 1/(1 + [H^-]_0 / K_a) \quad (3-13)$$

A power series solution for $\varepsilon \ll 1$ was derived from Equation (3-12) (Martin and Reissner, 1961) and the solution obtained is expressed as

$$C = e^{-T(1-\alpha)} + \varepsilon C_1 \quad (3-14)$$

where the quantity $C_1$ is expressed as a power series in the form

$$C_1 = T^{0.6} \left( \sum_{n=1}^{\infty} (-1)^{n-1} T^n (1 - \alpha)^{n-1} \right) \prod_{i=1}^{n} (i + 0.6) \quad (3-15)$$

**Mechanism of drop breakup**

A plot of $C$ versus normalized time for values of $\alpha = 0.16$ and $\varepsilon = 0.0134$ is shown in Figure 3-11 along with the numerical solutions. Manipulation of the leakage term (second on the right of Equation (3-12)) reveals that

$$\varepsilon T^{0.6} \alpha (N^{0.72} t)^{0.6} \quad (3-16)$$

The increase in the leakage rate with time in Equation (3-16) is expected since the benzoic acid content of the internal aqueous phase increases with time during the extraction process. Other contributing factors are the entrainment of the external aqueous phase, osmotic transport, surfactant film drainage (Li, 1971) or the change in the globule diameter with time (Groeneweg et al., 1994). Previous authors have proposed leakage
terms as either constant with time (Chen and Lee, 1987) or linear with time (Borwankar et al., 1988; Bhowal and Datta, 1997).

The power of $N^{0.72}$ suggests that the rate of leakage is proportional to the Kolmogoroff eddy velocity $v_k$ where the quantity $v_k \propto p_M^{1/4} \propto N^{0.75}$ (Davies, 1972). This could also be interpreted as a turbulent mass transfer coefficient from the emulsion globule to the external phase.

3.3.6. Comparison with Stirred Tank

The minimum in total conductance obtained at different rotation rates was measured in Taylor-Couette flow. These data are plotted versus the Taylor number as shown in Figure 3-12 where

$$ Ta = \frac{2\pi R N d_g}{\nu} \sqrt{\frac{d_g}{R}} \quad (3-17) $$

$R$ is the radius of the rotor and $d_g$ is the annular gap width. The data points for $Ta < 2000$ are influenced by poor dispersion arising from the buoyancy of the emulsion globule. There is some improvement in the total extraction, however, for a $Ta > 5,000$. All of the data in Figure 3-12 correspond to turbulent flow.

Similar measurements were made in a stirred tank as shown in Figure 14 for the same values of power input per unit volume as the data in Figure 3-12. The tank Reynolds number corresponding to turbulent flow in Figure 3-13 is defined.
Figure 3-12. Effect of Taylor number on minimum benzoic acid concentration. Same conditions as Figure 3-2.
Figure 3-13. Effect of Reynolds number for a stirred tank on minimum benzoic acid concentration.
\[ \text{Re} = \frac{ND_{im}^2}{v} \]  

(3−18)

where \( D_{im} \) is the impeller diameter of a six bladed impeller in a tank with four baffles.

A comparison of the data for the total electrical conductance from both Figure 3-12 and 3-13 are replotted in Figure 3-14 versus the power input per unit volume. Figure 3-14 supports the conclusion that lower maximum shear rates in Taylor-Couette flow contribute to greater droplet stability.

A final comparison between Taylor-Couette flow and a stirred tank is shown in Figure 3-15 which represents a plot of total conductance versus time for each device. At the same power per unit volume the stirred tank creates smaller emulsion droplets and thus decreases the time scale for extraction. The emulsion is far less stable, however, with a substantial increase in leakage rate for the stirred tank compared to the Taylor-Couette geometry.

3.4. ACKNOWLEDGEMENT

This work was supported by an NSF grant # CTS-9729849.
Figure 3-14. Comparison of minimum conductance versus power per unit volume for both Taylor-Couette and stirred tank data. Same conditions as Figure 3-2.
Figure 3-15. Comparison of conductance versus time for both Taylor-Couette and stirred tank data for equal power per unit volume, 545 kg/ms$^3$. Same conditions as Figure 3-2.
NOTATION

\( a = \) globule surface area per unit volume of total fluid, \( \text{m}^2/\text{m}^3 \)

\( C = \) total normalized benzoic acid + anion concentration in the external phase, \( c/c_o \)

\( c = \) solute concentration in the external phase, \( \text{M} \)

\( c_o = \) solute concentration in the external phase at time zero, \( \text{M} \)

\( c_t = \) solute concentration in the external phase at time \( t \), \( \text{M} \)

\( D = \) solute diffusivity, \( \text{m}^2/\text{s} \)

\( D_{im} = \) impeller diameter, \( \text{m} \)

\( d_g = \) annular gap width in Taylor-Couette flow, \( \text{m} \)

\( d = \) mean globule diameter, \( \text{m} \)

\( K = \) constant proportional to the mass transfer coefficient (\( \propto a k_m \)), \( 1/\text{s} \)

\( K_a = \) acid dissociation for benzoic acid

\( K_w = \) acid dissociation for water

\( k_e = \) external convective mass transfer coefficient, \( \text{m/s} \)

\( k_l = \) leakage mass transfer coefficient, \( \text{m/s} \)

\( k_m = \) interfacial mass transfer coefficient, \( \text{m/s} \)

\( k_t = \) overall mass transfer coefficient, \( \text{m/s} \)

\( m = \) an equilibrium partition coefficient

\( N = \) rotational speed, \( \text{rps} \)

\( n = \) constant

\( p_M = \) power per unit mass, \( \text{m}^2/\text{s}^3 \)

\( R = \) radius of the rotor in Taylor-Couette flow, \( \text{m} \)
\( Re = \) Reynolds number

\( T = \) normalized time (= \( Kt \))

\( Ta = \) Taylor number

\( t = \) time, s

\( t_m = \) time at which the conductance reaches a minimum, s

\( t^* = N^{1.2}t_m \)

\( v_k = \) Kolmogoroff eddy velocity, m/s

**Greek Symbols**

\( \alpha = \) initial fraction of the benzoic acid species dissociated in the external phase

\( \varepsilon = \) constant coefficient

\( \lambda = \) ion conductance coefficient

\( \nu = \) kinematic viscosity, \( m^2/s \)

\( \Phi = \) leakage coefficient, \( 1/s \)

\( \Phi_o = \) leakage coefficient at 900 rpm in Taylor-Couette flow, \( 1/s \)

\( \phi = \) volume of emulsion per unit volume of total fluid

**Concentrations**

\( [HA] = \) concentration of benzoic acid, M

\( [A^-] = \) concentration of benzoate, M

\( [OH^-] = \) concentration of \( \text{OH}^- \), M

\( [H^+] = \) concentration of \( \text{H}^+ \), M

\( [Na^+] = \) concentration of \( \text{Na}^+ \), M
REFERENCES


CHAPTER 4

REMOVAL OF PHENOL AND SUBSTITUTED PHENOLS BY
NEWLY DEVELOPED EMULSION LIQUID MEMBRANE
PROCESS

ABSTRACT

Emulsion liquid membrane (ELM) stabilized by non-Newtonian conversion of the liquid membrane phase and dispersed in a Taylor-Couette flow was applied to treat model industrial wastewaters containing phenols and selected substituted phenols (hydroquinone, three chlorophenols and two nitrophenols) at relatively high concentrations. Under optimized operating conditions, all the compounds except hydroquinone were extracted with the maximum extraction efficiency of over 96% and the time to reach maximum extraction ranged from 2 to 30 min. For 2-chlorophenol, 2,4-dichlorophenol, and 2-nitrophenol, maximum extraction efficiency of over 99% was reached in less than 2 min of contact time. Extraction of these compounds from the mixture was also highly efficient. Factors that affected the overall extraction efficiency such as acid-base speciation of the target compounds and the affinity between the target compounds and the membrane phase were determined. This study suggested that the

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newly developed ELM process might provide a promising alternative technology to treat industrial wastewaters containing high concentrations of phenolic compounds.

4.1. INTRODUCTION

Emulsion liquid membranes (ELMs) consist of an aqueous phase (internal receptor phase) stabilized by oil soluble surfactants and dispersed as very fine droplets (1-10 μm) inside an oil phase (membrane phase). The resulting liquid membrane, or water-in-oil emulsion, is further dispersed as emulsion globules (0.1-2 mm) in another aqueous solution (external donor phase). Target solutes in the external donor phase (e.g. contaminants in industrial wastewater) are transferred across the membrane phase into the internal receptor phase during an extraction process. In this water-oil-water ELM (i.e. in contrast to an oil-water-oil type ELM), the oil phase functions as a selective barrier, or membrane. The solute mass transfer is driven by the concentration difference between the external donor phase and the internal receptor phase. Activity of target solutes in the internal phase is typically kept at near zero by using a trapping agent in order to maintain the concentration gradient, although it gradually decreases, until most of target solutes are extracted from the external phase. After a desired level of extraction is achieved, the external phase and the ELMs are gravimetrically separated. The ELMs are further demulsified for separation of the internal phase from the membrane phase which is typically regenerated and reused for successive extraction processes.
A separation process employing ELMs is characterized by: 1) relatively low energy consumption especially compared to other separation processes such as thermal evaporation, electrodialysis and pressure-driven membrane processes (Naim and Monir, 2003), 2) rapid extraction with relatively high efficiency due to large surface area available for mass transfer (Frankenfeld and Li, 1987), and 3) high selectivity especially when carrier agents are used in the membrane phase that bind exclusively with target compounds (Frankenfeld and Li, 1987). As a result, the ELM has been considered a promising alternative technology for diverse separation processes including removal and recovery of various heavy metals such as copper, zinc, and cadmium (Mikucki and Osseasare, 1986; Reis and Carvalho, 1993; Urtiaga et al., 2000), separation of organic acids and bases (Baird et al., 1987; Wang and Bunge, 1990), and pharmaceutical separations (Frankenfeld and Li, 1987; Thien et al., 1988; Itoh et al., 1990). The ELMs have also received special interest for the treatment of industrial wastewaters containing a wide range of toxic contaminants such as phenol, chlorophenol, and nitrophenol (Teramoto et al., 1983; Zhang et al., 1988; Gadekar et al., 1992; Devulapalli and Jones, 1999; Correia and de Carvalho, 2000).

Unfortunately, widespread use of the ELM processes has been limited due to instability of emulsion globules against fluid shear. Breakup of emulsions and subsequent release of the internal receptor phase to the external donor phase would nullify the extraction process. As a result, several attempts to enhance the stability of ELMs have been made in past decades. Adding more surfactants might increase the stability of emulsion globules, but the presence of surfactants at membrane interface
hinders the mass transfer across the interface (Li, 1971). Excess amount of surfactant is also known to cause swelling of ELMs (Kinugasa et al., 1989). Employing a highly viscous oil as membrane phase has also been attempted, but reduced diffusivity of solutes and consequential decrease in extraction rate have been identified as problematic (Terry et al., 1982; Wang and Bunge, 1990; Park et al., 2004). Other studies have investigated optimization of the operational conditions such as agitation speed, temperature, and composition of ELMs (Pfeiffer et al., 1992; Correia and De Carvalho, 2003; Chakraborty et al., 2004). Using a polymeric porous membrane in a hollow fiber configuration to support the liquid membrane has also been proposed (Nanoti et al., 1997; Breembroek et al., 1998; Hu and Wiencek, 1998). While supported liquid membrane has been considered relatively successful compared to other approaches to avoid emulsion instability problem, a hollow fiber contactor inevitably suffers from fouling during long-term operation and lower removal rate due to much smaller surface area available for mass transfer.

A couple of novel solutions to this decades-old emulsion instability problem were recently proposed by the authors and their collaborators. The first solution involves a conversion of the membrane phase into a suitable non-Newtonian form (i.e., pseudo-plastic) by dissolving high molecular weight polymers such as polyisobutylene. The resulting shear-rate-thinning fluid exhibits increased apparent viscosity under low shear rate conditions which are typical for extraction process. Contrary to a Newtonian fluid, increased viscosity is not accompanied by the decrease in diffusivity of solutes in non-Newtonian fluid as long as the polymer content in the membrane phase is lower than a
critical concentration (Skelland and Meng, 1999; Park et al., 2004). Increased viscosity enables stable emulsion formation with less surfactants which might otherwise negatively affect the diffusion of solutes across the membrane interface. In addition, smaller internal phase droplets and corresponding large mass transfer area can be achieved during water-in-oil emulsion preparation, since the apparent viscosity of shear-rate-thinning fluid decreases under high shear rate conditions. The second solution involves using a Taylor-vortex column as a contacting device instead of conventional mixing reactors equipped with impellers (Forney et al., 2002). Taylor-Couette flow provides relatively uniform shears throughout the fluid, thus minimizing the rupture of the ELMs due to local, intensive form drags that are common near the impellor regions of stirred tanks (Forney et al., 2002). In addition, the Taylor-vortex column requires less power per unit volume than conventional stirred tanks in order to disperse emulsions throughout the external phase (Forney et al., 2002; Park et al., 2004).

A novel ELM process that combined these two innovative modifications has been proven highly successful for the extraction of a model organic contaminant, benzoic acid, from a model industrial wastewater in our previous study (Park et al., 2004). However, applicability of this newly developed process for the removal of various other contaminants would require further studies. Contaminants of particular interest in this study are phenol and substituted phenols such as chlorophenol and nitrophenol. These compounds are widely used in manufacture of various industrial and agricultural chemicals such as dyes, adhesives, plastics, pesticides, germicides, and chemical intermediates (Howard, 1989; Prager, 1995; Spero, 2000). Typical treatment options
include biological processes (*e.g.* activated sludge), activated carbon adsorption, reverse osmosis, ion exchange, coagulation-precipitation, and electrodialysis. (Sakurai et al., 2003; Gupta et al., 2004). However, construction and operation costs could be prohibiting for most existing processes especially when these compounds occur at very high concentrations (*e.g.* 3,000 to 50,000 mg/L) in wastewaters generated from industries such as heavy chemical, petrochemical, and oil refining industries (Nanoti et al., 1997; Lin et al., 1999).

The overarching objective of this study is to evaluate the applicability of the newly developed ELMs for the removal of phenol and selected substituted phenols. Target compounds and their relevant properties are presented in Table 4-1. Of particular interest in this study was elucidating the factors affecting the extraction efficiencies of various compounds including octanol-water partitioning coefficient of target compounds, pH of external phase, and the amount of surfactant used as an emulsifier. Key operational conditions such as volume fraction of internal phase, agitation speed, and dosage of a non-Newtonian additive were also determined.

### 4.2. EXPERIMENTAL

#### 4.2.1. Materials

Analytical reagent grade chemicals and water (>20 μΩ/cm at 25°C) purified by a Milli-Q Ultrapure Gradient Water System (Millipore, Billerica, MA) were used
Table 4-1. Relevant properties of tested compounds (Schwarzenbach et al., 2003)

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Molecular Formula</th>
<th>M.W., g/mol</th>
<th>Log$K_{ow}^*$</th>
<th>p$K_a^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>C₆H₅O</td>
<td>94.1</td>
<td>1.44</td>
<td>9.95</td>
</tr>
<tr>
<td>2-Chlorophenol</td>
<td>C₆H₅ClO</td>
<td>128.6</td>
<td>2.19</td>
<td>8.44</td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>C₆H₅ClO</td>
<td>128.6</td>
<td>2.42</td>
<td>9.29</td>
</tr>
<tr>
<td>2,4-dichlorophenol</td>
<td>C₆H₄Cl₂O</td>
<td>163</td>
<td>3.09</td>
<td>7.85</td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>C₆H₅NO₃</td>
<td>139.1</td>
<td>1.78</td>
<td>7.15</td>
</tr>
<tr>
<td>3-nitrophenol</td>
<td>C₆H₅NO₃</td>
<td>139.1</td>
<td>2.00</td>
<td>8.36</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>C₆H₆O₂</td>
<td>110.1</td>
<td>0.59</td>
<td>9.85</td>
</tr>
</tbody>
</table>

* At 25 °C
throughout the study. The membrane phase consisted mainly of Soltrol 220 (Chevron Philips Chemical, Spring, TX). A non-ionic surfactant, Span 80 (Emulsion Engineering, Sanford, FL), was used as an emulsifier and polyisobutylene (PIB) EL-100 with average molecular weight of 1,250,000 (ExxonMobil Chemical, Houston, TX) as a polymeric additive. Internal phase was made of 0.5 N NaOH.

4.2.2. Experimental Procedure

Emulsion was prepared by first dissolving 5 g of Span 80 in 45 mL to 85 mL of Soltrol 220 under a gentle mixing by a magnetic stirrer. For selected experiments, a varying amount of PIB (0 g to 0.5 g) was also dissolved. The prepared membrane phase was then placed in a 200 mL beaker immersed in an ice bath and a varying volume of internal phase \( (i.e. \ 10 \text{ mL to } 50 \text{ mL of } 0.5 \text{ N NaOH}) \) was slowly added under a vigorous mixing under sonication. Detailed procedure is described in Park et al. (2004).

Solute extraction was performed using a custom-built Taylor-vortex column shown in Figure 3-1. The Taylor-vortex column consisted of an inner cylinder made of polytetrafluoroethylene with a diameter of 49.3 mm and a height of 94.0 mm and an outer cylinder made of glass with an inner diameter of 80.5 mm and a height of 100.9 mm. The inner cylinder was housed inside the fixed outer cylinder and connected to a variable speed motor. An aqueous donor phase \( (i.e. \ model \ industrial \ wastewater) \) of 150 (or 200) mL containing target compound was kept in the annular gap between the inner cylinder and the outer cylinder. While rotating the inner cylinder at a rotational velocity of 300 to
700 rpm, 25 (or 50) mL of emulsion prepared was injected for the initiation of the extraction process. Temperature was controlled at 20°C.

4.2.3. Sample Collection and Analysis

Samples (5 mL) were periodically collected from the solution agitated in the Taylor-vortex column using a micropipette. Collected samples were immediately transferred into glass tubes (12×75 mm) for gravimetric separation of emulsions from the donor phase. After 2 min, 1 mL of donor phase was carefully collected from the bottom of the glass tube into a syringe. The sample was further filtered using a nylon syringe filter with nominal pore size of 0.2 µm (Fisher Scientific, Pittsburgh, PA). The filtered samples were analyzed by an Agilent Model 1100 HPLC (Agilent, Santa Clara, CA) installed with an Agilent 8453 UV-Vis Diode Array detector and a 4.6×150 mm Zorbax Eclipse XDB-C8 column. A gradient mobile phase containing varying proportions of acetonitrile and 0.01 M phosphate buffer at flow rate of 1.0 mL/min was used. Note that the amount of target solutes transferred from the donor phase into ELMs during gravimetric separation period up to 10 min was found to be negligible from separate experiments.
4.3. RESULTS AND DISCUSSION

4.3.1. Optimization of Factors Affecting ELM stability

Experiments presented in this section were performed using 1,000 mg/L of phenol as a representative contaminant, since the effects of variables of interest were likely to be independent of the type of the target solute. First, the ratio of internal phase volume to membrane phase volume ($V_i/V_m$) was varied from 0.12 to 1.11 by increasing the internal phase volume and decreasing the membrane phase volume during emulsion preparation with the fixed Span 80 amount. Experimental results showed that extraction efficiency increased significantly as volume fraction was increased from 0.12 to 0.46 (Figure 4-1). These might have resulted since the larger internal phase volume increased the number of droplets in the membrane phase and consequently provided larger surface area for the mass transfer (Frankenfeld and Li, 1987). Since the amount of surfactant used was fixed, less surfactant might have accumulated per unit interface area between the external phase and the membrane phase also contributing to increase in extraction efficiency (Wan and Zhang, 2002; Park et al., 2004). In addition, increase in the internal phase volume could have decreased the thickness of the membrane and consequently increased the rate of mass transfer across the membrane (Hanna and Larson, 1985; Gadekar et al., 1992; Luan and Plaisier, 2004). It is noteworthy that larger $V_i/V_m$ might have additional advantages during electrostatic demulsification processes (Hsu and Li, 1985). As $V_i/V_m$ was further increased beyond 0.46, little increase in the mass transfer rate was observed. This might have resulted because emulsion globules ruptured more easily by the fluid shear as the
Figure 4-1. Effect of the ratio of internal phase volume to membrane phase volume ($V_i/V_m$) on phenol extraction (Initial phenol concentration = 1,000 mg/L; Span 80 concentration = 5 % w/v; no PIB; $V_e/V_f = 0.33$; Inner cylinder rotational speed = 500 rpm; Temperature = 20°C).
membrane phases became thinner, nullifying the extraction process (Luan and Plaisier, 2004).

The hydrodynamic condition in Taylor-Couette flow is dependent on the rotational speed of the inner cylinder. As the rotational speed increases, the solute extraction rate may increase since: 1) emulsion globules are more uniformly dispersed throughout the external donor phase (Park et al., 2004), 2) larger surface area for mass transfer becomes available as the size of emulsion globules is reduced due to fluid shear (Correia and De Carvalho, 2003), and 3) the thickness of the mass transfer boundary layer at the interface of the emulsion globules and external phase is reduced (Sahoo and Dutta, 1998). On the contrary, as rotational speed increases, the rate of the membrane breakage due to fluid shear and feed phase entrainment may increase (Mok et al., 1995; Correia and de Carvalho, 2000; Wan and Zhang, 2002). Therefore, optimal agitation speed exists, the value depending on the geometry of the contactor and the type of the emulsion.

Experimental results obtained for the phenol extraction with the rotational speed of the inner cylinder varying from 300 rpm to 700 rpm are shown in Figure 4-2. These rotation speeds correspond to a dimensionless Taylor Number, $Ta$, of approximately 5,200 to 12,000. $Ta$ is defined as follows:

$$ Ta = \frac{2\pi R \Delta d_g}{\nu} \sqrt{\frac{d_g}{R}} $$ (4-1)
Figure 4-2. Effect of agitation speed of Taylor-vortex column on phenol extraction (Initial phenol concentration = 1,000 mg/L; Span 80 concentration = 5 % w/v; no PIB; $V/V_m = 0.46$; $V_e/V_f = 0.33$; Temperature = 20°C).
where \( R \) = radius of the rotor [L]; \( N \) = rotational speed [T\(^{-1}\)]; \( d_g \) = annular gap width [L]; \( \nu \) = kinematic viscosity of the external phase at \( 20^\circ \text{C} \) [LT\(^{-1}\)] estimated based on Skelland and Ramsay (1987). At 300 rpm or \( Ta = 5,200 \), (results not shown), it was observed that most emulsion globules were not properly dispersed throughout the contactor but remained near the water surface resulting in unacceptably low extraction rate.

As the agitation speed was increased beyond 400 rpm (\( Ta = 6,900 \)), emulsion globules became uniformly dispersed throughout the external phase and dramatic decrease in phenol concentration in the external phase was observed (Figure 4-2). The initial extraction rate, estimated from the slope of curve during initial phase of extraction, was also enhanced. However, at 600 (\( Ta = 10,000 \)) and 700 rpm (\( Ta = 12,000 \)), phenol concentration in the external phase increased after the minimum concentration (i.e. maximum extraction efficiency, \( R_{max} \)) was reached. Increase in phenol concentration during the later phase of extraction resulted because the rate of release of phenol from the internal phase to the external phase due to ELM rupture by fluid shear was greater than the rate of extraction of phenol by the intact ELMs as previously described in Park et al. (2004).

The rate of phenol extraction was greatly enhanced by the addition of PIB as shown in Figure 4-3. Increase in the rate was caused by increased stability of ELMs and subsequent reduction in the rate of ELM rupture as previously described (Skelland and Meng, 1999; Park et al., 2004). Note again that the experimental curves shown in Figure 4-3 are the combined effect of the extraction and emulsion breakage. Alternatively, this
Figure 4-3. Effect of non-Newtonian additive (PIB) concentration on phenol extraction (Initial phenol concentration = 1,000 mg/L; Span 80 concentration = 5 % w/v; $V_i/V_m = 0.73; V_e/V_f = 0.33; Temperature = 20^\circ C$).
enhancement of the initial extraction rate might have been partly caused by the change of an internal structure of the solvent (i.e. Soltrol 220) due to the dissolved polymer which facilitates the diffusivity of solute (Osmers and Metzner, 1972). At 700 rpm, since the initial extraction rate was already high without PIB, increase in mass transfer rate was relatively small. But at this high shear rate condition, release of solutes from the ELMs due to breakage might dominate extraction, as evidenced by increase in phenol concentration in the external phase after passing the minimum value. Such undesirable effect was greatly reduced by adding 5 g/L of PIB. When larger amount of PIB was added (i.e. 10 g/L), the rate of extraction was decreased (results not shown), possibly due to the “blocking effect” by the excessive polymer against solute mass transfer (Osmers and Metzner, 1972). Based on the experimental results discussed above, all experimental results discussed below were obtained with \( \frac{V_e}{V_m} \) of 0.46, rotational speed of 500 rpm, and PIB concentration of 5 g/L.

### 4.3.2. Extraction of Substituted Phenols

Experiments were performed to evaluate the extraction efficiency of a few selected substituted phenols present at 1,000 ppm. The ratio of ELM volume (\( V_e \)) to external phase volume (\( V_j \)) was either at 1:6 (25 mL of ELM and 150 mL of external phase) or 1:3 (50 mL of ELM and 150 mL of external phase). Experimental results were summarized in Table 2 in terms of the maximum removal efficiency (\( R_{max} \)) and the contact time (\( t_R \)) required to reach \( R_{max} \). For most compounds investigated, \( R_{max} \) was relatively high at over 90%. \( R_{max} \) was even over 99% for some compounds. The
Table 4-2. Results obtained from experiments performed with the external phase containing a single solute at two different $V_e/V_f$ values. (*Initial compound concentration* = 1,000 mg/L; *Span 80 concentration* = 5 % w/v; *PIB concentration* = 5 g/L; $V/V_m$ = 0.46; *Inner cylinder rotational speed* = 500 rpm; *Temperature* = 20°C).

<table>
<thead>
<tr>
<th>Target Compound</th>
<th>25/150 ($V_e/V_f$)</th>
<th>50/150 ($V_e/V_f$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_{max}$ (%)</td>
<td>$t_R$ (min)</td>
</tr>
<tr>
<td>Phenol</td>
<td>90.82</td>
<td>30</td>
</tr>
<tr>
<td>2-Chlorophenol</td>
<td>97.43</td>
<td>6</td>
</tr>
<tr>
<td>4-Chlorophenol</td>
<td>95.32</td>
<td>6</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>98.44</td>
<td>2</td>
</tr>
<tr>
<td>2-Nitrophenol</td>
<td>98.62</td>
<td>4</td>
</tr>
<tr>
<td>3-Nitrophenol</td>
<td>94.74</td>
<td>30</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>16.89</td>
<td>30</td>
</tr>
</tbody>
</table>
extraction rate was also relatively fast (i.e. most compounds were extracted less than 8 min). For compounds such as 2,4-dichlorophenol, maximum extraction might have been reached before 2 min, the first sampling time. The only compound that showed low extraction efficiency was hydroquinone, i.e. phenol derivative with possibly the lowest affinity to the membrane phase and the strongest hydrogen bond with water. For all the compounds investigated, \( R_{\text{max}} \) was higher at higher \( V_e:V_f \). It was interesting to note that the difference was smaller for the compounds with higher \( R_{\text{max}} \), with the greatest difference observed with hydroquinone. Since demulsification of ELM and subsequent treatment of the internal phase are required after the completion of the extraction process, the smaller \( V_e:V_f \) is generally preferred. Therefore, increasing \( V_e:V_f \) might need to be considered only for compounds with lower \( R_{\text{max}} \).

Note that these results were obtained without adjusting pH of the external phase. Initial pH of external phase individually containing 1,000 mg/L of hydroquinone, phenol, 2-chlorophenol, and 2,4-dichlorophenol were 5.05, 5.45, 5.40, and 4.98, respectively. The external phase pH increases during extraction process due to release of internal phase by ELM breakage. Quantitative analysis on the rate of ELM breakage is available in Park et al. (2004). Since all the compounds tested are weak acids (Table 4-1) and charged species does not readily partition into the membrane phase (Wan et al., 1997), pH affects the extraction efficiency. Additional experiments were performed individually with hydroquinone, phenol, 2-chlorophenol and 2,4-dichlorophenol after lowering the external phase pH to 1.5 (from unadjusted pHs of 5.05, 5.45, 5.40, and 4.98, respectively) in order to convert all the ionic species into their neutral, protonated forms. Experimental
results shown in Figure 4-4 suggested that once all the species presented as neutral form, the extraction was generally more efficient. It is noteworthy that lowering the pH suppressed the increase in external phase concentration more effectively during the later stage of extraction when pH change would have become more significant due to ELM breakage if pH had been unadjusted. As expected, this phenomenon was most pronounced with 2,4-dichlorophenol which had the lowest pK\textsubscript{a}. Also note that this particular series of compounds exhibited a wide range of octanol-water partition coefficient (\(K_{ow}\) = the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature) (Table 4-1). This parameter is widely used to represent relative hydrophobicity of a compound. Hydrophobicity might be related to the affinity of a compound to the membrane phase and especially to the initial rate of extraction. Figure 4-5 compares the initial extraction rate (\(i.e.\) defined as the rate of decrease in normalized concentration during initial 2 min of extraction) obtained with two different \(V_e:V_f\) ratios. This result suggests that a parameter such as \(K_{ow}\) might be useful in evaluating extraction efficiency of similar classes of compounds.

4.3.3. Competitive Transport in Mixture

The performance of the ELM process was evaluated for a mixture of target compounds, which might be common in many industrial wastewaters (Gupta et al., 2004; Luan and Plaisier, 2004). A set of experiments was performed using an external phase that contained phenol, 2-chlorophenol, and 2,4-dichlorophenol simultaneously at initial
Figure 4-4. Effect of external phase pH on extraction of hydroquinone, phenol, 2-chlorophenol, and 2,4-dichlorophenol (Initial compound concentration = 1,000 mg/L; Span 80 concentration = 5% w/v; PIB concentration = 5 g/L; \(V_i/V_m = 0.46\); \(V_e/V_f = 0.33\); Inner cylinder rotational speed = 500 rpm; Temperature = 20\(^\circ\)C).
Figure 4-5. Relationship between octanol-water partition coefficients ($K_{ow}$) and initial extraction rates of hydroquinone, phenol, 2-chlorophenol, and 2,4-dichlorophenol (Initial compound concentration = 1,000 mg/L; Span 80 concentration = 5% w/v; PIB concentration = 5 g/L; $V_e/V_i = 0.46$; External phase pH = 1.3 ~ 1.6; Inner cylinder rotational speed = 500 rpm; Temperature = 20°C).
concentration of 1,000 mg/L each. Experimental results in Figure 4-6 showed that extraction curve for each compound followed the trend similar to those obtained with the individual compound (shown as dotted lines). A closer examination suggested that the initial extraction rate (i.e., up to 2 min) was the fastest for 2,4-dichlorophenol, followed by 2-chlorophenol and the slowest for phenol. This order was consistent with that of $K_{ow}$ values of these compounds. It is interesting to note that the effect of affinity of the solute to the membrane phase, presumably strongly dependent on $K_{ow}$, was more pronounced when the solutes were present as a mixture. Such a phenomenon is thought to be caused by competitive effect on the mass transfer. Accordingly, extraction of phenol (i.e., the compound with the lowest $K_{ow}$) was significantly retarded by the presence of other compounds that had stronger affinity to the membrane phase. On the contrary, little decrease in the initial extraction rate was observed for 2,4-dichlorophenol.

After reaching the minimum extraction, the concentration of solute in the external phase increased due to the ELM breakage. Since the initial pH of the mixture was lower than the solution made of a single compound, the fraction of species present in the neutral form was greater in the mixture, which resulted in better overall extraction efficiency. Note that the extraction of solutes even at such a high concentration was not limited by the capacity of the internal phase because the internal phase contained a sufficiently large amount of hydroxide ions to shift the equilibrium toward negatively charged forms nearly completely. Some studies reported that extraction rates decreased for the extraction of mixtures when the amount of stripping agents was not sufficiently provided compared to
Figure 4-6. Comparison of the removal rates of phenol, 2-chlorophenol and 2,4-dichlorophenol when present individually (dashed lines, the same data from Figure 5) and when present in a mixture (symbols and lines) (Initial compound concentration = 1,000 mg/L; Span 80 concentration = 5% w/v; PIB concentration = 5 g/L; \( V_i/V_m = 0.46; V_e/V_f = 0.33 \); External phase pH = 1.3 ~ 1.6; Inner cylinder rotational speed = 500 rpm; Temperature = 20°C).
the amount of the target compounds (Teramoto et al., 1983; Baird et al., 1987; Wang and Bunge, 1990).

4.3.4. Effect of Surfactant Dissolved in the Liquid Membrane Phase on the Extraction Rates

Surfactants affect the physical characteristics of ELMs as previously described, and such effects are most likely to be independent of the nature of the target solutes. This presumption seemed valid when a mixture of 2-chlorophenol and 4-chlorophenol (1,000 mg/L each) was treated with the ELMs with varying amount of Span 80. As shown in Figure 4-7, slightly more hydrophobic 4-chlorophenol showed slightly better extraction efficiency than 2-chlorophenol. In addition, since $pK_a$ of 4-chlorophenol is higher, larger fraction existed as neutral forms that were able to partition into the membrane phase.

However, similar experiments performed with a mixture of 2-nitrophenol and 3-nitrophenol showed the opposite trend (Figure 4-8). Even though 2-nitrophenol has lower $K_{ow}$ and lower $pK_a$, both the initial rate of extraction and overall extraction efficiency was higher. This unexpected result might be related to change in the affinity of the solute to membrane phase due to the presence of surfactants that were accumulated at the membrane-water interface. At lower surfactant concentration, this effect played a major role since the amount of surfactants might have been a limiting factor. Therefore, as surfactant concentration was increased, the difference became smaller.
Figure 4-7. Effect of surfactant concentration on the extraction of 2-chlorophenol and 4-chlorophenol present in a mixture (Initial compound concentration = 1,000 mg/L each; PIB concentration = 5 g/L; \( V/V_m = 0.46 \); \( V_d/V_f = 0.33 \); Inner cylinder rotational speed = 500 rpm; Temperature = 20°C).
Figure 4-8. Effect of surfactant concentration on the extraction of 2-nitrophenol and 3-nitrophenol present in a mixture (Initial compound concentration = 1,000 mg/L each; PIB concentration = 5 g/L; $V_i/V_m = 0.46$; $V_e/V_f = 0.33$; Inner cylinder rotational speed = 500 rpm; Temperature = 20°C).
Only few studies in the literature have reported the similar phenomena with respect to interaction of the solute with surfactants in liquid membranes. Wang and Bunge (1990) observed that the partitioning of both phenol and phenylacetic acid into a liquid membrane increased as oil-soluble surfactant was added, and the increase in the partition coefficient was much larger for phenylacetic acid. Note that these compounds have nearly the same log $K_{ow}$ values ($\log K_{ow} = 1.41$ for phenylacetic acid). In order to verify this effect in our ELM system, additional experiments were performed using the mixture containing 1,000 mg/L of each compound. In order to exclude the effect of species ionization, external phase pH was lowered to approximately 1.4. Experimental results in Figure 4-9 confirmed that phenylacetic acid was much more efficiently removed by the ELM. This large difference could be only explained by the large affinity of the phenylacetic acid to the membrane phase due to the presence of surfactants as previously reported. Currently, the exact nature of the interaction between the solute with the surfactant is unknown, while it might be presumably related to the polarity of the liquid membrane (Teramoto et al., 1983; Wang and Bunge, 1990).

4.4. CONCLUSION

The novel ELM process was shown highly efficient in treating model industrial wastewaters that contained phenol and substituted phenols at relatively high concentrations (1,000 ppm). Extraction of these compounds from the mixture was also highly efficient, while a minor level of mass transfer retardation due to competitive effect was observed. Since these compounds were weakly acidic, the overall extraction was
Figure 4-9. Extraction of phenol and phenylacetic acid present in a mixture (Initial compound concentration = 1,000 mg/L each; Span 80 concentration = 5 % w/v; PIB concentration = 5 g/L; V_i/V_m = 0.46; V_e/V_f = 0.33; Inner cylinder rotational speed = 500 rpm; Temperature = 20°C).
greatly affected by the external phase pH. When the pH was kept low and most species were present in neutral forms, the overall extraction efficiency was found to be closely related to their affinity to the membrane phase, represented in this study by octanol-water partition coefficient. In case of nitrophenols and phenylacetic acid, however, the surfactant present in the membrane phase was found to play a critical role in determining the affinity between the target solute and the membrane phase.

Relatively high extraction efficiency observed in this study for phenol and selected substituted phenols was consistent with previous observation that the stability of the ELM was greatly enhanced and higher extraction efficiency could be achieved by converting the membrane phase into a suitable non-Newtonian form and employing the Taylor-Couette flow. The results obtained in this study suggested that the newly developed ELM process might be effective to remove these contaminants from industrial wastewaters even at very high concentrations. Applicability of this process on real industrial wastewaters might require future targeted study considering specific water quality conditions and treated water quality goals.

4.5. ACKNOWLEDGEMENTS

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REFERENCES


CHAPTER 5

SELECTIVE SEPARATION OF VARIOUS HEAVY METALS FROM SYNTHESIZED PHOSPHORIC ACID SOLUTIONS

ABSTRACT

Phosphoric acid is produced mainly through the so-called wet processes, in which phosphate ore reacts with sulfuric acid to form phosphoric acid and calcium sulfate solids. With the phosphate ore, impurities including metallic ions and anions enter the production process. Some of these impurities end up in the product acid. Separation of these impurities from the phosphoric acid solutions has been a big challenge in phosphoric acid purification because the current technologies such as solvent extraction are very costly. Therefore, in this study, emulsion liquid membranes (ELMs) were employed as an alternative technology for the purification of phosphoric acid solutions because of their outstanding selectivity, high extraction efficiency, and relatively low energy consumption compared to the other separation methods. As a first step, several different types of carrier agents commercially available were evaluated to find the most suitable one in extracting various metallic ions and anions in order to develop and optimize a Type II emulsion liquid membrane system in Taylor-vortex column. The carrier agents studied were Cyanex 301, Cyanex 302, Cyanex 923, Acorga M-5774, D2EHPA, Alamine 336, dicyclohexano-18-crown-6, dibenzo-18-crown-6, 18-crown-6,
and 15-crown-8. At moderate pH (> 2), ELMs with Alamine 336 were the most efficient (almost 100 % of metal removal efficiency); however, their removal efficiency significantly decreased for the simulated phosphoric acid solution (40 wt% of phosphoric acid). Only ELMs with Cyanex 301 showed a potential to separate some of the tested metal, such as cadmium, lead, and zinc from synthesized phosphoric acid. Observed failure of the ELM process for the extraction of multiple metals might have resulted from either lack of proper bonding between carrier agents and metals or instability of emulsion membranes under extreme pH conditions. In order to rule out the stability problem, solvent extraction experiments were performed to focus on interaction between carriers and metals. Based on the results obtained with 20:1 of molar ratio of Cyanex 301 to total metals, the tested metals could be categorized into three classes – fast extracted metals (As, Cd, Cu, Pb, and Zn), moderately extracted metals (Fe, Ni, and V), and rarely extracted metal (Cr) under the conditions studied.

5.1. INTRODUCTION

Selective separation of metallic cations (e.g. cadmium, chromium, nickel, zinc, lead, and copper) as well as anions (e.g. sulfate and chloride) from phosphoric acid solution is a recurring problem in phosphoric acid manufacturing processes. These ions are required to be removed to very low concentrations during a phosphoric acid purification process since they are harmful to human health. Accordingly, various methods including solvent extraction, ion exchange, extraction by liquid membrane, precipitation, and reverse osmosis have been previously investigated for the removal of
these heavy metals (Ahmed et al., 1998; Koopman et al., 1999; Kislik and Eyal, 2001; Park et al., 2004; Qdais and Moussa, 2004).

Emulsion liquid membranes (ELMs) has been considered a promising process for the removal of various types of heavy metals and anions from aqueous phase for industrial wastewater treatment and solution purification due to their outstanding selectivity, high extraction efficiency, and relatively low energy consumption compared to the other separation methods (Reis and Carvalho, 1993; Breembroek et al., 1998; Hu and Wiencek, 1998; Schwarzenbach et al., 2003). ELMs consist of three distinct phases: a feed phase, a liquid membrane (oil) phase, and a stripping phase. The liquid membrane phase functions as a selective barrier that allows transport of only target solutes (i.e., impurities) from the feed phase to the stripping phase. The solutes are subsequently trapped in the stripping phase to maintain the driving force for mass transfer, i.e. the concentration difference between the feed phase and stripping phase. ELMs can be categorized into either Type I or II depending on whether a mobile carrier is absent (Type I) or present (Type II) in the liquid membrane phase. In Type II system, a mobile carrier selectively shuttles target solutes (i.e., cations and anions) through the liquid membrane. There are two types of transport mechanisms - symport and antiport. Both cations and anions are transported by a carrier simultaneously in symport mechanism, whereas either cations or anions can form a complex with a carrier to diffuse across the liquid membrane in antiport mechanism. Regardless of transport mechanisms, the complex form in liquid membrane has to maintain charge neutrality (Pedersen, 1967). Metal extractions have
been carried out exclusively by Type II system and the nature and performance of carriers
govern the mechanism and the overall efficiency of extraction process, respectively.

It should be noteworthy that a widespread use of the ELM processes has been
limited due to instability of emulsion globules against fluid shear. Breakup of emulsions
and subsequent release of the internal receptor phase to the external donor phase would
nullify the extraction process. As a result, several attempts to enhance the stability of
ELMs have been made in past decades. Adding more surfactants might increase the
stability of emulsion globules, but the presence of surfactants at membrane interface
hinders the mass transfer across the interface (Li, 1971). Excess amount of surfactant is
also known to cause swelling of ELMs (Kinugasa et al., 1989). Employing a highly
viscous oil as membrane phase has also been attempted, but reduced diffusivity of solutes
and consequential decrease in extraction rate have been identified as problematic (Terry
et al., 1982; Wang and Bunge, 1990; Park et al., 2004). Other studies have investigated
optimization of the operational conditions such as agitation speed, temperature, and
composition of ELMs (Pfeiffer et al., 1992; Correia and De Carvalho, 2003; Chakraborty
et al., 2004). Using a polymeric porous membrane in a hollow fiber configuration to
support the liquid membrane has also been proposed (Nanoti et al., 1997; Breembroek et
al., 1998; Hu and Wiencek, 1998). While supported liquid membrane has been
considered relatively successful compared to other approaches to avoid emulsion
instability problem, a hollow fiber contactor inevitably suffers from fouling during long-
term operation and lower removal rate due to much smaller surface area available for
mass transfer.
A couple of novel solutions to this decades-old emulsion instability problem were recently proposed by the researchers at Georgia Institute of Technology. The first solution involves a conversion of the membrane phase into a suitable non-Newtonian form (i.e. pseudo-plastic) by dissolving high molecular weight polymers such as polyisobutylene. The resulting shear-rate-thinning fluid exhibits increased apparent viscosity under low shear rate conditions which are typical for extraction process. Contrary to a Newtonian fluid, increased viscosity is not accompanied by the decrease in diffusivity of solutes in non-Newtonian fluid as long as the polymer content in the membrane phase is lower than a critical concentration (Skelland and Meng, 1999; Park et al., 2004). Increased viscosity enables stable emulsion formation with less surfactant which might otherwise negatively affect the diffusion of solutes across the membrane interface. In addition, smaller internal phase droplets and corresponding large mass transfer area can be achieved during water-in-oil emulsion preparation, since the apparent viscosity of shear-rate-thinning fluid decreases under high shear rate conditions. The second solution involves using a Taylor-vortex column as a contacting device instead of conventional mixing reactors equipped with impellers (Forney et al., 2002). Taylor-Couette flow provides relatively uniform shears throughout the fluid, thus minimizing the rupture of the ELMs due to local, intensive form drags that are common near the impellor regions of stirred tanks (Forney et al., 2002). In addition, the Taylor-vortex column requires less power per unit volume than conventional stirred tanks in order to disperse emulsions throughout the external phase (Forney et al., 2002; Park et al., 2004).
The main objective of the proposed research was to optimize the previously developed emulsion liquid membrane (ELM) process for the removal of metallic cations from synthesized phosphoric acid solutions. Research tasks specifically focused on selecting appropriate carriers and stripping agents as well as optimizing operating conditions in order to remove the metallic cations most efficiently by ELM process. Solvent extraction experiments were performed in parallel to screen the candidate carrier agents.

5.2. EXPERIMENTAL

5.2.1. Materials

All the chemicals purchased either from Acros Organic (Morris Plains, NJ) or Sigma-Aldrich (St. Louis, MO) were of analytical reagent grade. The membrane phase consisted of either Soltrl 220 (i.e. an isopraffin oil, a mixture of C13-C17 hydrocarbons) obtained from Chevron Philips Chemical (Spring, TX), nitrobenzene, chloroform or toluene from Acros Organic (Morris Plains, NJ). A non-ionic surfactant, Span 80 (sorbitan mono-oleate) purchased from Emulsion Engineering (Sanford, FL), was used as an emulsifier. Polyisobutylene (PIB) EL-100 with average molecular weight of 1,250,000 (ExxonMobil Chemical, Houston, TX) was used as a polymeric additive that converted the membrane into non-Newtonian fluid. Internal phase was made of concentrated HCl or NaOH. A water (>20 µΩ/cm at 25°C) purified by a Mili-Q Ultrapure Gradient Water System (Millipore, Billerica, MA) was used to prepare both
internal and external phase solutions. The detailed information of the carrier agents used in this study is shown Table 5-1.

5.2.2. Experimental Procedure

Emulsion Liquid Membranes

Membrane Preparation – 70 mL of Soltrol 220 (membrane phase) was measured by a graduated cylinder (100 mL) and transported into a beaker (200 mL). A certain amount (e.g. 2 mL) of a carrier agent (e.g. CYANEX 301 and 302) and 3 g of surfactant (Span 80) were taken and then dissolved in the membrane phase. A relatively slow agitation was provided by a multi-stirrer (200 RPM). Sufficient time was allowed to dissolve all the additives in the membrane phase.

Emulsion Formation – The membrane phase was poured into a 200-mL beaker placed in an ice-water bath and rigorously stirred using a magnetic stir bar. The ultrasound probe was lowered into the solution at a depth of 1 inch. A 25 ml of the internal phase (e.g. 2 N of HCl), prepared by diluting a concentrated strong acid (e.g. 6 N HCl) with Milli-Q water, was transferred into the membrane phase using a pipette. As the internal phase was added, the mixture was emulsified with an Ultrasonicator, Model 2020 (Heat Systems) with the setting at 3.2, which corresponds to approximately 20% of available power. The ultrasonicator is run for 7 minutes, with a 3-s on, 2-s off program to
Table 5-1. List of carrier agents employed in ELMs or solvent extraction

<table>
<thead>
<tr>
<th>Carrier Agents</th>
<th>Active Components</th>
<th>Manufacturer Or Vendor</th>
<th>Formula</th>
<th>Formula Weight (g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanex 301</td>
<td>Bis(2,4,4-trimethylpentyl)dithiophosphinic acid</td>
<td>Cytec</td>
<td>C_{16}H_{35}PS_{2}</td>
<td>322.55</td>
</tr>
<tr>
<td>Cyanex 302</td>
<td>Bis(2,4,4-trimethylpentyl)monothiophosphinic Acid</td>
<td>Cytec</td>
<td>C_{16}H_{35}PSO</td>
<td>306.49</td>
</tr>
<tr>
<td>Cyanex 923</td>
<td>Trihexylphosphine oxide Dihexylmonooctylphosphine oxide Dioctylmonohexylphosphine oxide Trioctylphosphine oxide</td>
<td>Cytec</td>
<td>C_{19}H_{39}OP</td>
<td>302.48</td>
</tr>
<tr>
<td>D2EHPA</td>
<td>di(2-ethylhexyl)phosphoric acid</td>
<td>Alfa Aesar</td>
<td>C_{19}H_{38}O_{3}P</td>
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<tr>
<td>Acorga M-5774</td>
<td>5-Nonyl-2-hydroxybenzaldoxime</td>
<td>Cytec</td>
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<td>Alamine 336</td>
<td>Tri-octyl/decyl amine</td>
<td>Cognis</td>
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<td>N/A</td>
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<td>Dicyclohexano-18-crown-6</td>
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<td>Acros</td>
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<tr>
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<td>15-crown-5</td>
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<td>Sri Hari Labs</td>
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<td>220.27</td>
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</tbody>
</table>
keep the emulsion from overheating. The ice-water bath kept the emulsion temperature around 25 °C.

*Metal Extraction* – A predetermined mass of solute was dissolved in Mill-Q water for preparation of the external phase. Taylor-vortex column was then placed in a constant temperature bath of 20 °C. 200 ml of the external phase was first poured into the Taylor-vortex column. After the system reaches the agitation speed of 500 RPM, 20 ml of the prepared emulsion was added into the system by a graduated cylinder for the initiation of extraction process. During extraction, samples were periodically collected by an auto-pipetter. The samples were further filtered using a polypropylene syringe filter with nominal pore size of 0.2 µm (Pall Corporation, East Hills, NY) for analysis with ICP-AES. Figure 3-1 shows a schematic diagram of metal extraction by emulsion liquid membranes.

*Analysis* – Concentrations of the tested metals were measured using an Inductively Coupled Plasma Mass Spectrometer-Atomic Emission Spectroscopy (ICP-AES) (Model ICAP 61E Trace Analyzer, Thermo Jarrell Ash, Franklin, MA) equipped with an autosampler. Samples were introduced into a cross-flow nebulizer, contained within a room temperature spray chamber, at a pump speed of 100 rpm. A sipper was used to induce the sample to the reactor. Prior to analysis, trace metal grade nitric acid was added to sampling vials to meet 1% v/v of nitric acid concentration. The studied metals (wavelength for ICP-AES, nm) are As (193.696), Cd (226.502), Cr (324.754), Cu (324.754), Fe (259.940 or 271.441), Pb (220.353), Ni (231.604), V (292.402), and Zn.
For instrument calibration, standard solutions of each species were prepared using High-Purity Standards (Charleston, SC) and Milli-Q water in polyethylene or polytetrafluoroethylene bottles. Analyses were performed four times for each sample and the average value was recorded.

**Solvent Extraction**

For each solvent extraction experiment as shown in Figure 5-1, 20 mL of the feed phase was added to 20 mL of the extractant in a 100 ml wide mouth bottle. The bottle was capped and placed in the shaker bath agitating at 200 rpm at 20 °C. Samples of feed phase (0.5 mL) were collected periodically by immersing the pipette or syringe into the feed layer and transferring to 15 mL tubes. To the samples in tubes were added 9.3 mL Milli-Q water and 0.2 mL of 70 wt% nitric acid. The tubes were capped and shaken a few times. The concentrations of metal ions were analyzed by ICP-AES.

**5.3. RESULTS AND DISCUSSION**

**5.3.1. Removal of Metallic Ions by ELMs**

*Removal of Single Solute with Cyanex 301*

Cyanex 301 is a dialkylidithiophosphinic acid extractant. This sulfur-containing compound is a much stronger acid than its analogous oxy-acid, Cyanex 272
Figure 5-1. Schematic diagram of metallic ion removal by a shaker test.
(Kargari et al., 2004). As such, it is capable of extracting many metallic ions at low pH (< 2). Therefore, Cyanex 301 has been studied as a carrier agent or an extractant in ELMs, supported liquid membranes, and solvent extraction (Ocio et al., 2004; Bourget et al., 2005; Dimitrov et al., 2005; Madaeni and Zand, 2005; Wentink et al., 2005).

In this study, this carrier agent was first tested with the ELMs in order to selectively remove metallic ions dissolved in Mill-Q water or a simulated phosphoric acid solution. For cadmium removal with ELMs, an external feed phase was prepared by dissolving 0.025 g of CdSO$_4$ into 500 mL of Milli-Q water to represent 50 ppm of CdSO$_4$ in the water of pH of 4.92 without phosphoric acid. Figure 5-2a shows the results obtained from the cadmium removal by ELMs. Within 2 minutes of a contacting time with ELMs, most cadmium was found to be removed. This suggests that Cyanex 301 is a highly suitable carrier agent in the removal of cadmium at moderate pH (= 4.92). However, as shown in Figure 5-2b, ELMs with Cyanex 301 were not very efficient in removing chromium under the similar experimental conditions applied for the cadmium removal, except that 0.025 g of Cr(NO$_3$)$_3$.9H$_2$O was dissolved into 500 mL of Milli-Q water to prepare an external feed phase and its initial pH was slightly lower at 3.74.

In addition to cadmium and chromium, other metallic ions – copper, iron, lead, nickel and zinc were tested to be removed by ELMs with Cyanex 301 under the similar conditions. Figure 5-3 and 5-4 show the results obtained. Most metallic ions were removed during 30 minutes of a contacting time with ELMs; however the copper
Figure 5-2. (a) Cadmium and (b) chromium removal by ELMs with Cyanex 301. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-3. (a) Copper and (b) iron removal by ELMs with Cyanex 301. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
(70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
extraction rate was relatively slower than the ones of the other metals such as cadmium, iron, lead, nickel and zinc. Based on results obtained, it was found that ELMs with Cyanex 301 were very efficient in removing these metallic ions except chromium in terms of their removal ratios and rates.

Cyanex 301 vs. Cyanex 302

Cyanex 302 extractant is a monothiophosphinic acid. Similar to Cyanex 301, Cyanex 302 can perform selective metal separations at a lower pH than is possible with its oxy-acid analogue, Cyanex 272. Cyanex 302 has also been studied in ELMs, supported liquid membranes, and solvent extraction (Dongbei et al., 2004; Reddy et al., 2004; Ribeiro Jr et al., 2004; Dimitrov et al., 2005; Wentink et al., 2005; Wu et al., 2005).

Several sets of experiments with Cyanex 302 were conducted under the same conditions above to remove single metallic ion from the external feed phase. Then, the results obtained were compared to the ones from single metal removal by emulsion liquid membranes with Cyanex 301. Figures 5-5 to 5-7 show the comparison of ELMs with Cyanex 301 and Cyanex 302 in terms of the removal rates of a single metal.

As for the removal of cadmium, lead and zinc, Cyanex 302 was as effective as its analogue, Cyanex 301. These metals were quickly removed once they were brought into contact with ELMs. However, chromium was not removed using Cyanex 302.
Figure 5-5. Cyanex 301 vs. Cyanex 302 for (a) cadmium and (b) chromium removal by ELMs. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-6. Cyanex 301 vs. Cyanex 302 for (a) copper and (b) iron removal by ELMs. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-7. Cyanex 301 vs. Cyanex 302 for (a) lead, (b) nickel, and zinc removal by ELMs. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Chromium was identified as a problematic metal which was not easily removed by ELMs with Cyaenx 301 or 302 unlike the other metals.

For iron and nickel, the removal rates with Cyanex 302 were considerably retarded compared to those with Cyanex 301 presumably because Cyanex 301 is stronger acid than Cyanex 302. However, as for the copper removal, the results were opposite. The removal rate with Cyanex 302 was faster. There seem other factors involved in this phenomenon, for example bonding strength difference between the carrier agents and copper, but no clear explanation was available at this stage. It was found that both carrier agents could remove the tested metals except chromium very efficiently and the overall removal efficiency with Cyanex 301 was relatively higher than the ones with Cyanex 302 under the same conditions tested.

Effect of Initial Metal Concentration on the Removal Efficiency of ELMs with Cyanex 301 and Cyanex 302

It is known that the overall removal efficiency of ELMs can decrease as an initial solute concentration increases. This phenomenon results mainly due to the limitation in amounts of available carrier agents in the membrane phase and/or stripping agents in the internal phase. Five different heavy metals – cadmium, chromium, lead, nickel and zinc were studied with ELMs containing Cyanex 301 or 302. Cadmium sulfate, chromium nitrate, lead nitrate, nickel nitrate and zinc sulfate were used to prepare the feed phases and initial concentrations of each metal salt compound were adjusted at 500 mg/L. Same
The results obtained were presented in Figures 5-8 and 5-9. For cadmium and lead, the higher initial concentration (500 mg/L) did not have any measurable impact on their removal efficiencies and rates. They were easily removed by ELMs with Cyanex 301 or 302 when initial concentrations were high. However, the removal rates of nickel and zinc were impaired when initial concentrations of these metals were higher (compare to Figures 5-7b and 5-7c). Notably, removal efficiency of nickel significantly decreased especially when Cyanex 302 was used as a carrier agent and initial concentration was high. Overall, Cyanex 301 appeared to be less sensitive to initial metal concentrations than Cyanex 302.

Effect of Phosphoric Acid

Effect of the amount of phosphoric acid in an external feed phase on the metallic ion removal was studied. Two different initial concentrations (50 and 500 mg/L of each metal salt compound in the external feed phase) were tested with Cyanex 301 and 302 in the presence and absence of phosphoric acid.

For the cadmium removal, 5 wt% of phosphoric acid in the external feed phase did not affect its high removal rate with Cyanex 301 as shown in Figure 5-10. However, the cadmium removal rate with Cyanex 302 was significantly affected by adding 5 wt%
Figure 5-8. Effect of the initial concentrations of (a) cadmium and (b) chromium on the removal efficiency of ELMs. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-9. Effect of the initial concentrations of (a) lead, (b) nickel, and (c) zinc on the removal efficiency of ELMs. (70% v/v of Soltrol 220; 2% v/v of Cyanex 301 or 302; 3% w/v of Span 80; 25% v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-10. Effect of phosphoric acid on cadmium removal. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
of phosphoric acid to the external feed phase. Moreover, for the higher initial concentration (500 mg/L) of cadmium sulfate, the removal rate with Cyanex 302 was retarded and the cadmium concentration in the external feed phase even increased after 10 minutes of contacting time probably due to the leakage of emulsion globules (Park et al., 2004). These results reaffirmed that Cyanex 301 was more efficient than Cyanex 302.

Figure 5-11 shows the results of chromium removal under the similar conditions. Consistent with the previous experimental results, no significant removal of chromium was detected. Lead was also tested under the same conditions and the results obtained (Figure 5-13) had a similar trend compared to cadmium. But in this case, overall removal efficiency was affected largely by addition of phosphoric acid even when initial concentration of lead nitrate was as low as 50 mg/L.

Figure 5-12a shows the results of copper removal by ELMs. Though its removal rate with Cyanex 302 decreased at 5 wt% of phosphoric acid, most copper was removed by ELMs at the end of all the experiments. Figure 5-12b and 5-14 present the results of iron and nickel removal. It was found that both metal removal rates were significantly affected by phosphoric acid. At 5 wt% phosphoric acid, there was iron and nickel concentrations in the external feed phase did not decrease during extraction with both carrier agents. Zinc removal was less sensitive to phosphoric acid compared to some other metals such as iron and nickel when Cyanex 301 was used as a carrier agent (Figure 5-15).
Figure 5-11. Effect of phosphoric acid on chromium removal. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-12. Effect of phosphoric acid on (a) copper and (b) iron removal. (70 % v/v of Soltron 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-13. Effect of phosphoric acid on lead removal. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-14. Effect of phosphoric acid on nickel removal. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-15. Effect of phosphoric acid on zinc removal. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
**Binary Solute Extraction**

When two different solutes are dissolved in an external feed phase simultaneously and brought into contact with Type II ELMs, they could be either competing each other for the carrier agents or forming a complex to result in synergistic effect on transport. Several sets of experiments were conducted to evaluate how the presence of different metals affects each other on their removal rates.

For the removal of binary metals – cadmium and chromium, there were negligible effects on each metal removal rates as shown in Figure 5-16. Because chromium does not react with Cyanex 301 and 302, cadmium removal efficiency and rate was not much affected in the presence of chromium. However, cadmium and lead affected each other’s removal rate as shown in Figure 5-17. In Figures 5-10 and 5-13, it had been shown that the concentration of each metal in the external feed phase quickly decreased down to almost zero by ELMs with Cyanex 301. In contrast, lead concentration in the external feed phase did not decrease equally fast in Figure 5-17.

The competitive effects of metals were more evident when cadmium and zinc were present together (Figure 5-18). In the absence of zinc, it was previously shown that cadmium was completely removed by ELMs with Cyanex 301 and relatively effectively even with Cyanex 302 at 5 wt% of phosphoric acid. However, in the presence of zinc, the overall removal efficiency and rate were considerably affected especially when extracted with Cyanex 302 at 5 wt% of phosphoric acid.
Figure 5-16. Binary solute (Cd and Cr) extraction. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-17. Binary solute (Cd and Pb) extraction. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301 or 302; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-18. Binary solute (Cd and Zn) extraction. (70% v/v of Soltrol 220; 2% v/v of Cyanex 301 or 302; 3% w/v of Span 80; 25% v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Additional experiments were performed with phosphoric acid content of up to 40 wt%. Even at 40 wt% of phosphoric acid, the concentrations of cadmium and lead in the feed phase decreased greatly within 2 minutes (Figure 5-19). But lead removal ratio was found to be slightly affected by such a high concentration of phosphoric acid. For the mixture of cadmium and zinc, it was found that zinc removal rates were greatly affected by the increase of phosphoric acid content in the external feed phase. At 20 and 40 wt% of phosphoric acid, only about 30 % of zinc was removed as shown in Figure 5-20.

Unlike the other binary solutes, cadmium and copper were removed well at even 40 wt% of phosphoric acid. No retardation on the removal rate of either metal was detected as presented in Figure 5-21. Another combination of binary metals, cadmium and iron were also studied. Iron removal rate (Figure 5-22) was greatly impacted with increase of phosphoric acid content in the external feed phase, but cadmium removal rate was not much affected.

The results obtained suggested that retardation of mass transfer due to competitive effect existed for a few couples of metals. It is currently not clear what factors govern observed competitive effects on the interactions of metals with specific carriers. No synergistic effects were observed in the cases tested in this study.
Figure 5-19. Binary solute (Cd and Pb) extraction. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-20. Binary solute (Cd and Zn) extraction. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-21. Binary solute (Cd and Cu) extraction. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-22. Binary solute (Cd and Fe) extraction. (70 % v/v of Soltrl 220; 2 % v/v of Cyanex 30; 3 % v/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Multi Solute Extraction with Various Extractants

Further studies were conducted to examine the case where multiple metals are present as a mixture, a case that is more likely to represent the case with industrial phosphoric acids. Seven different metals with same initial molar concentrations in the feed phase, 0.00045 M, were treated with ELMs with Cyanex 301 in the presence and absence of phosphoric acid (40 wt%). The results obtained are presented in Figure 5-23. In the absence of phosphoric acid, cadmium, copper, lead, and zinc were very efficiently removed by ELMs. However, in the presence of 40 wt% of phosphoric acid in the external phase, zinc and lead removal was significantly retarded.

Additional experiment was performed with metal concentrations representing an actual phosphoric acid solution (Figure 5-24). Without phosphoric acid in the external phase, cadmium, copper, lead and zinc were very effectively removed. However, overall removal rates for most metals were significantly impacted by the increase in phosphoric acid content. At 20 or 40 wt% of phosphoric acid, only iron was removed up to a certain level.

Through the results presented in Figure 5-24, it was suspected that some metals might have been hindering the extraction of other metals by Cyanex 301. Therefore, four different conditions were studied and the results obtained are presented in Figure 5-25. In the absence of iron in the external feed phase, the removal rates of cadmium, copper, and lead were dramatically improved, but that of zinc was not much changed. The other
Figure 5-23. Multi solute extraction. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-24. Effect of phosphoric acid on multi solute extraction. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-25. Treatment of various mixture solutions by ELMs. (70 % v/v of Soltrol 220; 2 % v/v of Cyanex 301; 3 % w/v of Span 80; 25 % v/v of HCl (2M) as an internal stripping phase; 40% w/w of phosphoric acid as a external feed phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
results also supported that iron was the metal ion dominantly hindering the other metal removal because of its high initial concentration in the feed phase and its relatively strong binding with Cyanex 301. Chromium and nickel was not removed at all regardless the condition applied (results not shown).

A different carrier agent was explored as the extraction of multiple metals in the presence of phosphoric acid was not readily achieved with Cyanex 301 and 302. Alamine 336 was therefore tested, since it is known as a suitable carrier agent for extraction of cadmium, chromium, iron, and vanadium from the aqueous phase (Kontrec et al., 2003; Lee et al., 2004; Lozano et al., 2005; Someda et al., 2005). In the absence of phosphoric acid in the external feed phase, all the tested metals were quickly removed by ELMs with Alamine 336 (Figure 5-26). However, at 40 wt% of phosphoric acid, only cadmium concentration showed appreciable decreased.

Since the overall removal rates of heavy metals tested were greatly affected by 40 wt% of phosphoric acid, it was necessary to understand whether this undesirable phenomenon was caused by the unique characteristics of phosphoric acid or simply by extremely low pH of the external feed phase. Therefore, additional sets of experiments were conducted with adding 1 mL of 70 wt% of HNO₃ to 250 mL of the external phase to provide lower pH of the external phase. Alamine 336 was used as a carrier agent. The results obtained are presented in Figure 5-27. The results suggested that overall removal rates of the tested metals were also significantly affected by addition of nitric acid to the feed phase. Only iron showed any measurable decrease in concentration (around 95 % of
Figure 5-26. Multi metal extraction by ELMs with Alamine 336. (70 % v/v of Soltrol 220; 2 % v/v of Alamine 336; 3 % w/v of Span 80; 25 % w/v of NaOH (4M) as an internal stripping phase; 0.4 %v/v of concentration HCl (37 %w/w) in the external feed phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-27. Multi metal extraction by ELMs with Alamine 336. (70 % v/v of Soltrol 220; 2 % v/v of Alamine 336; 3 % w/v of Span 80; 25 % v/v of NaOH (4M) as an internal stripping phase; 0.4 %v/v of concentration HCl (37 %w/w) and 0.4 %v/v of concentration HNO₃ in the external feed phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
iron removal ratio after 30 minutes) (Figure 5-27). Additional sets of experiments were conducted with an external feed phase contained only iron or multi metals of chromium, iron, and zinc. The results obtained are shown in Figure 5-28.

Further efforts were made in order to improve the overall removal rates of multi metals by ELMs: (1) using different types of a membrane phase, (2) using different types of a carrier agent than Cyanex and Alamine, and (3) converting a membrane phase into a non-Newtonian form. It is known that a type of a membrane phase plays an important role in an emulsion liquid membrane system. Depending on a type of a membrane phase, solute mass transfer rate and emulsion stability are greatly affected. First, xylene, a less viscous solvent than Soltrol 220, was tested under the same conditions – at 0 or 40 wt% of phosphoric acid using Alamine 336 as a carrier agent. Figure 5-29 shows the results obtained.

At 0 wt% of phosphoric acid, the overall removal rates of all the tested metal enhanced greatly compared to the results shown in Figure 5-26. However, at 40 wt% of phosphoric acid, only cadmium was extracted and other metals were not extracted (Figure 5-29). Cyanex 923, Acorga M-5774, and Dicyclohexano18-Crown-6 were also tested as an alternative carrier agent. However, there was no significant improvement on the overall removal rates of the tested metals (results not shown).

It was noticed that emulsion stability were significantly affected by phosphoric acid addition to the external phase. Therefore, polymer (i.e. polyisobutylene) was
Figure 5-28. Single and multi metal extraction by ELMs with Alamine 336. (70 % v/v of Soltrol 220; 2 % v/v of Alamine 336; 3 % w/v of Span 80; 25 % v/v of NaCl (2M) as an internal stripping phase; 0.4 %v/v of concentration HNO₃ (70 %w/w) in the external feed phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Figure 5-29. Multi metal extraction by ELMs with Alamine 336 in xylene. (70 % v/v of xylene; 2 % v/v of Alamine 336; 3 % w/v of Span 80; 25 % v/v of NaOH (4M) as an internal stripping phase; 0.4 %v/v of concentration HCl (37 %w/w) in the external feed phase; no polymer; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
dissolved in the membrane phase to enhance its strength against shear rate in a Taylor-vortex column. A representative experimental result among several tested is shown in Figure 5-30. It was found that the emulsion stability was not much improved by converting a membrane phase into a non-Newtonian form.

5.3.2. Removal of metallic Ions by Solvent Extraction

*Multi Metal Extraction with Various Extractants*

Observed failure of the ELM process for the extraction of multiple metals might have resulted from either lack of proper bonding between carrier agent and metals or instability of emulsion membranes under extreme pH conditions. In order to rule out the stability problem, solvent extraction experiments were performed to focus on interaction between carriers and metals.

A set of a shaker tests was conducted following orthogonal matrix of different metals, different carrier agents, and varying phosphoric acid contents in aqueous phase. The experimental results are summarized in Table 2. The values given in the table represent the concentration of metals in aqueous phase after 60 min of exposure to the solvent that contains equal molar amount of extractant (carrier).

At 5 wt% of phosphoric acid, Cyanex 301 sufficiently extracted cadmium, copper, lead and zinc. Cyanex 302 was able to extract cadmium and copper. Alamine 336 did
Figure 5-30. Effect of non-Newtonian conversion of the membrane phase. (70 % v/v of Soltrol 220; 2 % v/v of Alamine 336; 3 % w/v of Span 80; 25 % v/v of NaOH (2M) as an internal stripping phase; 5 g/L of polyisobutylene; inner cylinder rotational speed = 500 rpm; temperature = 20°C).
Table 5-2. Results of metal removal with various extractants by a simplified solvent extraction.

<table>
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<tr>
<th>wt% of PA</th>
<th>Cd (mg/L)</th>
<th>Cr (mg/L)</th>
<th>Cu (mg/L)</th>
<th>Fe (mg/L)</th>
<th>Pb (mg/L)</th>
<th>Ni (mg/L)</th>
<th>Zn (mg/L)</th>
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<td>14.11</td>
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<td>7.19</td>
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</tr>
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<td>8.15</td>
<td>15.85</td>
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<td>34.17</td>
<td>191.77</td>
<td>1.16</td>
<td>4180</td>
<td>15.58</td>
<td>15.37</td>
</tr>
<tr>
<td>AcorgaM7554</td>
<td>40</td>
<td>49.97</td>
<td>186.77</td>
<td>20.9</td>
<td>4116.66</td>
<td>14.66</td>
<td>14.91</td>
</tr>
</tbody>
</table>
extract only cadmium. For the other extractants, there was only negligible change in the concentrations of the tested metals in the external feed phase after 60 minutes. At 40 wt% of phosphoric acid, the results were similar to the ones obtained from the experiments at 5 wt% of phosphoric acid. It was interesting to notice that extraction of lead and copper with Cyanex 302 and 923, respectively, was better at phosphoric acid content of 40 wt% than at 5 wt%, while no explanation is currently available for this phenomenon.

Crown ethers are well known as an effective extractant in ELMs and solvent extraction due to their selectiveness and capability of co-transporting cations and anions (Ramkumar et al., 2000; Gherrou et al., 2002a; Haddaoui et al., 2004). In this task various types of crown ethers were tested to evaluate their potentials as an extractant for phosphoric acid purification.

First, dicyclohexano-18-crown-6 and 15-crown-5 were used. Soltrol 220 was used as a membrane phase. The same initial molar concentrations of the metals according to Table 1 were used and samples were taken periodically (15, 30, 60, and 1080 minutes). The results obtained are shown in Figure 5-31. Removal efficiencies of most metals tested were less 10 % and only lead removal ratios with dicyclohexano-18-crown-6 and 15-crown-5 at 5 wt% of phosphoric acid were as high as 30 to 45 %.

In the subsequent experiments, considering relatively low solubility of dibenzo-18-crown-6 in soltrol 220, different solvents were evaluated. First, chloroform was used
Figure 5-31. Multi (6) metal extraction by solvent extraction at 5 wt% and 40 wt% of phosphoric acid with dicyclohexano-18-Crown-6 and 15-crown-5 in Soltrol220 (carrier to metal ratio =1:1, pH of external phase = 0.76 and 0.07 for 5 and 40 wt% of phosphoric acid, respectively).
a membrane phase instead. Figure 5-32 presents the results obtained. Only approximately 20% of lead was extracted at 5 wt% of phosphoric acid and the extractions of the other metals were very low at 5 wt% and 40 wt% of phosphoric acid.

Nitrobenzene was also tested as a membrane phase. Four different crown ethers were used as an extractant. The results obtained are presented in Figures 5-33 and 5-34. For 18-crown-6 and 15-crown-5 (Figure 5-33), most metals tested showed less than 10% removal at 5 wt% and 40 wt% of phosphoric acid, while lead removal efficiency reached almost 30% at 5 wt% of phosphoric acid. For dicyclohexano18-crown-6 and dibenzo-18-crown-6 (Figure 5-34), the lead removal efficiency was even higher than the ones with 18-crown-6 and 15-crown-5. Unfortunately, there was no significant enhancement on the other metal extraction rates under these conditions.

Toluene was also used as a membrane phase and three different crown ethers were used as an extractant. The results are shown in Figures 5-35 and 5-36. Similar to experimental results obtained with chloroform and nitrobenzene, it was found that there was no benefit of using toluene as a membrane phase. From the results obtained, it was found that crown ethers were not suitable extractants to remove various metals from simulated phosphoric acid solutions.

A normally applied stoichiometry ratio of an extractant to a metallic ion to form a complex ranges from two to three. It was postulated that increasing this ratio might affect the removal efficiency of multiple metals. Several sets of experiments were
Figure 5-32. Multi (6) metal extraction by solvent extraction at 5 wt% and 40 wt% of phosphoric acid with dibenzo-18-Crown-6 in chloroform (carrier to metal ratio =1:1, pH of external phase = 0.76 and 0.07 for 5 and 40 wt% of phosphoric acid, respectively).
Figure 5-33. Multi (6) metal extraction by solvent extraction at 5 wt% and 40 wt% of phosphoric acid with 18-Crown-6 and 15-crown-5 in nitrobenzene (carrier to metal ratio = 1:1, pH of external phase = 0.76 and 0.07 for 5 and 40 wt% of phosphoric acid, respectively).
Figure 5-34. Multi (6) metal extraction by solvent extraction at 5 wt% and 40 wt% of phosphoric acid with dicyclohexano-18-Crown-6 and dibenzo-18-crown-6 in nitrobenzene (carrier to metal ratio =1:1, pH of external phase = 0.76 and 0.07 for 5 and 40 wt% of phosphoric acid, respectively).
Figure 5-35. Multi (6) metal extraction by solvent extraction at 5 wt% and 40 wt% of phosphoric acid with 18-Crown-6 and 15-crown-5 in toluene (carrier to metal ratio =1:1, pH of external phase = 0.76 and 0.07 for 5 and 40 wt% of phosphoric acid, respectively).
Figure 5-36. Multi (6) metal extraction by solvent extraction at 5 wt% and 40 wt% of phosphoric acid with dicyclohexano-18-Crown-6 in toluene (carrier to metal ratio =1:1, pH of external phase = 0.76 and 0.07 for 5 and 40 wt% of phosphoric acid, respectively).
conducted with D2EHPA as an extractant in order to evaluate the effect of extractant-metal molar ratio. It was found that the removal efficiency of iron dramatically increased at 5 wt% of phosphoric acid with 5:1 of mole concentration ratio of D2EHPA to total metal tested, while extraction of other metals showed no appreciable change (Figure 5-37).

Since Cyanex 301 is a more suitable extractant than D2EHPA in the external phase of low pH (or with higher phosphoric acid content in the feed phase), further studies were performed varying the concentration of Cyanex 301 at 40 wt% of phosphoric acid. Figure 5-38 shows the results obtained. As the concentration of Cyanex 301 increased, the overall removal ratios of the tested metals dramatically increased except chromium.

With varying Cyanex 301 concentrations, several sets of additional experiments were conducted with an external feed phase containing nine different metallic ions. Figure 5-39 and 5-40 presents the results obtained. As the Cyanex 301 concentration increased, the overall removal ratio of the tested metals increased. Based on the results obtained, the tested metals could be categorized into three classes – fast extracted metals (As, Cd, Cu, Pb, and Zn), moderately extracted metals (Fe, Ni, and V), and rarely extracted metal (Cr) under the conditions studied.
Figure 5-37. Multi (6) metal extraction by solvent extraction at 5 wt% and 40 wt% of phosphoric acid with D2EHPA in soltrol 220 (carrier to metal ratio =5:1, pH of external phase = 0.76 and 0.07 for 5 and 40 wt% of phosphoric acid, respectively).
Figure 5-38. Multi (6) metal extraction by solvent extraction at 40 wt% of phosphoric acid with Cyanex 301 in soltrol 220 (carrier to metal ratio = 7, 10, or 14:1; pH of external phase = 0.76 and 0.07 for 5 and 40 wt% of phosphoric acid, respectively).
Figure 5-39. Multi (9) metal extraction by solvent extraction at 5 wt% and 40 wt% of phosphoric acid with Cyanex 301 in soltrol 220 (l) (carrier to metal ratio =5 or 10:1; pH of external phase = 0.76 and 0.07 for 5 and 40 wt% of phosphoric acid, respectively).
Figure 5-40. Multi (9) metal extraction by solvent extraction at 5 wt% and 40 wt% of phosphoric acid with Cyanex 301 in soltrol 220 (II) (carrier to metal ratio =15 or 20:1; pH of external phase = 0.76 and 0.07 for 5 and 40 wt% of phosphoric acid, respectively).
5.4. CONCLUSION

The following conclusions were made from the study presented in this report:

1. An extraction process using the Type II ELMs stabilized in Taylor-vortex column with Alamine 336, Cyanex 301 and 302 as carrier agents provided an extremely efficient way of separating various metallic ions from an aqueous phase at moderate pH ranges (>2). Among these carriers, metal extraction with Alamine 336 was most efficient and occurred most rapidly. While Cyanex 301 was also very efficient, chromium was identified as a problematic metal which was not easily extracted by both Cyanex 301 and 302; reasons for this are not apparent. The anomalous behavior of chromium identified here is a subject for further study.

2. When initial metal concentrations were increased, the overall removal efficiencies were observed to deteriorate. This might have resulted because of limitation in the amount of carrier agents available for binding with metals and shortage of stripping agents. In particular, the removal rates of nickel and zinc were significantly affected when Cyanex 302 was used as a carrier agent.

3. Phosphoric acid in the external phase significantly reduced the efficiency and rate of the metal removal in the ELM process. This phenomenon was more
apparent with iron and nickel than cadmium, lead, and zinc, and with Cyanex 302 than Cyanex 301.

4. When more than two metals co-existed in the external phase, retardation presumably due to competitive effect was observed. This phenomenon was more apparent with cadmium-iron, cadmium-lead, cadmium-zinc couples than cadmium-chromium and cadmium-copper couples.

5. For 40 wt% of phosphoric acid which simulated the industrial phosphoric acid, Cyanex 301 was the most suitable carrier agent. But ELM process under optimized condition only extracted cadmium, lead, and zinc. It was found that the high concentration of iron in simulated phosphoric acid solution might be the major cause of low removal efficiency for other metals presumably by occupying most of available carrier agents and hindering transport of other metals.

6. Simplified solvent extraction tests suggested that, among many factors tested, increasing the molar ratio of extractant to target metal up to 20:1 (for the case of Cyanex 301) dramatically enhanced extraction of all the metals except chromium.

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REFERENCES


Dongbei, W., Chunji, N., Deqian, L. and Yan, B. (2004) Solvent extraction of scandium(III), yttrium(III), lanthanum(III) and gadolinium(III) using Cyanex 302 in heptane from hydrochloric acid solutions, pp. 442-446, Elsevier, Geneva, Switzerland.


CHAPTER 6

HEAVY METAL REMOVAL BY NOVEL NON-NEWTONIAN EMULSION LIQUID MEMBRANE DISPERSED IN TAYLOR-COUETTE FLOW: EXPERIMENTS AND MODELING

ABSTRACT

Extraction of selected heavy metals from aqueous solutions was investigated using newly developed emulsion liquid membranes (ELMs). These ELMs had been stabilized by converting the liquid (oil) membrane phase into non-Newtonian fluid through the addition of high molecular weight polymers. The resulting ELMs were further dispersed in a Taylor-Couette flow to minimize the emulsion breakage. In this type II ELM process, Cyanex 301, 302, and 923 were applied as a carrier agent to facilitate the transport of metals across liquid (oil) membrane. A mathematical model to predict metal extraction was developed by taking into account the pH change in the external phase, the effect of agitation speed on the size of emulsion globules and leakage rate based on a classical shrinking core model. The proposed mathematical model was found to match with the experimental results reasonably well and shown useful to predict the performance of this particular ELM process under diverse operating conditions.
6.1. **INTRODUCTION**

Heavy metals such as cadmium, lead, nickel and zinc are present in wastewaters produced from many metal processing industries including metal mining, electroplating, extractive metallurgy, and metal treatment finishing, with typical concentration ranging from 100 to 750 mg/L (Loaec et al., 1997; Dutra et al., 2000; Schwuger et al., 2001; Chakraborty et al., 2004). The proper treatment of industrial wastewaters containing these heavy metals has been considered critical because of their serious impact on natural environment as well as human health (Loaec et al., 1997; Zouboulis et al., 2005). Common methods to remove heavy metals from wastewater include carbon adsorption, ion-exchange, electrodialysis, electrolytic extraction, solvent extraction and reverse osmosis (Loaec et al., 1997). However, these technologies have been faced with a number of challenges such as high constructional and operational costs, considerable energy consumption, additional purification processes required, and relatively low removal efficiency and operational complication (Veeken et al., 2003; Zouboulis et al., 2005).

A separation process employing emulsion liquid membranes (ELMs) has been widely studied because of its relatively low energy consumption especially compared to processes such as electrodialysis and reverse osmosis (Naim and Monir, 2003) and high extraction rate and high efficiency owing to the large surface area available for mass transfer (Frankenfeld and Li, 1987). In particular, the ELM has been considered as a promising alternative technology for removal and recovery of various heavy metals such
as cadmium, chromium, copper, nickel, and zinc, (Izatt et al., 1985; Reis and Carvalho, 1993; Raghuraman et al., 1995; Schwarzenbach et al., 2003; Chakraborty et al., 2004; Valenzuela et al., 2005) taking advantage of high selectivity. The high selectivity is achieved by using carrier agents in the membrane phase which exclusively bound with target heavy metals and selectively shuttles them through the liquid membrane (Frankenfeld and Li, 1987).

Unfortunately, the widespread use of the ELM processes has been limited due to the instability of emulsion globules against fluid shear. Breakup of emulsions and subsequent release of the internal stripping phase to the external feed phase would nullify the extraction process. As a result, several attempts to enhance the stability of ELMs have been made in the past decades. Adding more surfactants can increase the stability of emulsion globules, but the presence of surfactants at membrane interface hinders the mass transfer across the interface (Li, 1971). Excess amount of surfactant is also known to cause swelling of ELMs (Kinugasa et al., 1989). Employing a highly viscous oil as membrane phase has also been attempted, but reduced diffusivity of solutes and consequential decrease in extraction rate have been identified problematic (Terry et al., 1982; Skelland and Meng, 1996; Hou and Papadopoulos, 1997). Other studies have investigated optimization of the operational conditions such as agitation speed, temperature, and composition of ELMs (Pfeiffer et al., 1992; Correia and De Carvalho, 2003; Chakraborty et al., 2004). Using a polymeric porous membrane in a hollow fiber configuration to support the liquid membrane has also been proposed (Nanoti et al., 1997; Breembroek et al., 1998; Hu and Wiencek, 1998). While supported liquid membrane has
been considered relatively successful compared to other approaches to avoid emulsion instability problem, a hollow fiber contactor inevitably suffers from fouling during the long-term operation and from lower removal rate due to its much smaller surface area available for mass transfer.

A couple of novel solutions to this decades-old emulsion instability problem were recently proposed by the authors and their collaborators. The first solution involves a conversion of the membrane phase into a suitable non-Newtonian form (i.e., pseudo-plastic) by dissolving high molecular weight polymers such as polyisobutylene. The resulting shear-rate-thinning fluid exhibits increased apparent viscosity under low shear rate conditions which are typical in extraction process. Contrary to a Newtonian fluid, increased viscosity is not accompanied by the decrease in diffusivity of solutes in non-Newtonian fluid as long as the polymer content in the membrane phase is lower than a critical concentration (Skelland and Meng, 1996, 1999). Increased viscosity enables stable emulsion formation with less surfactant which might otherwise negatively affect the diffusion of solutes across the membrane interface. In addition, smaller internal stripping phase droplets and corresponding larger mass transfer area can be achieved during water-in-oil emulsion preparation, since the apparent viscosity of shear-rate-thinning fluid decreases under high shear rate conditions. The second solution involves using a Taylor vortex column as a contacting device instead of conventional mixing reactors equipped with impellers (Forney et al., 2002). Taylor-Couette flow provides relatively uniform shears throughout the fluid, thus minimizes the rupture of the ELMs due to local, intensive form drags that are common near the impellor regions of stirred
tanks (Forney et al., 2002). In addition, the Taylor-vortex column requires less power per unit volume than conventional stirred tanks in order to disperse emulsions throughout the external feed phase (Forney et al., 2002; Park et al., 2004).

In the present study, applicability of the newly developed ELMs for removal of common heavy metals such as cadmium, lead, nickel, and zinc from the simulated industrial wastewater was investigated. The effect of membrane composition (e.g., type of carrier agent) and operating conditions (e.g., the external feed phase and the agitation speed of Taylor vortex column) on the metal extraction rate were also examined. A mathematical model was developed to predict the removal rates of metal ions from unbuffered solutions by ELMs. In particular, the model incorporated the effect of change in external phase pH, which was found to be critical to determine the extraction efficiency of metal species with the carrier of choice.

6.2. MATHEMATICAL MODEL DESCRIPTION

A mathematical model presented in this study was developed based on a shrinking core model previously proposed by (Liu and Liu, 2000)) for emulsion liquid membrane extracting a model amino acid. A schematic description of a single emulsion globule and the projected concentration profile of metal in the external feed phase and inside the emulsion globule are shown in Figure 6-1. Since bulk phase is relatively well mixed and mass transfer through film is not rate-limiting, there is no concentration gradient in the external phase. Furthermore, because Biot number is usually larger than 20 under a good
mixing conditions in which a high mass transfer surface area is provided due to the decrease of emulsion globule size, the mass transfer coefficient in the external feed phase is significantly high compared with that in the membrane phase (Ho and Sirkar, 1992). The Biot number \( \text{Bi} = \frac{k_e R_{em}}{m D_c} \), where \( k_e \) = mass transfer coefficient in the external phase film around the emulsion globule (m/s); \( R_{em} \) = radius of an emulsion globule (m); \( m \) = ratio of metal in the external feed phase to that in the membrane phase; \( D_c \) = diffusivity of the metal-carrier complex in the membrane phase (m\(^2\)/s)) represents the ratio of the mass transfer resistance inside emulsion globules to that of the external feed phase (Yan et al., 1992; Goswami et al., 1993). As the carrier in the membrane phase complexes with the metal at the interface of emulsion and external phase, the complex first transports through the thin oil layer devoid of internal droplets (Liu and Liu, 2000; Chakraborty et al., 2004). As the metal-carrier complex further moves toward the center of the emulsion globule, carrier quickly exchanges the bound metal with proton present in the internal phase. Since the high viscosity of membrane phase and the presence of surfactants in the matrix of internal droplets, internal droplets are relatively motionless (Borwankar et al., 1988; Chowdhury and Bhattacharya, 1997; Chakraborty et al., 2004) and as a result the protons in the internal droplets located away from the center of the globules are consumed first. As the exchange of metal and proton proceeds, a boundary forms inside the emulsion globule between the region containing exhausted internal droplets and that containing unused internal droplets (Figure 6-1). This boundary, or reactive front, proceeds toward the center of the emulsion globule as extraction progresses.
Figure 6-1. Schematic of an emulsion globule and concentration profile. ($R$, $R_I$, and $R_F$ represent the radius of an emulsion globule, inner core, and reaction front, respectively.)
A mass balance of metal in the external phase results in the following equation:

$$\frac{dC_e}{dt} = -k_r a \cdot C_e + \Phi \cdot C_{em}$$  \hspace{1cm} (6-1)

where $C_e$ = concentration of metal in the external phase (mol/L); $C_{em}$ = concentration of metal in the emulsion globule (mol/L); $t$ = time (s); $k_T$ = overall mass transport coefficient (m/s); $a$ = specific surface area = $4 \cdot \pi \cdot r_e^2 \cdot N \div V_e$ (m$^{-1}$); $k_T a$ = overall volumetric mass transfer coefficient (s$^{-1}$); $r_e$ = radius of single emulsion globule; $N$ = total number of emulsion globules; $V_e$ = volume of the external phase (m$^3$); and $\Phi$ = leakage rate coefficient (s$^{-1}$). The first term and second term on the right side describe extraction of metal by the ELM and release of metal due to ELM leakage, respectively. It was assumed that emulsion globules are the spheres of uniform size and swelling, coalescence and redispersion of emulsions are negligible.

From the overall mass balance on the metal:

$$C_{em} \cdot (V_m + V_i) = (C_{e0} - C_e) \cdot V_e$$ \hspace{1cm} (6-2)

where $C_{e0}$ = initial concentration of metal in the external feed phase (mole/L); $V_m$ = volume of the membrane phase (m$^3$); and $V_i$ = volume of the internal phase (m$^3$), equation (6-1) can be rewritten to eliminate $C_{em}$ as follow:

$$\frac{dC_e}{dt} = -k_r a \cdot C_e + \Phi \cdot \frac{(C_{e0} - C_e) \cdot V_e}{V_m + V_i}$$ \hspace{1cm} (6-3)

The overall mass transport coefficient, $k_T$, is further expressed as (Borwankar et al., 1988; Geankoplis, 1993):
\[
\frac{1}{k_T} = \frac{1}{k_e} + \frac{m}{k_{em}} \equiv \frac{1}{k_{em}} \left[ \frac{(R_{em} - R_e)}{D_c} + \frac{(R_e - R_f)}{D_{em}} \right] \cdot m
\]  

(6-4)

\(k_e\) = mass transfer coefficient in the external phase film around the emulsion globule (m/s); \(k_{em}\) = mass transfer coefficient in the emulsion globule (m/s); \(R_{em}\) = radius of a emulsion globule (m); \(R_e\) = radius of inner core of an emulsion globule (m); \(R_f\) = radius of reaction front (m); \(D_c\) = diffusivity of the metal-carrier complex in the membrane phase (m²/s); \(D_{em}\) = effective diffusivity of the metal-carrier complex in the emulsion (m²/s); \(m\) = ratio of metal in the external feed phase to that in the membrane phase. The estimated \(k_e\) is several hundred times larger than \(k_{em}\), so the resistance \((1/k_e)\) in the external feed phase is neglected.

Additional mass balance can be formulated by recognizing that metals extracted from the external phase primarily exist in a portion of the emulsion liquid membranes that contain exhausted internal droplets:

\[
\frac{(C_{e0} - C_e)}{V_e} = \frac{4}{3} \pi \left( R_e^3 - R_f^3 \right) \cdot \frac{V_i}{V_m + V_i} \cdot \left( \frac{R_{em}}{R_e} \right)^3 \cdot \alpha \cdot C_{s0} \cdot N \quad (0 \leq R_f \leq R_e)
\]  

(6-5)

where \(C_{s0}\) = initial concentration of internal stripping agent; and \(\alpha\) = molar ratio of stripping agent reacting with metal-carrier complex. Note that \((R_e \div R_f)^3\) was multiplied to account for the fact that thin oil layer at the outer rim of the globule does not contain internal droplets. A set of equations (6-3), (6-4) and (6-5) was numerically solved through finite step-wise integration.
6.3. EXPERIMENTAL

6.3.1. Materials

Analytical reagent grade chemicals and water (>20 μΩ/cm at 25°C) purified by a Milli-Q Ultrapure Gradient Water System (Millipore, Billerica, MA) were used throughout the study. Cyanex 301, 302 and 923 (Cytec Industries Inc., West Paterson, NJ) and DEHPA (Alfa Aesar, Ward Hill, MA) were used as a carrier agent. Relevant information for these compounds is presented in Table 6-1. The membrane phase consisted mainly of Soltrol 220 (Chevron Philips Chemical, Spring, TX). A non-ionic surfactant, Span 80 (Emulsion Engineering, Sanford, FL), was used as an emulsifier and polyisobutylene (PIB) with average molecular weight of 1,250,000 (ExxonMobil Chemical, Houston, TX) as a polymeric additive. Internal stripping phase was made of 2 M of HNO₃.

6.3.2. Experimental Procedure

A Newtonian form of a solvent (Soltrol 220) was previously converted into a non-Newtonian form by PIB addition (5 g/L) in order to enhance a membrane’s viscosity. Then, emulsion was prepared first by dissolving Span 80 (5 % w/v) and a carrier agent (0.1 M) into the membrane phase under a gentle mixing by a magnetic stirrer. The prepared membrane phase was then placed in a 200 mL beaker immersed in an ice bath
Table 6-1. List of carrier agents employed in ELMs (Kargari et al., 2004).

<table>
<thead>
<tr>
<th>Carrier Agents</th>
<th>Active Components</th>
<th>Manufacturer Or Vendor</th>
<th>Formula</th>
<th>pKa</th>
<th>Formula Weight (g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanex 301</td>
<td>Bis(2,4,4-trimethylpentyl) dithiophosphinic acid</td>
<td>Cytec</td>
<td>C_{16}H_{35}PS_{2}</td>
<td>2.61$^*$</td>
<td>322.55</td>
</tr>
<tr>
<td>Cyanex 302</td>
<td>Bis(2,4,4-trimethylpentyl) monothiophosphinic Acid</td>
<td>Cytec</td>
<td>C_{16}H_{35}PSO</td>
<td>5.63$^*$</td>
<td>306.49</td>
</tr>
<tr>
<td>Cyanex 923</td>
<td>Trihexylphosphine oxide Dihexylmonoctylphosphine oxide Dioctylmonohexylphosphine oxide Trioctylphosphine oxide</td>
<td>Cytec</td>
<td>C_{18}H_{39}OP</td>
<td>302.48</td>
<td></td>
</tr>
</tbody>
</table>

* At 24 °C
and 25 ml of internal stripping phase (2 M of HNO$_3$) was slowly added under a vigorous mixing with sonication. Detailed procedure is described in Park et al. (2004).

Solute extraction was performed using a custom-built Taylor vortex column shown in Figure 6-2. The Taylor vortex column consisted of an inner cylinder made of polytetrafluoroethylene with a diameter of 49.3 mm and a height of 94.0 mm and an outer cylinder made of glass with an inner diameter of 80.5 mm and a height of 100.9 mm. The inner cylinder was housed inside the fixed outer cylinder and connected to a variable speed motor. An aqueous donor phase (i.e., model industrial wastewater) of 200 mL containing heavy metals was kept in the annular gap between the inner cylinder and the outer cylinder. While rotating the inner cylinder at a rotational velocity of 400 to 600 rpm, 20 mL of emulsion prepared was injected for initiation of the extraction process. Temperature was controlled at 20°C.

6.3.3. Sample Collection and Analysis

Samples (3 mL) were periodically collected from the solution agitated in the Taylor vortex column using a micropipette. Collected samples were immediately filtered using a polypropylene syringe filter with nominal pore size of 0.2 µm (Pall Co., East Hills, NY). Concentrations of heavy metals studied were analyzed by an Inductively Coupled Plasma Mass Spectrometer-Atomic Emission Spectroscopy (ICP-AES) (Model ICAP 61E Trace Analyzer, Thermo Jarrell Ash, Franklin, MA) equipped with an autosampler. The detection wave lengths for cadmium, lead, nickel and zinc were
Figure 6-2. Schematic of experimental apparatus.
226.502, 220.353, 231.604, and 206.200 nm, respectively. 1% of nitric acid was used as a rinse solution. For instrument calibration, standard solutions of each species were prepared with High-Purity Standards (Charleston, SC) and Mili-Q water. Analyses were performed four times for each sample and the average value was recorded.

Nitrate concentration of samples collected from emulsion leakage experiments was measured using a Dionex DX-600 Ion Chromatography (IC) system (Sunnyvale, CA) which consisted of a GP50 gradient pump, IonPac AG9 HC guard column, IonPac AS9 HC analytical column (4 mm x 250 mm), Anionic Atlas Electrolytic suppressor (AAES) and ED50 conductivity detector. The collected samples were injected with an AS50 autosampler. 9.0 mM Sodium carbonate (Na$_2$CO$_3$) was used as an eluent and its flow rate was 1.3 mL/min. The applied current was 100 mA and the diction time of nitrate was 9.5 minutes.

6.4. RESULTS AND DISCUSSION

6.4.1. Effect of Carrier Type and pH

A set of initial experiments was performed to extract zinc from the aqueous phase using the ELMs containing three different types of carrier agents: Cyanex 301, Cyanex 302, Cyanex 923. They are commercially available and often used for the selective removal of metal ions by solvent and liquid membrane extraction processes (Koopman et al., 1999; Gupta et al., 2003; Sze and Xue, 2003; Van De Voorde et al., 2004; Lozano et
al., 2005; Rodriguez et al., 2005). Experiments were performed individually under the same condition: $C_{e0} = 0.01$ M zinc; $C_{s0} = 2$ M HNO$_3$; $C_c = 0.1$ M (different carriers); concentration of Span 80 = 5 % w/v; concentration of PIB = 5 g/L; $V_e/V_m = 0.33$; $V_e/V_f = 0.1$; agitation speed = 500 rpm; temperature = 20 °C. Experimental results shown in Figure 6-3 suggested that Cyanex 923 was not effective for zinc removal. While Cyanex 923 binds strongly to zinc and therefore might useful in solvent extraction (Regel et al., 2001; Cierpiszewski et al., 2002), its exceedingly high affinity to zinc does not allow later separation during stripping (Miesiac and Szymanowski, 2004). Inefficient stripping in the internal phase makes this chemical not suitable as a carrier in the ELM extraction process. Cyanex 302 which has one thio group was found to be less effective than Cyanex 301 which has two thio groups.

The observed difference in extraction efficiency between carriers became more evident when external pH was varied. Experiments were performed using Cyanex 301 and 302 as carrier agents with external phase pH adjusted by nitric acid addition (the adjusted pHs by adding 0, 0.1, 0.5, and 1 M of HNO$_3$ were initially 5.17, 1.63, 0.54, and 0.35, respectively). The experimental results shown in Figure 6-4 suggested that the zinc removal with Cyanex 302 was more strongly affected by pH decrease than that with Cyanex 301 for the range of pH tested. This might have resulted since Cyanex 302 had a higher acid-base dissociation constant $pK_a$ at 5.63 compared to Cyanex 301 ($pK_a = 2.61$) (Kargari et al., 2004) such that more thio groups in Cyanex 302 were protonated and became less efficient in binding metals. Note that proton is exchanged during the
Figure 6-3. Zinc extraction with various types of carrier agents ($C_{e0} = 0.01$ M; $C_c = 0.1$ M, each; $C_{s0} = 2$ M, HNO$_3$; Span 80 concentration = 5 % w/v; PIB concentration = 5 g/L; $V_i/V_m = 0.33$; $V_e/V_f = 0.1$; agitation speed = 500 rpm; Temperature = 20 °C).
Figure 6-4. Effect of the pH of the external feed phase adjusted by nitric acid addition on zinc extraction ($C_{e0} = 0.01$ M; $C_c = 0.1$ M, Cyanex 301 or 302; $C_{s0} = 2$ M, HNO$_3$; Span 80 concentration = 5 % w/v; PIB concentration = 5 g/L; $V_i/V_m = 0.33$; $V_e/V_f = 0.1$; agitation speed = 500 rpm; Temperature = 20 °C).
extraction and pH is continuously decreased during the extraction process (Reis and Carvalho, 1993; Gherrou et al., 2002b; Kargari et al., 2004). In addition, leakage of emulsion globules adds stripping agent (HNO$_3$) to the external phase, which further contributes to pH decrease. Therefore, the rate (slope) of metal extraction in Figure 6-3 and 6-4 continuously decreased (i.e., curves were concave upward) due to not only decrease in the concentration difference between external and internal phases as extraction proceeded (i.e., decrease in driving force), but also decrease in external phase pH which results from proton exchange and ELM leakage. The effect of pH change during metal extraction, however, has not been well addressed in the past studies. The model presented in the previously section was therefore developed to account for the pH dependent equilibrium of metal and carrier complexation. In subsequent section, this model will be tested using Cyanex 301, apparently the most suitable carrier agent in the chosen system.

6.4.2. Model Parameter Evaluation

Key model parameters were estimated empirically or theoretically. The average radii of emulsion globules ($R_{em}$) and internal droplets ($R_i$) were directly measured by a photographic method. The average radius of emulsion globules was determined as $1.5 \times 10^{-4}$ m at an inner cylinder rotation speed of 500 rpm by first photographing with a digital camera and subsequent digital magnification and analysis of more than 200 individual globule images. The measurement of dispersed internal droplet size was performed within 10 minutes after preparing W/O emulsions ($C_e = 0.1$ M, Cyanex 301;
\( C_{so} = 2 \text{ M}, \text{HNO}_3; \) Span 80 concentration = 5 \% w/v; PIB concentration = 5 g/L; \( V_i/V_m = 0.33 \). The prepared emulsion samples (< 0.5 mL) were taken and left on a glass slide. Then the sample was covered with a thin cover glass and the photomicrographs were taken using a Leica DM IRM Differential Interference Contrast (DIC) microscope (Wetzlar, Germany) operated in a reflective index mode and a Hamamatsu EM-CCD C9100 CCD camera (1000×1000 pixels, 0.53 \( \mu \)m resolution/pixel, Hamamatsu city, Japan). In the reflected light DIC microscopy, the discontinuity on the surface of water in oil creates the optical path difference, which reveals the topographical profile. This microscopic technique provided relatively clean images of individual internal droplets. The average radius of internal droplets was estimated at 1.0\( \times 10^{-6} \) m.

From these experimentally determined \( R_{em} \) and \( R_i \) values, the thickness of the thin oil layer (\( R_{em} - R_e \)) and hence the radius of initial reaction front (\( R_e \)) were estimated at 9.5\( \times 10^{-7} \) m and 1.4530\( \times 10^{-4} \) m, respectively, according to the following equation (Kataoka et al., 1989):

\[
R_e - R_e = \left( \frac{4\pi}{3} \right)^{\frac{1}{3}} \left( \frac{V_i}{V_m + V_i} \right)^{-\frac{1}{3}} \left[ R_i \left( \frac{V_i}{V_m + V_i} \right)^{\frac{1}{3}} - 1 \right]
\]

(6–6)

The diffusivity of the metal-carrier complex in the membrane phase (i.e., thin oil layer) was estimated to be 7.5783\( \times 10^{11} \) (m\(^2\)/s) using the Hayduk and Minhas correlation (Reid et al., 1987).

\[
D_e (m^2/s) = 13.3 \times 10^{-8} \frac{T^{1.47}}{V_c^{0.71}} \mu_e^{0.57}
\]

(6–7)
where $T =$ absolute temperature (K); $\mu_m =$ viscosity of membrane (cP); $V_c =$ molar volume of complex at its normal boiling point (cm$^3$/mol), which was estimated at 881.6 (cm$^3$/mol) according to the Le Bas method (Reid et al., 1987) assuming that the molar volume of the tested metals is negligible. A value of 10.7 cP was used for the membrane viscosity ($\mu_m$) according to (Skelland and Meng, 1996).

The effective diffusivity of the metal-carrier complex in the emulsion was estimated to be $3.9442 \times 10^{11}$ m$^2$/s by the following Jefferson-Witzell-Sibbitt correlation (Chakraborty et al., 2004).

$$D_{em} (m^2/s) = 10^4 D_c \left[ \frac{4(1 + 2p)^2 - \pi}{4(1 + 2p)^2} \right]$$

(6 – 8)

where $p = 0.103 \left( \frac{V_i}{V_m + V_i} \right)^{-\frac{1}{2}} - 0.5$.

A separate set of batch extraction experiments was performed to evaluate the stoichiometry of metal-carrier reaction (Figure 6-5). An aqueous solution (200 mL) containing four different metals (individually) at initial concentration of 0.01 M was contacted with a membrane phase (Soltrol 220, 15 mL) containing 0.1 M of Cyanex 301. The membrane phase also contained 5 g/L of polyisobutylene but not surfactant. A gentle mixing was provided by a magnetic stirrer at 20°C and concentration change in the aqueous donor phase was monitored. After reaching the equilibrium and from the concentration of metal remaining in the aqueous phase, the mole ratio of Cyanex 301 to cadmium, lead, nickel, and zinc were determined as 2.16, 2.02, 2.19, and 2.32,
Figure 6-5. Metal extraction by a shaker test with Cyanex 301 – a. metal concentration decrease during a shaker test and b. complexation mole ratio of Cyanex 301 with cadmium, lead, nickel and zinc \((C_{e0} = 0.01 \text{ M}; \ C_c = 0.1 \text{ M}, \text{Cyanex 301}; \text{PIB concentration} = 5 \text{ g/L}; \ V_m/V_e = 0.075; \text{Temperature} = 20 ^\circ C)\).
respectively. From this result, the following equilibrium reaction with the correct stoichiometry was written:

\[ M^{2+} + 2\overline{HL} \Leftrightarrow \overline{ML}_2 + 2H^+ \]  

(6 - 9)

where \( M^{2+} \) = metal in the external phase; \( \overline{HL} \) = carrier in the membrane phase (bound to proton); \( \overline{ML}_2 \) = metal-carrier complex in the membrane phase. Note that since the carrier is present in protonated form in the membrane phase, one mole of carriers release two moles of protons, and therefore \( \alpha \) in equation (6-5) is equal to 2. From this equilibrium relationship, distribution coefficient \( m \) in equation (6-4) is further defined as:

\[ m = \frac{C_{M^{2+}}}{C_{\overline{ML}_2}} = \frac{C_{H^+}^2}{K_{ex} \cdot C_{ HL}^2} \]  

(6-10)

where \( C_{M^{2+}} \) = concentration of metal in the external phase (mol/L); \( C_{\overline{ML}_2} \) = concentration of metal-carrier complex in the membrane phase (mol/L); \( C_{H^+} \) = concentration of proton in the external phase (mol/L); and \( C_{HL} \) = concentration of carrier in the membrane phase (mol/L); and \( K_{ex} \) = equilibrium constant for metal-carrier complex formation (i.e., equilibrium constant for the reaction (6-9)). In excess carrier to metal condition, \( C_{HL} \gg C_{\overline{ML}_2} \), and \( C_{HL} = C_{HL,0} \), initial carrier concentration in the membrane phase.

Another set of experiments was performed to determine the leakage rate coefficient (\( \Phi \)). The concentration of nitrate in the external phase originating from the internal phase during ELM breakage was measured as a function of time. Since the pH of the external feed phase during the metal extraction in this study typically ranged from 2.5 to 1.6, four different acidic buffer solutions (0.36 M HCl, 0.12 M HCl, 0.2 M H\(_3\)PO\(_4\),
and 0.2 M CH\textsubscript{3}COOH, pH =1.13, 1.44, 1.71, and 2.65, respectively) were used as an external feed phase. In this study, only acid components were used to provide specific initial pHs of the external feed phase because metal ions can make a complex with basic components, which results in precipitation. The relatively high buffer capacity of the solutions examined minimized the change of pH of the external feed phase during metal extraction that resulted from hydrogen ion release by the leakage of emulsion and by extraction and stripping reactions driven by a carrier. The experimental results are shown in Figure 6-6. The rate of leakage was constant over the time period up to over 30 min (i.e., linear slope) with the rate varying from 2.876×10\textsuperscript{-7} to 5.387×10\textsuperscript{-7}. The average leakage rate coefficient (= 4.156×10\textsuperscript{-7}) was used in the mathematical modeling prediction of a metal removal rate.

In the modeling prediction, there were still two key unknown parameters – the change of hydrogen concentration in the external feed phase (i.e., the pH decrease) throughout the ELM process and an equilibrium reaction constant, K\textsubscript{ex}. For the former, a separate experiment was conducted to get the profile of the pH change of the external feed phase

6.4.3. Model Verification

Figure 6-7 shows the extraction of four different heavy metals by the ELM process experimentally determined versus that predicted with the proposed model. Note that equilibrium constant K\textsubscript{ex} is still an unknown. For the K\textsubscript{ex} estimation, the
Figure 6-6. Leakage experiment results for various types of the external feed phase ($C_e = 0.1$ M, Cyanex 301; $C_{so} = 2$ M, HNO$_3$; Span 80 concentration = 5 % w/v; PIB concentration = 5 g/L; $V_e/V_m = 0.33$; $V_e/V_f = 0.1$; agitation speed = 500 rpm; Temperature = 20 °C).
Figure 6-7. Comparison of the modeling prediction with the experimental results of the extraction rates of cadmium, lead, nickel and zinc ($C_{e0} = 0.01$ M; $C_e = 0.1$ M, Cyanex 301; $C_{s0} = 2$ M, HNO$_3$; Span 80 concentration = 5 % w/v; PIB concentration = 5 g/L; $V_i/V_m = 0.33; V_o/V_f = 0.1$; agitation speed = 500 rpm; Temperature = 20 °C).
concentration of a solute-carrier complex in the liquid membrane phase is needed to be measured, however, it is not a simple work for a particular ELM system. Therefore, the equilibrium constants of zinc, lead, cadmium, and for complexation with Cyanex 301 obtained by a least-square approach were 0.0034, 0.0018, 0.0005, and 0.00023, and, respectively. The model curves matched the experimental results very well.

Figure 6-8 shows the experimental data for zinc extraction under varying rotation speed of the inner cylinder in the Taylor-vortex column. These rotation speeds correspond to a dimensionless Taylor Number, $Ta$, of approximately 6,900 to 10,000. $Ta$ is defined as follows:

$$
Ta = \frac{2\pi R' S d_g}{\nu} \sqrt{\frac{d_g}{S}}
$$

where $R'$ = radius of the rotor (m); $S$ = rotational speed (rpm); $d_g$ = annular gap width (m); $\nu$ = kinematic viscosity (m/s) of the external feed phase at $20^\circ C$ in an ELM system (Skelland and Ramsay, 1987). As the rotation speed increases, the size of emulsion globules becomes smaller (subsequently total available reaction surface area increases) and rate of leakage increases both due to increase in fluid shear. The radii of emulsion globules at 400 and 600 rpm were measured as $1.8 \times 10^{-4}$ m and $1.0 \times 10^{-4}$ m, respectively, following the same procedure that was used at 500 rpm. The leakage rates at 400 and 600 rpm were estimated as $3.138 \times 10^{-7}$ and $5.108 \times 10^{-7}$ according to a correlation, $\Phi \propto S^{1.2}$, where $S$ = rotation speed of the inner cylinder (Park et al., 2004). Other model parameters remain constant. The model predictions in Figure 6-8 showed reasonably good match with the experimental data. Some underprediction in extraction rate was
Figure 6-8. Comparison of the model prediction with the experimental results for the effect of agitation speed on metal extraction ($C_{e0} = 0.01$ M, zinc; $C_c = 0.1$ M, Cyanex 301; $C_{s0} = 2$ M, HNO$_3$; Span 80 concentration = 5 % w/v; PIB concentration = 5 g/L; $V_i/V_m = 0.33$; $V_e/V_f = 0.1$; agitation speed = 400, 500, and 600 rpm; Temperature = 20 °C).
observed at higher rotation speed, presumably due to inaccuracy in photographic size measurement for the emulsion globules at higher speed as they become smaller.

Experiments in this section were performed to evaluate the efficiency of ELMs with Cyanex 301 ($C_c = 0.1$ M) for the treatment of a mixture solution containing cadmium, lead, nickel and zinc ($C_{eo} = 2.5$ mM, each metal). Figure 6-9 presents the results obtained through the experiments. It was noticed that the orders of the removal rate of metals tested are Pb > Cd >> Zn > Ni. The removal rates of zinc and nickel was found to be greatly influenced when they treated with the other competing metal ions, i.e., lead and cadmium (compared with the results shown in Figure 6-7). This phenomenon can be explained by the selectivity (affinity) of the carrier to the metal (Bartsch et al., 1999). Therefore, it is assumed that, in modeling prediction, the selective transports of metals by ELMs were mainly related to the amount of available carriers applied. With manipulating of the carrier concentration (i.e., actual concentration of carriers available, $C_c' = \beta \cdot Cc$, where $\beta =$ empirical constant) in the model, the removal rate of each metal from the mixture solution was estimated and then compared with the experimental data (Figure 6-9). The empirical constants used in the modeling prediction for cadmium, lead, nickel and zinc were 1, 1, 0.1, and 0.055, respectively. It was noticed that the model prediction underestimated the removal rate of cadmium by ELMs with Cyanex 301.
Figure 6-9. Comparison of model prediction with experimental results of multi-metal removal by ELMs ($C_{e0} = 0.0025$ M, each; $C_c = 0.1$ M, Cyanex 301; $C_s0 = 2$ M, HNO$_3$; Span 80 concentration = 5 % w/v; PIB concentration = 5 g/L; $V/V_m = 0.33$; $V_e/V_f = 0.1$; agitation speed = 500 rpm; Temperature = 20 °C).
6.4.4. Model Application

The model developed in this study could be useful as a tool to predict the performance of the newly developed ELM process in diverse operating conditions. An example model application is shown in Figure 6-10 in which zinc extraction efficiency, expressed in terms of the removal ratio after 10 min of contact time, under varying zinc and Cyanex 301 concentrations at 500 rpm. A dosage of carrier agent in proportion to the concentration of target metal is one important operating parameter to be considered in real application. The other model parameters were the same as used in the above section. The removal ratios of zinc calculated at 10 minutes of contact time in Taylor-Couette flow are presented in Figure 6-10. The applied initial concentrations of zinc and Cyanex 301 were 0.002 M to 0.02 M and 0.020 M to 0.200 M, respectively. It was predicted that as applied carrier concentration increases at fixed metal concentration, or as metal concentration decreases at a fixed carrier concentration, the ELM removal efficiency for the zinc solution was enhanced. In order to achieve more than 90% removal of metals in this example ELM system (at 10 minutes of contact time), this graph suggests that the carrier concentration should be adjusted from 0.06 M (for 0.002 M of zinc) to 0.2 M (for 0.02 M of zinc). That is, when treating higher concentration of zinc, higher concentration of carrier is required to achieve to a certain level of ELM removal efficiency. In addition, the zinc removal ratio by ELMs enhances at longer contact time. For example, under the conditions of 0.002 M of initial zinc concentration and 0.06 M of carrier concentration, the estimated zinc removal ratios is 91.9% and 98.2% (not presented in this paper) at 10 and 30 minutes of contact time, respectively.
Figure 6-10. Modeling prediction of zinc removal ratio (%) by ELMs with Cyanex 301 at 10 minutes of contact time.
6.5. CONCLUSION

The newly developed non-Newtonian ELM dispersed in Taylor-Couette flow was shown to be a very promising technology for the extract a relatively large amount of heavy metal (10 mM) from model industrial wastewaters. Among the carriers tested, Cyanex 301 was the most suitable carrier. pH dependency of the extraction was taken into consideration to develop a modified version of shrinking-core model that predicts the extraction rate of metal by ELMs. The model prediction matched the experimental data reasonably well, while fitting with the unknown equilibrium constant remains as the major drawback for the proposed model. Nonetheless, the model should provide a very useful tool to predict the performance of the metal extraction process by this particular ELM system as shown in the sample application to estimate metal extraction efficiency under varying metal and carrier concentrations.

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CHAPTER 7

CONCLUSIONS

This research was first focused on the development, application, and optimization of a novel ELM process using Taylor-Couette column as a new contacting device and the membrane converted into non-Newtonian fluid by polymer addition. Then the newly developed ELM process was applied for the extraction of various compounds (i.e. phenolic compounds and metallic cations) from simulated industrial wastewater and a concentrated phosphoric acid solution. Besides, two mathematical models were proposed to predict the solute extraction rate in the ELM process investigated, each for different process (i.e. Type I and Type II). The followings summarize major findings from this research.

In Chapter 3, a novel ELM process was newly developed employing a non-Newtonian fluid as a membrane phase and a Talor-Couette flow as a mixing pattern. Benzoic acid was used as a target solute in optimizing the ELM process.

1. As the surfactant (Span 80) concentration in the emulsion increased up to 5 %w/v, the stability of emulsion increased because of the reduction in interfacial tension which provides smaller internal droplets. However, the stability decreased for the further increase in the surfactant concentration due to the swelling of emulsion globules facilitated by an excessive amount of surfactant.
2. Similar to surfactant, the optimum conditions of an internal volume fraction and temperature for the particular ELM process investigated were found to be at around 20% and 293 K.

3. It was demonstrated that non-Newtonian conversion of the membrane phase by dissolving a proper amount of polymer (i.e. polyisobutylene) enhances the stability of emulsion without sacrificing the membrane permeability.

4. A Taylor-vortex column as a mixing contactor proved to be very effective in an ELM process compared with a conventional stirred tank in terms of energy consumption and emulsion stability.

5. A mathematical model for the extraction rate of benzoic acid by Type I ELMs was proposed, and the model prediction predicted the experimental results very well. In addition, it was found that the size of emulsion globules and the leakage rate of ELMs were proportional to $N^{-1.2}$ and $N^{1.2}$ (where $N =$ rotation speed, rps).

In Chapter 4, the applicability of the newly developed ELMs in Chapter 3 was evaluated for the removal of phenol and selected substitute phenols from model industrial wastewater.

1. The stability of ELMs was greatly enhanced and higher extraction efficiency could be achieved by converting the membrane phase into a suitable non-Newtonian form and employing the Taylor-Couette flow.

2. The novel ELM process optimized was shown highly efficient in treating model industrial wastewaters that contained phenol and substituted phenols at relatively high
concentrations (1,000 ppm). Extraction of these compounds from the mixture (= 1000 ppm of phenol, 2-chlorophenol, 2,4-dichlorophenol, each) was also highly efficient, while a minor level of mass transfer retardation due to competitive effect was observed.

3. Since these compounds were weakly acidic, the overall extraction was greatly affected by the external phase pH. When the pH was kept low and most species were present in neutral forms, the overall extraction efficiency was found to be closely related to their affinity to the membrane phase, represented by octanol-water partition coefficient in this study.

4. In case of nitrophenols and phenylacetic acid, however, the surfactant present in the membrane phase turned out to play a critical role in determining the affinity between the target solute and the membrane phase.

In Chapter 5, the ELM technology was applied for the extraction of various metallic cations from synthesized phosphoric acid solutions. Solvent extraction experiments were performed in parallel to find out appropriate carrier agents.

1. An extraction process using a Type II ELM system with Alamine 336, Cyanex 301 and 302 as a carrier agent provided an extremely efficient way of separating various metallic ions from an aqueous phase at moderate pH ranges (>2). Among these carriers, metal extraction with Alamine 336 was the most efficient and rapid. While Cyanex 301 was also very efficient, chromium was identified as a problematic metal which was not easily extracted by both Cyanex 301 and 302.
2. When initial metal concentrations were increased, the overall removal efficiencies were observed to decrease. This might have resulted from a limitation in the amount of carrier agents available for binding with metals and a shortage of stripping agents. In particular, the removal rates of nickel and zinc were significantly affected when Cyanex 302 was used as a carrier agent.

3. Phosphoric acid in the external phase significantly reduced the efficiency and rate of the metal removal in the ELM process. This phenomenon was more apparent with iron and nickel than cadmium, lead, and zinc, and with Cyanex 302 than Cyanex 301.

4. When more than two metals co-existed in the external phase, retardation presumably due to competitive effect was observed. This phenomenon was more apparent with cadmium-iron, cadmium-lead, cadmium-zinc couples than cadmium-chromium and cadmium-copper couples.

5. For 40 wt% of phosphoric acid which simulated the industrial phosphoric acid, Cyanex 301 was the most suitable carrier agent. But the ELM process under optimized condition extracted cadmium, lead, and zinc only. It was found that the high concentration of iron in simulated phosphoric acid solution might be the major cause of low removal efficiency for other metals presumably by occupying most of available carrier agents and hindering transport of other metals.

6. Simplified solvent extraction tests suggested that, among many factors tested, increasing the molar ratio of extractant to target metal up to 20:1 (for the case of Cyanex 301) dramatically enhanced extraction of all the metals except chromium.
In Chapter 6, the applicability of the newly developed ELMs for removal of common heavy metals such as cadmium, lead, nickel, and zinc from the simulated industrial wastewater was investigated.

1. The newly developed ELMs were shown to be highly efficient for extracting a relatively large amount of heavy metals (10 mM) from model industrial wastewaters.
2. Among the carriers (Cyanex 301, 302, and 923) tested, Cyanex 301 was the most suitable carrier for the metal extraction, even at low pH in the external feed phase.
3. The pH dependency of the extraction was taken into consideration to develop a modified version of shrinking-core model that predicts the extraction rate of metal by ELMs. The model prediction predicted the experimental data reasonably well, while fitting with the unknown equilibrium constant remains as a drawback of the proposed model.
4. The proposed model might provide a very useful tool to predict the performance of the metal extraction process by this particular ELM system as shown in the sample application to estimate metal extraction efficiency under varying metal and carrier concentrations.

Overall, an innovative ELM process was developed in this study by a unique combination of an unconventional contacting device (i.e. Taylor-Couette column) and a membrane with original characteristics (non-Newtonian). Combined with the experimental data obtained from various different applications and novel mathematical
predictive models, this study is expected to have a high impact on immediate practices of emulsion liquid membrane technologies in relevant industries.
CHAPTER 8

FUTURE WORK:

DEVELOPING A NOVEL DESALINATION PROCESS USING
SUPPORTED LIQUID MEMBRANES IN A HOLLOW FIBER
CONTACTOR

ABSTRACT

Current desalination technologies such as thermal evaporation and reverse osmosis have been always challenged by high energy consumption and accompanying high costs of operation and maintenance. However, there have been few major technological outbreaks to significantly reduce the production costs in past several decades other than progressive evolutions of these decades-old process options. The objective of the proposed research is to develop a very innovative alternative desalination technology using a Supported Liquid Membrane (SLM) in a Hollow Fiber (HF) Microfiltration contactor as a key salt separation step. The mechanism of salt separation by the liquid membrane is fundamentally different from those by the other processes, since it aims at transporting salt ions (minor constituent) rather than water molecules (major constituent) across a physical barrier. In addition, a driving force for separation is the concentration gradient of salts which is maintained by chemical mechanism rather
than physical means such as evaporation and pressurization which require high energy. In the proposed research, the composition of the liquid membrane and design configuration will be first optimized for salt extraction. The ultimate goal is to construct a complete lab-scale system for sea water desalination including the SLM-HF as a key unit operation as well as pre- and post-treatment steps. The newly developed process will be validated with demonstration experiments and cost analysis.

8.1. INTRODUCTION

About one-third of the population in the world is suffering from shortage of fresh water supply. Accordingly, various technologies including thermal evaporation, electrodialysis (ED), and reverse osmosis (RO) have been developed to produce fresh waters from seawaters and brackish waters for human consumption and agricultural and industrial uses. Unfortunately, widespread use of these technologies has often been limited by high energy consumption and accompanying high costs of operation and maintenance. However, there have been few major technological outbreaks to significantly reduce the production costs in past several decades other than progressive evolutions of the abovementioned process options.

Liquid membranes embedded into and supported by porous and solid microfiltration membranes (frequently in a hollow-fiber (HF) configuration) have been receiving growing interest in various separation processes including removal, recovery, and purification of diverse organic and inorganic compounds in industrial wastewaters
due to their outstanding selectivity, high extraction efficiency, and relatively low energy consumption compared to the other treatment methods (Breembroek et al., 1998; Hu and Wiencek, 1998; Luo et al., 2004; Van De Voorde et al., 2004). Supported liquid membranes (SLM) consist of three distinct phases: a donor phase (aqueous phase), a liquid membrane phase (oil phase), and a receiving phase (aqueous phase). The liquid membrane phase functions as a barrier that allows selective transport of target solutes from the donor aqueous phase to the receiving aqueous phase. The solutes are subsequently trapped by a stripping agent in the receiving phase that reduces the activity of solutes and maintains the driving force for mass transfer, \( i.e. \) the concentration (activity) difference between the donor phase and the receiving phase. The mass transfer is often facilitated by using a carrier agent dissolved in the membrane phase, which also enables exclusive extraction of specific solutes.

The mechanism of extraction of metallic cations such as silver, copper, zinc, and potassium in SLM process that has been proposed in previous studies (Dernini et al., 1992; Gherrou et al., 2001b, 2001a) is expected to be the same for that of extraction of sodium and chloride ions. Figure 8-1 illustrates the fundamental mechanism of salt extraction which the proposed study is based on. In brief, (1) \( \text{Na}^+ \) in the interface of the donor phase and the membrane surface partitions into the liquid membrane phase (accompanied by \( \text{Cl}^- \) to maintain electroneutrality) and forms a complex with the a carrier agent, represented by circles (Figure 8-1); (2) \( \text{Na}^+ \)-carrier complex and \( \text{Cl}^- \) pair moves across the liquid membrane following the concentration gradient (always in the direction of donor phase to receiving phase); (3) \( \text{Na}^+ \) and \( \text{Cl}^- \) are released to the receiving phase;
Figure 8-1. Mechanism of salt transport across SLM
(4) Na\(^+\) is sequestered by the stripping agent to lower the activity of Na\(^+\); (5) the carrier returns back to the membrane phase to repeat the cycle.

In essence, contrary to other desalination techniques such as thermal evaporation, RO and ED, the SLM process operates without a need for heat, high external pressure or electric field as a driving force for the separation. In SLM, the driving force is a concentration gradient which is maintained by lowering the activity of target solutes in receiving phase, even after the total number of solutes in the receiving phase exceeds that in the donor phase. In addition, the large surface area available for mass transfer, provided by the surface area of the hollow fibers, is expected to allow a rapid separation of target solutes. It is also noteworthy that, contrary to thermal evaporation and RO in which the water molecules are the target of transport, the SLM process aims at transporting the salts, which is the minor constituents in seawater compared to water. Currently, no attempts have been made to apply SLM in a HF contactor for desalination of seawaters or brackish waters. Only a preliminary study using liquid membranes supported by a flat sheet cellophane membrane to examine transport of salts in a simple batch-type reactor has been recently reported in the literature (Naim and Monir, 2003).

8.2. RESEARCH OBJECTIVES

The primary objective of the proposed research is to develop a very innovative alternative desalination technology using the SLM-HF as a key salt separation step. The final outcome of the project will be very practical and obvious – construction and
validation of a complete lab-scale demonstration unit for sea water desalination. The overall research objective will be addressed by performing the following four individual yet highly correlated tasks. The organization of the overall research is shown schematically in Figure 8-2.

**Task 1.** Optimizing SLM tailored for salt extraction. Specific tasks include selecting carrier and stripping agents effective for transport of and sequestration of salts, respectively, and determining their optimal doses as well as evaluating liquid membranes made with different materials and additives including polymeric additives for non-Newtonian conversion

**Task 2.** Developing SLM apparatus using a HF module tailored for desalination purpose and determining optimal operation conditions

**Task 3.** Designing pre- and post-treatment for the complete process train including a separate step for stripping agent recovery and performing lab-scale demonstration runs over a relatively long period of time

**Task 4.** Analyzing the equipment and operating costs and comparing to those of existing desalination technologies.
Task 1. Optimizing Supported Liquid Membrane Recipes

Optimizing Liquid Membranes (Carrier and Stripping Agents / Materials/Additives) ➔ Batch Experiments using Flat-Sheet SLM Apparatus

Task 2. Developing and Evaluating Hollow-Fiber Contactor

Optimizing Membranes and Operating Conditions ➔ Flow-through Experiments using Hollow-Fiber SLM Apparatus

Task 3. Developing Complete SLM Desalination System

Lab-Scale Demonstration Operation ➔ Task 4. Cost Analyses

Figure 8-2. Overall Structure of the Proposed Research Project
8.3. TECHNICAL APPROACH

Task 1. Optimizing Supported Liquid Membranes

The carrier and stripping agents are critical for efficient transport of the salts across the organic membrane phase and maintenance of driving force (\textit{i.e.} concentration gradient), respectively. Carrier agents are required 1) to form relatively stable complexes with cations (\textit{e.g.} \(\text{Na}^+\)) to extract cations from the donor phase (note: exceedingly high complex stability retards the process of cation release to the receiving phase), 2) to have a negligible solubility in the water phase to avoid loss of agents and possible contamination of product water, and 3) to have a sufficiently solubility in the membrane phase to achieve the target extraction rate, and 4) to exhibit low toxicity. Dibenzo-18-crown-6 is proposed considering the above concerns (Pedersen, 1967; Frensdorff, 1970; Izatt et al., 1985) and will be used at the initial phase of the project. Starch is chosen as a stripping agent to start with. Starch typically consists of amylase (10-20 \%) and amylopectin (80-90 \%) which have a molecular weight of 10-60 K and 30-1,000 K, respectively (Brautlecht, 1953), although composition varies greatly depending on the source. Sequentially arranged hydroxyl groups in starch molecules form a relatively stable complex with cations such as sodium ion (Rendeleman, 1966; Angyal, 1989) to lower the activities of ions in the aqueous phase. Furthermore, it is relatively inexpensive and highly biodegradable to minimize environmental concerns for concentrate treatment and disposal. During this phase of the project, other types of carrier agents such as
(Cyclohexyl-15-crown-5, Dicyclohexyl-18-crown-6, cryptant [2,2,2]) and carbohydrates will be also examined as candidates for carrier and stripping agents.

Mass transfer rate as measured in effective diffusivity ($D_{eff}$) and the overall efficiency of extraction through the liquid membranes prepared in different compositions will be first evaluated using a flat-sheet SLM (FS-SLM) apparatus (Figure 8-3). The liquid membrane will be prepared by dissolving a carrier agent and a surfactant (if necessary, such as Span 80, i.e. sorbitan monooleate) in a few different organic solvents such as Soltrol 220 (a mixture of C$_{13}$-C$_{17}$ aliphatic hydrocarbons), chlorobenzene, chloroform, and nitrobenzene. Previous study by the PI and collaborators suggested that a polymeric additive such as polyisobutylene (average MW of 1,250 K) which induces conversion of oil phase to non-Newtonian and increase in viscosity has dramatically increased the stability of emulsion liquid membranes without reducing solute transport rates (Park et al., 2004). Accordingly, non-Newtonian conversion will be also attempted to increase the viscosity and the stability of liquid membranes in capillary pores of polymeric membrane support. In the FS-SLM setup, the liquid membrane will be supported by a flat-sheet coupon of hydrophobic, micro-porous polymeric membrane (e.g. polypropylene microfiltration (MF) membrane with nominal pore sizes of 0.2 µm) which separates the donor and receiving phases. In order to minimize the loss of SLM to water phase during extraction, coating the SLM surface with a polyamide top layer produced from interfacial polymerization of piperazine and trimesoyl chloride will be tested following the procedure developed by Kemperman et al. (Kemperman et al., 1998). Each vessel will be filled with either an organic-free synthetic seawater or brackish water and a
Figure 8-3. Schematic diagram of flat-sheet-supported liquid membrane (FS-SLM) apparatus.
stripping solution (*e.g.* pure water containing stripping agents), respectively. Note that stripping solution for these experiments will be prepared by adding stripping agents to pure water to enhance the mass transfer rate and more accurate measurement of effective diffusion coefficient. But the stripping solutions will be made from seawater or brackish water in the actual systems since no pure water shall be available in real situation.

Experiments will be performed first with the synthetic water containing only sodium chloride (34,000 mg/L) but later with the synthetic seawater containing other major ionic species to better simulate the seawater composition. Synthetic seawater will contain 26.71 g/L NaCl, 2.03 g/L MgSO$_4$, 3.74 g/L MgCl$_2$ and 1.53 g/L CaSO$_4$ to yield a solution of 10,500 mg/L sodium, 19,000 mg/L chloride, 1,350 mg/L magnesium, 450 mg/L calcium, and 2,700 mg/L sulfate (*i.e.* total dissolved solids of 34,000 mg/L). Synthetic brackish waters will be prepared by diluting the synthetic seawaters. In the presence of other ionic species, multiple carrier agents will be added to the membrane phase to attempt simultaneous removal of major divalent ions such as Mg$^{2+}$ and Ca$^{2+}$. Mechanical agitations in both vessels will be provided by magnetic stirrers and experimental temperature will be controlled by a water bath at 5 to 30°C (with 20°C as a baseline condition). Samples will be taken periodically from the donor and receiving phases and concentrations of ions will be analyzed by inductive coupled plasma-atomic emission spectrometry (ICP-AES) for metallic cations and ion chromatography (IC) for anions to estimate effective diffusivity of various target ions.
**Task 2. Developing and Evaluating Hollow-Fiber Contactor**

A few selected liquid membrane that exhibited high performances in batch experiments will be further tested in a lab-scale flow-through HF reactor made with polymeric microfiltration membranes of different materials and nominal pore sizes (Figure 8-4).

Impregnation of liquid membranes on the polymeric support will be carried out by pumping the liquid membrane through the shell side for 1 hour at a relatively slow flow rate. The solvent will flow rapidly through the porous wall of the fibers and will be collected in the lumen side (Kulkarni et al., 2000). After washing both the lumen and pores with clean water for approximately 30 min, the organic-free synthetic seawater or brackish water and the stripping solution will be circulated from the separate container using peristaltic pumps through shell side and lumen side, respectively (i.e. outside-in operation transfer), or in an opposite configuration (i.e. inside-out transfer) (See Figure 8-4). Note that stripping solution is the same as the synthetic seawater or brackish water except that it contains stripping agent that effectively lowers the activity of cationic species. For accurate estimation of transport parameters, a few experiments will be performed using the stripping solution made without salts. The solutions will be directed toward opposite directions (i.e. counter-current mode). Samples will be taken periodically during experiments and the concentrations of salts in the feed and stripping phases will be determined by ICP-AES and IC. Possible contamination of the donor and receiving phase by release of membrane phase and carrier agent, although expected to be
Figure 8-4. Schematic diagram of lab-scale supported liquid membrane-hollow fiber reactor for salt extraction (for inside-out configuration).
very low, will be monitored by either high performance liquid chromatography (HPLC) or collectively as total organic carbon (TOC). If loss is significant, the method of interfacial coating as described above will be carefully examined (Kemperman et al., 1998). Operating parameters such as flow rates of both solutions and hydraulic pressure variations will be investigated. Flow rate and pressure will affect the shear rate at the interphase of the SLM and the donor/stripping solutions and therefore increasing flow rate might decrease the stability of the membranes. However, increasing the flow rate of stripping solution will increase the contact time with fresh stripping solution and therefore will increase the mass transfer rate. Therefore, careful optimization for flow rate and build-up of hydraulic pressure inside the module will be performed. Experiments will be performed at controlled temperatures from 5 to 30°C.

**Task 3. Developing Complete Supported Liquid Membrane Desalination System**

The ultimate goal of the proposed study is to develop a lab-scale demonstration SLM seawater desalination unit and to perform a continuous operation for system validation. Experiments will be first performed with a synthetic seawater to initially evaluate the system performance. Actual demonstration experiment will be performed for a relatively long term period (> 1 week) using the seawater collected from the Atlantic coast of the State of Georgia (i.e. sampling site is located approximately 4 hours from the laboratory). The following four additional components will be developed to accomplish a complete process.
1. Pre-Treatment with MF Membrane. The raw water might contain particulate matter that may clog the pores of hollow fibers and accumulate on the membrane surface. Accumulation of particulate matter will reduce the available mass transfer area and will reduce the rate of salt extraction. In addition, it is important to remove microorganisms in the feed in order to prevent any unwanted bacterial growth in the system. Depending on the quality of water in terms of concentration of particulate matter, cartridge-type dead-end microfiltration unit with nominal pore sizes ranging from 0.1 to 0.5 µm will be employed to pre-treat the seawaters. Note that MF is also often employed as a pre-treatment step for seawater desalination with RO.

2. Multiple-Stage SLM Application. It is desirable to have a relatively large extraction efficiency through one-stage SLM step. However, considering that mass transfer rate might not be sufficiently fast to achieve the target salt removal, it might be necessary to treat the seawater through several stage SLM processes. Note that overall extraction efficiency will increase as additional SLM steps are added to the whole process. Based on the results obtained in Task 2, multiple-stage SLM process will be devised to achieve the target removal efficiency of at least 99%.

3. Post-Treatment with Granular Activated Carbon Column. The product water might contain a very small amount of liquid membranes eluted from the SLM which will be closed monitored during Task 2. Since they are exceedingly hydrophobic (e.g. log $K_{ow}$’s of chlorobenzene and nitrobenzene are 2.78 and 1.85 respectively (Schwarzenbach et al., 2003)), removal by adsorption onto hydrophobic activated carbon surfaces is expected to
be very efficient. Initial attempt will be made using a glass column filled with granular activated carbons (GACs). Operational variables such as dimensions of column, type of GAC (different materials and pore sizes), and empty-bed contact time (EBCT) will be varied. In case the concentration of liquid membrane in the product water is relatively high and early breakthrough by GAC column is identified, an ultrafiltration (UF) membrane in a flow-through module (e.g. hollow-fiber configuration) with molecular weight cut-offs (MWCO) ranging from 10-300 K might be employed as a more reliable barrier.

4. Recycling Stripping Agents with UF Membrane. The stripping solution contains a large amount of stripping agents (e.g. starch) which must be treated before disposal. In order to reduce the cost and to be more environmentally sustainable, recycling the stripping agents is considered critical for the success of the system. Salt ions in the stripping solutions are relatively loosely bound to the stripping agents. Therefore, if the stripping solution is pressurized against the membrane with pore sizes smaller than the stripping agents, only salts ions and water will pass through the membrane while the stripping agents are retained. The stripping agents that have lost the salts will be then available to accept more salts ions transported from the SLM. Filtration with UF membranes of nominal MWCOs ranging from 10 – 300 K will be tested to retain and recycle starch in the stripping solution. Dead-end filtrations will be first carried out with an Amicon stirred cell (Millipore) housing a flat-sheet membrane. A constant trans-membrane pressure (10-50 psig depending on MWCO) will be provided by compressed extra-dry nitrogen gas. After the membrane with appropriate MWCO that exhibits
effective retain of starch molecules is determined, a hollow-fiber module with the same MWCO will be employed for the flow-through operation in the lab-scale demonstration unit. It should be noted that the starch may promote bacterial growth in the stripping solution. If any bacterial growth is identified as measured by heterotrophic plate count (HPC), small amount of free chlorine (HOCl) might be dosed or intermittent shortwave UV irradiation will be applied.

Figure 8-5 shows the projected schematic of the complete lab-scale demonstration unit that uses SLM as a key desalting step. It is envisioned that this lab-scale unit will be the first-step toward developing a bigger scale system that we will propose to develop upon completion of the proposed project.

**Task 4. Cost Analyses**

Overall costs of SLM desalination process for a range of output capacity will be analyzed and critically compared to those of existing desalination processes under typical design configurations and operating conditions. Budgetary costs will be developed based on the cost of equipment, construction cost, engineering, overhead, and finance charges. Capital cost estimates will be developed based on the prevailing interest rate. Operating costs will be calculated to include power, chemical usage, maintenance, membrane replacement, and labor. Power costs will be estimated based on the efficiency of commercially available pumps, power recovery turbines, and electric motors. Note that the PI is currently performing a comprehensive economic analysis of various design
Figure 8-5. A schematic of a complete lab-scale demonstration desalination process using the SLM separation as a key step ($Q_1$, $Q_2 =$ flow rates) and also including pre- and post-treatment steps as well as a UF process to recycle the stripping agents.
approaches currently used for seawater desalination by RO process as a part of the research project funded by U. S. Department of Interior, Bureau of Reclamation and the approach developed in that project will be applied for the cost analysis in the proposed project.
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VITA

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