Ionic Liquid-Based Composite Thin-Films for Selective Ion Separations in Electrodialysis

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IONIC LIQUID-BASED COMPOSITE THIN-FILMS FOR SELECTIVE ION SEPARATIONS

IN ELECTRODIALYSIS

A Thesis
Presented for the Degree of

Master of Science in Engineering Science

Department of Chemical Engineering

The University of Mississippi

Saloumeh Kolahchyan

December 2018
ABSTRACT

The onset of climate change and rising global population has caused greater water scarcity, a considerable problem which threatens our world. The demand for fresh water is pushing a fast development of water purification technologies. Among these technologies, membrane-based water desalination processes are playing an interesting role in both academia and industry. Electrodialysis (ED) is an electro-membrane separation process aimed at water treatment through ion removal, which is achieved through the selective control and transport of ionic species. ED is a popular water treatment method; however, it is limited by membrane scaling, lack of ion selectivity, and high energy consumption for high salinity feeds. This study is focused on the synthesis of unique ionic liquid-based anion exchange membranes in order to obtain ion-selectivity in Electrodialysis (ED) systems through the addition of a divalent ion repulsion layer. Thin films of polymerizable ionic liquids were coated and cured on the anion exchange membranes in order to enhance ion selectivity in (ED) system. The membrane characteristics were studied through FTIR, SEM, AFM, contact angle measurement, and ED performance. Results suggest that while imidazolium coatings were incompatible with ED system due to rapid degradation, phosphonium coatings exhibited enhanced monovalent ion selectivity.
DEDICATION

To my loving husband, Abolfazl, and my family for their unending support along the way.
# LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ED</td>
<td>Electrodialysis</td>
</tr>
<tr>
<td>EDI</td>
<td>Electrodionization</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic Liquid</td>
</tr>
<tr>
<td>PIL</td>
<td>Poly/Polymerized Ionic Liquid</td>
</tr>
<tr>
<td>BMED</td>
<td>Bipolar Membrane Electrodialysis</td>
</tr>
<tr>
<td>AEM</td>
<td>Anion Exchange Membrane</td>
</tr>
<tr>
<td>CEM</td>
<td>Cation Exchange Membrane</td>
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ACKNOWLEDGEMENTS

I would like to acknowledge my advisor, Dr. Alexander Lopez, for his support and mentorship during my graduate career.

I would like to acknowledge my committee members Dr. Paul Scovazzo and Dr. Sasan Nouranian for their support, guidance, and feedback throughout my graduate career.

I would like to acknowledge undergraduate students Matthew Edwards and Madelyn Barber who I had the pleasure to mentor during their studies.

Special thanks to the University of Mississippi Graduate School for funding this degree.
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CHAPTER I
INTRODUCTION

Motivation for Wastewater Treatment through Membrane Separations

The onset of climate change, rising population and urbanization has caused greater water scarcity around the world. Currently, two-thirds of the global population live under severe water shortage conditions during at least part of the year [1]. Increasing competition over water due to increased demands for industrial and agricultural purposes, water pollution, economic growth and population growth are the main factors affecting the global water resources [2]. In addition, according to a WHO/UNICEF JMP (Joint Monitoring Programme) report in 2017, 844 million people do not have access to the clean water which results in water-related illnesses and deaths. Consequently, solving the water-related hygiene issues and finding unconventional sources of fresh water is pushing a fast development of water production technologies.

Recently, there has been growing appeals for water treatment technologies in order to reduce the use of natural water sources and provide a solution to the water contamination issue. Recycling and reuse of water through efficient water treatment technology can be a great reduction in water resources utilization [3]. Hence, a variety of water treatment methods such as Distillation, Flocculation, Ion Exchange, Anaerobic Digestion, Reverse Osmosis (RO), Electrodialysis (ED), Electrodiionization (EDI) and Micro/Nano-filtration have been studied. Membrane-based separation processes are capable of replacing traditional energy-intensive separation techniques, such as evaporation and distillation. They are known as “Green” Technologies because of their
energy efficiency and environment friendly characteristics. It is also possible to achieve a higher selectivity, recovery factor, improved water quality, and cost reduction through combination of different membrane operations. These advantages along with water scarcity and high energy consumption of traditional separation processes soothed the development and commercialization of membrane-based water treatment methods during the last 40 years [4]. Membrane-based separation processes have played a leading role in both academia and industry in terms of water treatment applications. In the field of brackish water desalination, RO holds 60% to 90% of the global demand. In Gulf countries, multiple stage Distillation and Flash technologies are still popular due to the large availability of the heat needed for powering the thermal evaporative systems [5]. Electro-membrane processes, such as, ED and EDI have a small but stable market, especially in low salinity desalination applications [6]. The specific applications of electro-membrane processes are expanding by developing new IEMs and devices, which enlarges the potential for the application of these flexible technologies.

**Electrodialysis, a Mature Technology for Wastewater Treatment**

ED is an electro-membrane separation technique in which charged membranes are used in an alternate arrangement built on a plate and frame module. When an electrical potential is applied to the system, ions migrate towards the electrodes through semi-permeable membranes. The alternate pattern of the charged membranes, allows ions removal from one solution in to another [7], [8]. Due to its wide range of application, Electrodialysis has been maturing with a wealth of well-understood methods over the past 60 years. Reverse Electrodialysis (RED), Electroionization (EDI) and Bipolar Membrane Electrodialysis (BMED) are some modified version of ED system, being invented due to the specific applications. RED is the use of natural salinity gradients to create an electric current as opposed to using a current to create a salinity
gradient [9]. In EDI, ion exchange resins are used in the solution compartments in order to enhance the solution conductivity and it is useful when ultrapure water or high ion removal is needed [10]. ED can be used in combination with bipolar membranes (BMED) for the production of acids and bases from waste water containing salts [11]. In some specific industrial applications, the features of ED (or EDI) are more favorable than RO; For instance:

1. In pharmaceutical and food industry for applications such as deacidification of fruit juices, demineralization of whey protein, and removal of sodium from products
2. In electrical industry for ultra-pure water production [12]
3. Selective electrodialysis for selective salt separation from saline streams [13]

The popularity of ED in food and pharmaceutical industry stems from its ability to keep the health and nutritious properties of the final product and not endangering it by for example adding coagulants or regenerating agents. For separation at low salinities, ED and EDI are more suitable than RO. However, at high salinities, ED and EDI demonstrate high Specific Energy Consumption (SEC) which makes them uncompetitive for use in water recovery. Therefore, ED and EDI are
practical options for brackish water production as long as feed salinities are below 9000 ppm. [14][15]. Figure 1-1 shows the two regimes where the ideal separation process can be determined from feed condition. As the feed salinity decreases, ED and EDI become more favorable. However at moderate and high salinities RO is favored.

**Ion Exchange Membranes (IEMs): Charged Polymer Films for Perm-selective Separations**

IEMs are dense polymeric membranes containing fixed charged groups in the polymer backbone. Depending on the type of the charged groups attached to the polymer matrix, IEMs are either Cation Exchange Membranes (CEMs) or Anion Exchange Membranes (AEMs). AEMs consist of positively charged groups, such as $\text{–NH}_3^+$, $\text{–NR}_2H^+$, $\text{–NR}_3^+$, $\text{–PR}_3^+$, etc., attached to the membrane backbone. They allow the passage of anions but reject cations. While CEMs consist of negatively charged groups, such as $\text{–SO}_3^-$, $\text{–COO}^-$, $\text{–PO}_3^{2–}$, $\text{–PO}_2H^–$, $\text{–C}_6\text{H}_4O^–$, fixed to the membrane backbone and allow the passage of cations but reject anions [16][17]. When IEMs contact an ionic solution, they exclude co-ions (ions of the same charge as the fixed ions in the membrane) partially or completely from the membrane. Because of their perm-selectivity, IEMs are utilized in several industrial applications. Table 1 shows different processes that employ IEMs. Innovative research ideas has been developed by researchers on the characteristics of the IEMs in terms of efficiency, cost, and application [16]. Ion selectivity of IEMs plays a key role in expanding the application of these membranes and several industrial processes based on IEMs exist. For instance, in processes such as microbial fuel cells, ion exchange membrane bioreactors, diffusion dialysis, and flow batteries, high membrane perm-selectivity between counter-ions of different valences is crucial for system efficiency [18]. In addition, in some applications of treated
water separation of monovalent ions, such as K$^+$, Na$^+$, NH$^{4+}$, NO$_3^-$, and Cl$^-$ versus multivalent ions Mg$^{2+}$, Ca$^{2+}$, PO$_4^{3-}$, and SO$_4^{2-}$ is also important [19].

Table 1-1. Processes using IEMs [12]

<table>
<thead>
<tr>
<th>Process</th>
<th>Application</th>
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<tbody>
<tr>
<td>Electrodialysis</td>
<td>Water desalination, NaCl production</td>
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<td>Flow batteries</td>
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<td>Microbial Fuel Cells</td>
<td>Waste biomass treatment, energy conversion</td>
</tr>
<tr>
<td>Ion Exchange Membrane Bioreactor</td>
<td>Water treatment</td>
</tr>
</tbody>
</table>

Seta et al. studied such monovalent ion selectivity in ED system through incorporation of modified IEMs. In general, the mono/multivalent ion selectivity mechanisms are governed by exclusion, size and electrostatic repulsion [20]. Consequently, various membrane surface modification methods such as,

- formation of a highly cross-linked layer,
- introduction of a weakly basic anion exchange group layer on the membrane surface and controlling the hydrophilicity of the membrane
- formation of condensation-type polymer-aromatic amines and formaldehyde on the membrane surface or in the membrane matrix,

have been studied in order to obtain monovalent ion selectivity in IEMs [21][22]. However, a challenging problem which arises in this domain is that most of the materials used are either expensive or hazardous. There is also a further problem with undesired membrane resistance that can happen by introducing a highly cross-linked layer on the membrane. Therefore, there is a
demand to advance the development of mono/multivalent ion selective IEMs. In the present work, we aim to achieve a monovalent ion selectivity in AEM through incorporation of ionic liquids in electrodialysis system for water treatment applications.

**Ionic Liquids; Room Temperature Molten Salts**

Ionic Liquids (ILs) have been attracting researchers for decades due to the many unique properties they possess. They present negligible vapor pressure, which makes them non-flammable and are able to dissolve a large variety of organic and inorganic compounds (polar or non-polar). They display good conductivity which is useful in electrodialytic separation applications. ILs are molten salts at room temperature due to bulky cation and anion structures [23]. Previous studies show that ionic liquids can provide a wide range of application in chemical industries, such as, a good solvent for gas separation, extraction, and other separation processes as well as a liquid electrolyte in a battery and electrolysis process for their good conductance and stability. The most important factors building the relationship between properties and structures of ILs are melting point, viscosity, and conductivity. Cations and anions play a key role in designing the suitable IL. For instance, the viscosity of the ILs is significantly dependent on the nature of the anions [24], (eg. ILs containing [TF$_2$N]$^-$ anion have a lower viscosity compare to those containing [PF$_6$]). This is suggested to be related to the shape, size, molar mass and H-bond capability of the anion. Smaller, lighter, and more symmetric anions present more viscous ILs. The low melting point of ILs is related to the size, anisotropy, and internal flexibility of the ions. ILs with 4 to 10 N-alkyl chains have a wide liquid range with low melting points [25]. The conductivity of ILs is mainly important in electrochemical processes. Due to their salty structures, they have many charge carriers per mole, which makes them amongst the most concentrated organic electrolytes.
Imidazolium-based ILs present high conductivity while quaternary ammonium ILs exhibit lower conductivity. The conductivity of ILs has an inverse relationship with their viscosity [26].

The presence of water in ILs can considerably influence the viscosity, conductivity, polarity and solubility of other materials in ILs. T.Welton et al found that anions are mainly responsible for the solubility of water. For example, imidazolium-based ionic liquids demonstrate different water solubility depending on the anion; $[\text{BF}_4]^-$, $[\text{NO}_3]^-$, and $[\text{ClO}_4]^-$ are more water soluble, while $[\text{PF}_6]^-$, $[\text{SbF}_6]^-$, $[\text{OSO}_2\text{CF}_3]^-$, $[\text{OCOCF}_3]^-$, and $[\text{TF}_2\text{N}]^-$ have less water solubility [25].

In some applications such as small electronics devices, where ILs features are extremely favorable, film like electrolyte materials are required. Therefore, it is interesting to have ILs with polymerizable groups [28]. Polymerized ionic liquids (PILs) are a relatively new class of IL-based materials. They present a macromolecular structure which contains an ionic liquid (IL) monomer in each repeating unit, connected through a polymeric backbone. The most common way of polymerization is chain polymerization of IL monomers, which is described in Figure 2. Depending on the desired poly ionic liquid architecture, the polymerizable unit can be located either on the anion or cation. PILs are primarily used for gas separation membranes and ion conductive mediums in fuel cells [29]. Some other applications of PILs include: absorbent, precursor for carbon materials and porous polymers, powerful dispersant and stabilizer. The main reasons of using PILs instead of ILs are further mechanical stability, durability, and enhanced processability. Research reports that the ion mobility of PILs are at least two magnitudes lower than the corresponding IL monomer. Because for example, the mobility of the cation species after the polymerization of cations is negligible and the formed PIL can act as a single-ion conductor.
In this situation, the movement of the free anions is possible but limited to the free volume between the polymeric chains, resulting in lower ion mobility and conductivity [30].

Figure 1-2. Polymerization of ILs [29]

**Purpose and Hypothesis of the Research**

The purpose of this research is to obtain a monovalent anion selectivity in ED system via coating thin ionic liquid based composite thin-films on AEM surface. Selective removal of target ions from feed solutions, is specifically important in producing high quality water to meet water standards. Furthermore, monovalent selectivity can be of a great help to prevent scaling on the membrane. For instance, calcium sulfate can cause serious scaling problems in ED system as a scale. By making the AEMs impermeable to sulfate ion we can address this issue. The perm-selectivity of specific anions in to the anion exchange membrane is essentially related to the negative charge layer on the membrane surface [22]. Compare to monovalent anions, multivalent anions are less prone to transport on to the membrane surface and according to the Coulomb’s law, that is due to the higher electrostatic repulsion between a negatively charged surface potential and multivalent anions compare to the electrostatic repulsion between monovalent anions and a negatively charged surface potential. To our knowledge, no previous research has investigated the application of PILs in water separations.
We hypothesize that PIL modification of ion exchange membranes can increase the electrostatic repulsion of the AEM surface, resulting in monovalent ion selectivity. The electrostatic repulsion between multivalent anions and a negative surface potential is greater than that between monovalent anions and a negative surface potential according to Coulomb’s law, which means that multivalent anions are less likely to transport onto the membrane surface than monovalent anions.
CHAPTER II
BACKGROUND

Over the past 60 years, ED and ED-related processes have played an interesting role in water treatment technologies in terms of flexibility and range of application. In fact, research and developments on IEMs and ED system optimization are boosting the growth of this technology globally. In this chapter, a brief background of the ED evolution will be presented.

**Electrodialysis: From Early Steps to Commercialization**

In 1890, Ostwald, Maigrot and Sabates proposed an Electrodialysis (ED) system for the first time for the demineralization of the sugar syrup [31]. However, the actual ED was hypothesized when Donnan presented his exclusion principle in 1911. The Donnan exclusion principle helped pave the way for the development and manufacture of the first ion exchange membranes. This advancement opened the way for development of the actual multi-compartment ED. The first synthetic ion exchange membranes were produced in 1950 by W.Juda and W.A McRay. Ionics (USA) used them to make the first ED desalination plant for Aramco in Saudi Arabia [32][7]. Due to the lack of domestic salt sources, Japan has used ED system to concentrate sea water and produce salt for human consumption. During the 1950s to 1960s, the formation of scale on the ion exchange membrane surface was a severe problem. That was mainly occurring due to the unidirectional mode of operation in ED system. In this mode, the polarity of the electrodes and the position of the dilute and concentrated cells were fixed. Fixing this issue
required addition of anti-scaling chemicals to the feed water and pH adjustment. In early 1970s, Ionics established a breakthrough in ED system design called electrodialysis polarity reversal (EDR)[33][7]. In this design, the polarity of the DC power applied to the membrane electrodes and thus, the desalted water and brine chambers are also reversed two to four times per hour. Switching cells and reversing current direction resulted in scale flushing from the membrane before it can precipitate and scale the membranes. [8]

![Electrodialysis Configuration](image)

**Figure 2-1. Electrodialysis Configuration**

**Electrodionization (EDI)**

ED has some limitations in terms of energy efficiency. When ions are depleted in a solution, more power is needed to move current through that solution which results in larger power requirements for solutions of low salt content. A solid conductive ion medium introduced into the dilute compartment in the form of ion exchange resins eliminates this disadvantage. This reliable technique to treat low electrolyte content solutions is Electrodionization [34]. In 1953, the first patent was
applied for an EDI device by a Dutch company which was granted in 1957. They described an apparatus for the deionization of salt-containing liquids using an alternating pattern of anion and cation resins. A patent was also granted to Kollsman describing a Continuous EDI (CEDI) mechanism for the purification of acetone. Numerous patents were granted for various types of EDI devices during 1957 to 1960 [35]. In addition, the design and operating conditions of electrodeionization process has been extensively investigated by Glueckauf in the late 1950s and early 1960s. His two-staged theory was based on the diffusive transfer of ions from flowing solution to ion exchange resin beads and the transfer of ions along the chain of ion exchange beads [36]. In the 1970s to 1980 Matejka and Shaposhnik extended the investigation of CEDI into the deionization of brackish or tap water to produce ultra-pure water [37] Finally, the first commercially CEDI modules were introduced in 1987 under the trade name Ionpure, now sold by U.S. Filter Corporation (“U.S. Filter”) [38]. The configuration of an EDI is similar to ED except the usage of ion exchange resins or fibers in the diluate cell in order to increase the conductivity in the solvent-water and prevent the occurrence of the concentration polarization phenomenon. The main application of this technology is the production of ultrapure water for semiconductors and pharmaceutical manufacturing. Also, this technology may facilitate the separation of toxic metallic ionic species that are present in industrial waste effluents [33], [39]. Recently, Arora et al. and others developed ion exchange resin wafers that can enhance electrical conductivity in solutions similar to EDI process [40]. The benefit of using a wafer is that thinner electrode cells can be developed and resin regeneration can occur within the cell through water splitting. Consequently, the overall resistance in the electrodialytic stack is lower. The main difference of this technique is that a polymer is used to bond the ion exchange resins together.
**Bipolar Membrane Electrodialysis (BMED): Applications of Electrodialysis in the Food industry**

Bipolar membranes are consist of an anion zone, a cation zone and the interphase area where the two zones overlap. They can produce hydroxyl and hydrogen ions via water splitting. When they are used in conjunction with IEMs in an ED system, they produce acid and bases from salt. Bipolar membranes have been prepared by K.N.Mani et al. in the late 1970s [41]. The first commercial application of bipolar membranes was for generating spent hydrofluoric/nitric acid mixture used in stainless steel pickling, which was commercialized by AQUATECH systems in 1980 [42]. Attempts have been made by Strathmann et al. in order to improve the characteristics of the bipolar membranes [43]. BMED is a promising alternative technique for the valorization and treatment of industrial wastewaters of very different nature, such as, metal processing, production of rubber, wood processing, beverage industry, and production of acetaldehyde [44]–[48]. The key parameters in a bipolar membrane are high water dissociation rates, low electrical
resistance at high current density, high ion-selectivities, low co-ion transport rate and good chemical and thermal stability in strong acids and bases. Application of this technology in food industry has been extensively studied by Bazinet et al. [47]. For instance, milk protein production [48], juice deacidification [49], acidification of Kraft black liquor [50] and etc. BMED has been growing so fast recently due to its unique design and capability.

**Theoretical Background: Transport in Ion Exchange Membranes**

In separation processes using ion exchange membranes both electrical potential and concentration gradients are as driving forces, it is usually easier to study them in terms of the amount of charge transported than the amount of mass transported. Because both types of ion are present, anions and cations move in opposite directions under an electric potential gradient. In ED,
for example, when an electrical potential difference is applied to a NaCl solution, Cl\(^-\) will migrate to the anode (positive electrode) and Na\(^+\) will migrate to the cathode (negative electrode). Negative ions cannot pass the negatively charged membranes (anion exchange membrane) and positive ions cannot pass the positively charged membranes (cation exchange membrane). This allows the depletion of ions from a diluate or diluting solution and the concentration of ions in concentrate solution. The total amount of charge transported per second across a plane of given area can be measured using the following equation:

\[
\frac{I}{F} = c^+ (u) (+e) + c^- (-\nu) (-e) = ce (u+\nu) \quad (2-1)
\]

Where

- \(c^+\) is the concentration of sodium cations,
- \(c^-\) is the concentration of chloride anions,
- \(u\) is the velocity of the cations in an externally applied field of strength (cm/s),
- \(-\nu\) is the velocity of the anions measured in the same direction (cm/s),
- \(+e\) and \(-e\) are protonic and electronic charge, respectively,
- \(I\) is the current (A),
- and \(F\) is the Faraday constant which converts the transport of electric charge to a current density in amps (C/mol).

Equation 1 links the electric current with the transport of ions. The fraction of the total current transported by an ion is known as the transport number of that ion. The relationship between the transport number for the cations and anions is,

\[
t^+ + t^- = 1 \quad (2-2)
\]
which means by combining the equation 1 and 2 the transport number for both cation and anion can be calculated from Eq. (2-3) and (2-4), respectively:

\[
t^+ = \frac{c \, u \, e}{e \, u \, (u+\nu)} = \frac{u}{u+\nu} \quad (2-3)
\]

\[
t^- = \frac{u}{u+\nu} \quad (2-4)
\]

**Concentration Polarization in Electrodialysis**

Concentration polarization is a well-known phenomenon in membrane separation processes that occurs as a concentration gradient within the solution and perpendicular to the membrane surface. In ED system, electrical current is carried by anions and cations migrating through the solution in opposite direction. Conversely, current is carried mainly by counter-ions inside the membrane, while co-ions are (ideally) rejected [31]. The resistance of the membrane is often small compare to the resistance of the water-filled compartments, especially in the dilute compartment where the amount of ions carrying the current is low. The formation of ion-depleted regions next to the membrane in dilute compartments, places an additional limit on the flux of ions through the membrane. Ion transport through this ion-depleted aqueous boundary layer controls ED system performance. The thickness of this unstirred layer in ED system is 20-50 µm. Since only one of the ionic species is transported through ion exchange membrane, the concentration gradients will form in this layer [51].

**Limiting Current Density in Electrodialysis**

Due to the selective permeation of the ions in electrodialysis membranes, an immediate decrease in the concentration of some ions in the solution adjacent to the membrane surface will
occur. Comparing to the bulk solution concentration, this reduction is significant, which reflects that an increasing fraction of the voltage drop is being consumed to transport ions across the boundary layer rather than through the membrane. Consequently, the energy consumption associated with salt transportation increases dramatically [52]. The maximum transport rate of ions in the boundary layer can be presented by a point at the membrane surface where the ion concentration is zero. The limiting current density is the current through the membrane at this point, which is, current per unit area of membrane (mA/cm²). Any further increase in voltage difference across the membrane after reaching to the limiting current density, will not increase current or ion transport through the membrane. This extra power usually causes side reactions such as, water dissociation [31][6].

**Figure 2-4.** Schematic of the concentration gradients adjacent to a single cationic membrane in an ED stack. Reproduced from [31].

**Figure 2-5.** Typical current-voltage curve for an IEM immersed in an electrolyte solution. Reproduced from [11]
**Electrodialysis Performance**

The overall efficiency of an ED process is the energy consumption of the system to perform the desired separation which can be calculated from equation (2-5),

\[ E = I^2 R \quad (2-5) \]

where \( E \) is the power consumption in Kilowatts, \( I \) is the current through the stack and \( R \) is the resistance of the stack. Current efficiency is another important key factor determining the performance of ED system, which can be measured using equation (2-6),

\[ \eta = \frac{ZVF (C_i - C_f)}{NIt} \quad (2-6) \]

where \( Z \) is the ion valence, \( V \) is the system volume, \( F \) is Faraday’s constant, \( C_i \) and \( C_f \) are the initial and final ion concentration, respectively, \( I \) is the system current, and \( t \) is the operation time. In general, at low current densities the current efficiency is highest, while this results in low productivity. Since high productivity is often favorable, current densities are raised up to the point where power consumption can be justified by the economics of the process. In addition, further increase in current density above the limiting current density will cause water splitting rather than ionic movement [53].

**Monovalent Ion Selectivity in Electrodialysis**

Brackish water and sea water mainly consist of monovalent and multivalent ions such as sodium, chloride, calcium, magnesium, and sulfate. The separation of monovalent ions can be beneficial where the existence of a specific ion can cause issues in terms of either processing or final application. For instance, selective removal of sodium over calcium and magnesium is
important in agricultural applications. Because irrigation water with high sodium concentration can decrease water infiltration and permeability of soil, which results in reducing crop yield [19]. Another example is the formation of undesired precipitates by calcium, magnesium and sulfate (e.g. CaSO₄) which can clog parts of seawater desalination process equipment [54]. Also, in some countries, the concentration of nitrate in groundwater is increasing significantly due to excessive use of artificial fertilizers. Nitrate ion is harmful to human health and it needs to be removed when treating ground water [55]. Separation of ions with the same sign and valence is difficult and important in both industrial requirements and academia. ED system is one of the most promising methods for selective separation of monovalent ions over multivalent ions by using monovalent perm-selective IEMs. The perm-selectivity of ions through IEMs is governed by their specific transport rate in membranes and affinity of ions with membranes. Several theories have been proposed to clarify the perm-selectivity mechanism of specific ions. These studies are mainly classified as, a) control of the same charge ions perm-selectivity based on their hydrated ion size; b) particular interactions between the IEM’s functional groups and the mobile ions; c) rejection of specific ions by a thin surface layer on the IEM which has the same charge as ions [24–30]. Xu et.al developed a monovalent CEM by coating a polyethyleneimine layer on the membrane surface [19]. Mulyati et al. found the effect of a strong negative charge on the monovalent selectivity and anti-fouling properties of AEMs through layer-by-layer assembly of oppositely charged polyelectrolytes on the membrane [62]. Composite membranes composed of AEMs and Polypyrrole present a lower transport number ratio compare to those of membranes without polypyrrole layer [63]. Introducing anionic polyelectrolyte layers by immersing the AEMs in the electrolyte solution and providing ionic cross-linking on the membrane surface can also cause perm-selectivity in the AEM’s [59]. Monovalent perm-selective IEMs have been industrially used
to increase the efficiency of ED system. However, the current perm-selective membranes in industry are either costly, hazardous and/or have high potential for fouling and scaling. There is an urgent need to develop robust cost-effective monovalent perm-selective membranes.

**Ionic Liquid-based Composite Thin-films for Perm-selectivity in AEMs**

In AEMs, perm-selectivity can be discussed in terms of a transport number ratio between a target anion and a standard anion, which is usually chloride ion. Thus the perm-selectivity between anion X and chloride is defined as,

\[
P^X_{\text{Cl}} = \frac{t_x}{t_{\text{Cl}}} \cdot \frac{c_x}{c_{\text{Cl}}}\ 
\]

where, \(t_x\) and \(t_{\text{Cl}}\) are transport number of anion X and chloride in the membrane, respectively, and \(C_x\) and \(C_{\text{Cl}}\) are the concentrations of X and chloride in the diluate during ED process. \(P^X_{\text{Cl}}\) is also called the transport number of anion X relative to chloride ion [58]. It has been suggested that the transport number of sulfate ions relative to chloride ions in ED is dependent on the preparation methods of AEMs. For instance, MPDA anion exchange membranes which are made of the condensation of m-phenylenediamine, phenol and formaldehyde have extremely low \(P^{\text{SO}_4}_{\text{Cl}}\) while an AEM prepared by the condensation of tetraethylenepentamine, phenol and formaldehyde, permeates almost the same amount of sulfate ions as that of chloride [22]. AEMs made from 2-oxy-benzylidimethyleneamine, phenol and formaldehyde present higher permeation of sulfate ions compare to MPDA membrane [54]. Another way of membrane surface modification by the purpose of specific ion perm-selectivity is decreasing hydrophilicity of AEMs by introducing specific anion exchange groups in the membranes [61][22]. In this concept, the permeation of anions through the membranes becomes difficult with increasing the hydrophobicity of the membrane. Since for example, sulfate ions are bulky and hydrophilic compared with chloride ions,
it is reasonable that the hydrophilic ions are difficult to permeate through the hydrophobic membrane.

As far as we know, no previous research has investigated the usage of ILs to develop perm-selective AEMs for aqueous solutions in ED system. However, the application of these ILs in membrane-based gas separation processes has been investigated by researchers extensively. The earliest story about ionic liquids was in 1914, when Paul Walden was investigating salts and he found [EtNH$_3$][NO$_3$], with a melting point of 12°C [64]. After that several individual groups were working on molten salts without being aware of each other. In 1951, Hurley and Weir discovered 1-ethylpyridinium bromide-aluminum chloride ([C$_2$py]Br-AlCl$_3$) which was liquid in 2:1 M ratio mixture at room temperature [65]. Later, Bob Osteryoung’s group found 1-butylpyridinium chloride-aluminium chloride ([C$_4$py]-AlCl$_3$) being liquid at room temperature while they were studying the electrochemistry of two iron (II) diimine complexes ferrocene and hexamethylbenzene at room temperature [66]. Other low-melting systems with organic cations such as [Et$_4$N][GeCl$_3$], [Et$_4$N][SnCl$_3$], and [Et$_3$NH][CuCl$_2$] being studied by scientists as solvents for catalysts [16]. Finally, in 1980s, with new researchers such as Ken Seddon, Tom Welton and Charles L. Hussey interest in ionic liquids began to slowly spread [68]. Due to their ability to change the anion and cation components of the liquid, ionic liquids are considered as ‘designer solvents’; which makes them suitable for a broad range of application. Recent studies indicate that ionic liquids can be used as membranes in various separation processes. The initial use of ILs as membranes was as a supported IL membrane, in which their negligible vapor pressure solves one of the limitations of traditional liquid membranes [69]. Gelled structures are also a new morphology advancement of ILs that provides improved mechanical features compare to the liquid while keeping the diffusion properties of the liquid phase [70]. The utilization of ILs in
Electrodialysis system has been mostly conducted for ILs synthesis and purification. For example, Himmler et al. designed new ionic liquids through isolating an ionic liquid cation in BPED [53]. ED has been used by Haerens et al. in order to produce low concentrations of the ionic liquid choline dicyanamide from salt solutions [40].

Containing big charged groups, ILs are capable of having specific interactions with ions. In this work, we synthesized two ionic liquids, [VBMIM][TF$_2$N] and [P888VB][TF$_2$N], and studied the characterization and performance of the AEM after polymerization of the IL on the surface of the membrane. ILs containing [TF$_2$N]$^-$ show low water solubility and are suitable options when working with aqueous solutions. The hypothesis is that by polymerizing the ionic liquid on the surface of the AEM, the electrostatic repulsion between sulfate anions and the negative surface potential made by [TF$_2$N], is greater than that between chloride anions and the negative surface potential according to Coulomb’s law, which means that multivalent anions are less likely to transport onto the membrane surface than monovalent anions. This can be observed by a change in the transport number of sulfate ions relative to chloride ions when comparing neat and PIL coated AEMs results.
CHAPTER III
EXPERIMENTAL

Materials and Instrumentation

Experiments were conducted using a PCCell 64-4 (PCCell GmbH Co, Heusweiler, Germany) for ED experiments. The characteristics of the membranes used in this study are listed in Table 2. The Neosepta ASE (ASTOM Corporation, Tokyo, Japan) membrane is a standard AEM with no specific selectivity towards monovalent anions. All starting materials for ionic liquid synthesis have been purchased from Sigma-Aldrich Company except Acetonitrile. It was purchased from VWR Company. Sodium chloride (MW 58.44 g/mole, VWR International, LLC, USA) and sodium sulfate (MW 142.04 g/mole, VWR International, LLC, USA) were utilized for most of the membrane properties measurements. Nuclear Magnetic Resonance (NMR) spectra was performed using a 400 MHz Bruker Avance III HDTM NMR spectrometer. Fourier- transform infrared (FTIR) spectra were obtained using an Agilent Technologies Cary 630 FTIR spectrometer in attenuated total reflectance (ATR) mode. Surface characterization of both pristine and coated membranes was examined using SEM (JSM-5600 Scanning Electron Microscope, JEOL, USA Inc. Peabody, MS). Atomic Force Microscopy (AFM) was performed using a Bruker NanoScope V microscope. Contact Angle was measured using a Biolin Scientific Attention Theta instrument.
Table 3-1. Detailed Specification of Ion Exchange membranes

<table>
<thead>
<tr>
<th>Title</th>
<th>Anion Exchange Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard grade ASE</td>
</tr>
<tr>
<td>Type</td>
<td>Strong Base (Cl type)</td>
</tr>
<tr>
<td>Characteristics</td>
<td>High mechanical strength</td>
</tr>
<tr>
<td>Electric resistance (Ω.cm²)</td>
<td>2.6</td>
</tr>
<tr>
<td>Burst strength (MPa)</td>
<td>≥ 0.35</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>0.15</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>≤60</td>
</tr>
<tr>
<td>PH</td>
<td>0-14</td>
</tr>
</tbody>
</table>

**Ionic Liquids Synthesis**

**1-methyl-(4-vinylbenzyl) imidazolium bis(trifluoromethylsulfonyl)imide**

4-vinylbenzyle Chloride (17.16 mL) was added drop wise to a stirred solution of 1-methylimidazole (9.708 mL) in acetonitrile (30 mL) at 70 °C under an atmosphere of nitrogen. The reaction mixture was stirred at 70 °C for 24h. The resulting mixture was washed several times with diethyl ether. Rotary evaporation of the diethyl ether followed by evaporation in vacuum provided the clear liquid. The [VBMIM][TF2N] monomers were synthesized via anion-exchange of [VBMIM][Cl]. Lithium bis(trifluoromethylsulfonyl)imide was added to a solution of [VBMIM][Cl] in water (150 mL), and the resulting mixture was stirred for 48h at room temperature. Dichloromethane (150 mL) was then added, and the dichloromethane layer was washed with water (150 mL) until no halide was detected by the silver nitrate test. Rotary evaporation of the dichloromethane layer, followed by evaporation in vacuum, provided the product as a clear liquid.
Figure 3-1. Schematic of the 1-methyl-(4-vinylbenzyl) imidazolium bis(trifluoromethylsulfonyl)imide synthesis

**Trioctyl-3-(4-vinylbenzyl) phosphonium bis(trifluoromethylsulfonyl)imide**

4-vinylbenzyle Chloride (7.6 mL) was added drop wise to a stirred solution of Trioctylphosphine (24 mL) in acetonitrile (30 mL) at 70 °C under an atmosphere of nitrogen. The reaction mixture was stirred at 70 °C for 24h. The resulting mixture was washed several times with diethyl ether. Rotary evaporation of the diethyl ether followed by evaporation in vacuum provided the clear liquid. The [P888VB][TF2N] monomers were synthesized via anion-exchange of [P888VB][Cl]. Lithium bis(trifluoromethylsulfonyl)imide was added to a solution of [VBMIM][Cl] in water (150 mL), and the resulting mixture was stirred for 48h at room temperature. Dichloromethane (150 mL) was then added, and the dichloromethane layer was washed with water (150 mL) until no halide was detected by the silver nitrate test. Rotary evaporation of the dichloromethane layer, followed by evaporation in vacuum, provided the product as a clear liquid.
**Surface Modification of AEMs**

PILs coated AEMs were prepared via both solvent casting and sandwiching using the following general procedures: the [X][Tf2N] (X indicates either [VBMIM] or [P888VB]) monomers and 1 wt% 2-hydroxy-2-methylpropiophenone (radical photo-initiator) were combined and vortexed for 1 min. The mixture was then casted onto the AEM on a quartz plate coated with Rain-X and then sandwiched with a second quartz plate. The membrane was then irradiated with 365 nm light for 4 h. In solvent casting procedure acetonitrile was added to the mixture, coated the membrane and then left under the hood for 12h. The membrane was then irradiated with 365 nm light for 8h. Only one side of the membrane surface was modified and the thickness was measured using an electronic digital micrometer (Midland Scientific Inc, USA). Then the membranes were soaked in DI water for 24h before utilization in ED system.

**Electrochemical Properties Characterizations**

**Transport numbers**

The monovalent-ion selectivity of the AEMs is investigated by the transport number ratio between monovalent chloride and divalent sulfate ions. To get the bulk transport numbers, the
ionic fluxes of Cl\(^-\) and SO\(_4\)\(^{2-}\) through the membranes with time elapsed were measured in a four-cell testing module including two CEMs and one AEM. A mixture of 0.05 M NaCl and 0.05 M Na\(_2\)SO\(_4\) was used as the testing solution, and 0.2 M Na\(_2\)SO\(_4\) was used as the solution for electrodes. The voltage applied was held constant at 5 volt with the effective membrane area of 64 cm\(^2\). 2 mL of testing solutions were taken from compartments every 30 min. The concentration of Cl\(^-\) was analyzed by a Thermo Scientific Chloride Electrode. The concentration of SO\(_4\)\(^{2-}\) was calculated from conductivity versus concentration plot and conductivity was measured using a Thermo Fisher ion conductive probe. The corresponding ion flux of Cl\(^-\) and SO\(_4\)\(^{2-}\) passing through the membrane (\(J_i\)) is calculated based on the ions concentration change with time (d\(C_i\)/dt) in the dilute compartment as follows:

\[
J_i = \frac{V \frac{dC_i}{dt}}{A} \quad (3-1)
\]

where \(V\) is the volume of the circulated testing solution (cm\(^3\)) and \(A\) is the effective membrane area (cm\(^2\)). To evaluate the improvement of monovalent-ion selectivity of the membranes after modification, the transport number ratio between Cl\(^-\) and SO\(_4\)\(^{2-}\) was determined based on Eq.(3-2)

\[
P_{\text{Cl}^- \text{SO}_4^{2-}} = \frac{t_{\text{Cl}^-} / C_{\text{Cl}^-} - t_{\text{SO}_4^{2-}} / C_{\text{SO}_4^{2-}}}{t_{\text{Cl}^-} / C_{\text{Cl}^-} - t_{\text{SO}_4^{2-}} / C_{\text{SO}_4^{2-}}} \quad (3-2)
\]

where \(t_{\text{Cl}^-}\) and \(t_{\text{SO}_4^{2-}}\) are transport numbers of Cl\(^-\) and SO\(_4\)\(^{2-}\) ions, respectively; \(C_{\text{Cl}^-}\) and \(C_{\text{SO}_4^{2-}}\) are the average concentrations of Cl\(^-\) and SO\(_4\)\(^{2-}\) ions in the dilute solution, respectively. The transport number of ion (i), \(t_i\) is defined by Eq. (3-3),

\[
t_i = \frac{J_i}{\sum J_s} \quad (3-3)
\]
where $\sum J_s$ denotes the total ion flux through the membrane. The flux used in Eq. (3-3) is the absolute value. The transport of cations i.e. $\text{Na}^+$ was not considered in the present work.

**Limiting Current Density and Resistance of the Membranes**

To investigate limiting current density of the membranes, chronopotentiometry was conducted with a 0.17 M ($10$ g per L) $\text{NaCl}$ solution under direct current conditions to yield current-voltage (I-V) curve in the same four- compartment modules. A 0.2 M ($30$ g per L) $\text{Na}_2\text{SO}_4$ solution was used as the electrolyte. The solutions in each cell were circulated individually by a Masterflex L/S peristaltic pump (Cole-Parmar Instrument Company, USA). The applied voltage was raised step by step every 10s (i.e. 0, 0.5, 1,…, 10 V) and was provided by a power supply (Model GPS-3030DD DC power supply, GW Instek, Fotronic Corporation). The I-V curve was plotted by current density versus voltage across the membrane. Electrochemical impedance spectroscopy (EIS) measurement was applied to analyze the membrane conductivity using a Princeton Applied Research potentiostat/galvanostat model 263A.
CHAPTER IV
RESULTS AND DISCUSSION

Fourier-Transform Infrared (FTIR) Spectroscopy

Figures 4-1 show selected IR spectra for the PIL/IL prepared from radical photopolymerization of both imidazolium and phosphonium-based IL monomers. For [P888VB][TF2N] the C=C stretch at 828-926 cm\(^{-1}\) was used as the vinyl peak of interest and the integral of the area between 1142-1206 cm\(^{-1}\) was used as the reference peak. Integration of the IL and neat curable PIL signals was used to estimate the C=C bond conversion using Eq. (4-1) shown below. For [VBMIM][TF2N] the C=C stretch as 900-930 cm\(^{-1}\) was used as the vinyl peak of interest and the integral of the area between 1000-1100 cm\(^{-1}\) was used as the reference peak. The conversion percent for imidazolium and phosphonium-based PIL was 68 and 75 percent, respectively.

\[
\text{Polymerization Degree} = \frac{\left(\frac{\text{Area vinyl peak}}{\text{Area reference peak}}\right)_{\text{IL}}}{\left(\frac{\text{Area vinyl peak}}{\text{Area reference peak}}\right)_{\text{PIL}}} \quad (4-1)
\]
Membrane surface Characterization

As mentioned in previous chapters, [VBMIM][TF2N] coated ASE membrane did not have mechanical stability in water. After soaking the coated membrane in DI water for 24 hours, the coating layer started to delaminate from the membrane surface. Fig. 4-2 indicates the delamination of the coating layer after utilization in the ED system. The next chosen IL was [P888VB][TF2N]. Fig. 4-3 shows the surface SEM images of the pristine and [P888VB][TF2N] coated ASE membrane. Incomplete membrane coating has been occurring through the knife casting technique using 2 quartz plates. Then, in order to achieve a thinner PIL layer on the membrane, solvent casting technique has been used. The detectable thickness of coated films ranged from 8 µm to 35 µm. This inconsistency in the membrane thickness might be caused by the high compression of the 2 plates or the membrane surface tension. ASE and ILs have a yellow color, which makes the defects observation difficult. Fig. 4-4 implies the non-uniform coating layer through AFM images.

Figure 4-1. Overlay of the IR spectra of IL and PIL. The change in C=C stretch 900-930 cm⁻¹ in polymer indicates the degree of polymerization which is 68% for [VBMIM][TF2N] and 75% for [P888VB][TF2N].
**Figure 4-2.** Delamination of [VBMIM][TF2N] PIL from ASE membrane surface.

**Figure 4-3.** SEM images of the a) pristine and b) [P888VB][TF2N] coated membranes

**Figure 4-4.** AFM images showing non-uniform coated layer of the [P888VB][TF2N] on the AEM surface.
To determine the resultant changes on hydrophilic property of the membrane after surface modification, water contact angle measurements were conducted for both [VBMIM][TF2N] and [P888VB][TF2N] coated AEMs. Due to the hydrophobic nature of the [TF2N], it was expected to see an increase in the hydrophobicity of the AEMs. However, this can be justified as long as the membrane is still hydrophilic. Table 3 shows the contact angle of the pristine and coated membranes. The [P888VB][TF2N] coated AEM is more hydrophobic compare to [VBMIM][TF2N] coated AEM, which is resulted from hydrophobicity of the both cation and anion in IL [71].

**Table 4-1. Contact Angle measurements of the membranes**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine AEM</td>
<td>19.2 ± 1</td>
</tr>
<tr>
<td>[VBMIM][TF2N] Coated AEM</td>
<td>66.2 ± 1</td>
</tr>
<tr>
<td>[P888VB][TF2N]</td>
<td>88.5 ± 1</td>
</tr>
</tbody>
</table>

**Electrochemical Properties Characterization**

Electrical impedance spectroscopy (EIS) was conducted to investigate the material resistance. The applied voltage during testing was 10 mV with frequency range between 1 MHz and 1 Hz. The material resistance was obtained from locating the x-intercept of the generated Nyquist plot [72][73]. The ion conductivity was then calculated using Eq. (4-2) below,

$$\sigma = \frac{L}{RA}$$ (4-2)

where L is the thickness of the membrane, R is the membrane resistance and A is the membrane surface area. The conductivity of the modified membrane with thickness of 20 µm has been
reduced by 43%. However, providing thinner coating layer might improve the conductivity. Monovalent-ion selectivity of the membranes was investigated based on transport number ratio, which was calculated from Eq. (9). The larger \( \frac{P_{Cl}}{P_{SO_4^{2-}}} \) value is indicating the better monovalent ion selectivity [58]. As listed in Table 4, the modified AEMs have decreased sulfate flux and larger \( \frac{P_{Cl}}{P_{SO_4^{2-}}} \) values has been obtained. Since the repulsive force produced by a negatively charged surface against sulfate is stronger than that against Cl\(^-\) the negatively charged coated layers on the surface rejected SO\(_4^{2-}\) more intensively than Cl\(^-\) [21]. The impacts on the apparent perm-selectivity and Cl\(^-\) flux suggest that the negatively charged surface introduced by PIL exerted a weak repulsive force on Cl\(^-\). Also, perm-selectivity of the membranes have been obtained from the slope of the concentration versus time plot. Results indicates a 23% improve in the perm-selectivity of the coated membrane compare to the pristine membrane.

**Table 4-2.** Transport number ratios for the membranes

<table>
<thead>
<tr>
<th>Membranes</th>
<th>( J_{Cl^-} ) ( \times 10^{-6} ) mole/cm(^2)min</th>
<th>( J_{SO_4^{2-}} ) ( \times 10^{-6} ) mole/cm(^2)min</th>
<th>( t_{Cl^-} )</th>
<th>( t_{SO_4^{2-}} )</th>
<th>( P_{Cl^{-}SO_4^{2-}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine ASE</td>
<td>1.83</td>
<td>2.63</td>
<td>0.44</td>
<td>0.55</td>
<td>1.29</td>
</tr>
<tr>
<td>[P888VB][TF2N] coated ASE</td>
<td>2.48</td>
<td>2.55</td>
<td>0.49</td>
<td>0.50</td>
<td>1.61</td>
</tr>
</tbody>
</table>

![Average Monovalent Selectivity](image1)

![Average Transport Number](image2)
current efficiency of the pristine and modified membrane was calculated based on Eq. (4-3) below,

$$\eta = \frac{ZVF(C_i - C_f)}{NI_t}$$  \hspace{1cm} \text{Eq.(4-3)}$$

where $z$ is the ion valence, $V$ is the volume of the solution in diluate, $F$ is the Faraday’s constant, $C_i$ and $C_f$ are initial and finial concentration, respectively, $N$ is the number of stacks in ED system, $I$ is the average current density and $t$ is the time of experiment. The current efficiency of the modified membrane was about 30% higher than the pristine membrane. This might be due to the faster ion depletion and the reduction in the time of experiment. Figure 16 indicates the the conductivity reduction in diluate compartment versus time. Figure 16a shows the delamination of Imidazolium coating due to solubility of water within cured film. Phosphonium coating is stable and working properly. However, it is not as efficient as neat membrane to reduce the concentration of ion and reduce the conductivity. Figure 16b indicates faster conductivity reduction in coated membrane compared to pristine membrane. This is because of thinner coating layers.

\textbf{Figure 4-5.} Comparing a) average selectivity, b) average transport number and c) average current efficiency of the pristine and modified membrane. The average monovalent selectivity has been increased by 23%, average transport number by 24% and average current efficiency by 30%. The error bar is showing the standard deviation error.
Figure 4-6. Conductivity reduction over time in ED. a) Imidazolium and phosphonium coated membrane (20 µm) performance compared to pristine membrane b) Phosphonium coated (15 µm) performance compared to pristine membrane.
SUMMARY AND CONCLUSION

In this work, the surface of the standard AEM (ASE) was modified with PILs. [VBMIM][TF2N] and [P888VB][TF2N] were synthesized and coated on the AEMs. The surface characteristics and electrochemical properties of the membranes were determined. After surface modification, [VBMIM][TF2N] coated membranes were delaminated immediately after using in ED system due to solubility of water within cured film. However, [P888VB][TF2N] modified membranes indicated a slight improvement in monovalent-anion selectivity. This enhancement might be attributed to the strong negatively charged surface potential achieved by the PIL layer. The coated membrane with [P888VB][TF2N] PIL showed monovalent-anion selectivity comparable to that of the commercial ASE membranes. Also, there has been about 30% increase in current efficiency. Although the preliminary results suggest an improvement in the current efficiency and monovalent selectivity of the modified ASE membrane, more experiments need to be performed to prove the concept. On the other hand, the spacers stick to the modified membranes which clogged the water pathways on the spacer and after each trial cleaning procedure is needed. This is happening due to the sticky nature of the PILs and might be improved by a thinner PIL layer or coating a very thin layer of a non-sticky material on the PIL layer. It can also be related to the polymerization degree which might be enhanced by increasing the time of radiation or the amount of initiator needed for the polymerization reaction.
FUTURE WORK

Although preliminary data shows an improvement in the monovalent selectivity of the modified membranes in ED system, more experiments are needed to perform and prove the concept. Other coating procedures and materials such as, spin coating might be considered. More ILs such as, [HMIM][TF2N] and [EMIM][TF2N] might be tried to see if higher monovalent selectivity can be achieved. In order to achieve a thin, uniform coating layer on the membrane surface the surface tension of the pristine AEM might be studied. Also, applying more PIL layers on the membrane surface might be considered.
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[56] Y. Zhang, S. Paepen, L. Pinoy, B. Meesschaert, and B. Van Der Bruggen, “Selectrodialysis: Fractionation of divalent ions from monovalent ions in a novel


APPENDIX
Calculation of Sulfate Concentration:

Chloride concentration was calculated by a chloride probe. To calculate the sulfate concentration, the conductivity versus concentration data for both chloride and sulfate is needed. After measuring the concentration of the chloride ion by chloride probe we measured the total conductivity of the diluate compartment by a conductive probe. Sodium chloride conductivity was found from the conductivity versus concentration plot. This plot can be obtained by measuring the conductivity of the sodium chloride in the experiment concentration range. Then sodium sulfate conductivity was obtained by subtracting sodium chloride conductivity from total conductivity. The sulfate concentration was then calculated based on the sodium sulfate conductivity versus concentration plot.

![Graphs showing conductivity versus concentration](image)

Conductivity versus concentration. a) NaCl  b) Na₂SO₄
Monovalent Selectivity Results:

<table>
<thead>
<tr>
<th></th>
<th>Pristine Membrane</th>
<th>Modified membrane</th>
<th>Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average Transport Number Ratio</strong></td>
<td>1.29</td>
<td>1.61</td>
<td>24%</td>
</tr>
<tr>
<td>St Err</td>
<td>0.25</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td><strong>Average Selectivity</strong></td>
<td>0.85</td>
<td>1.05</td>
<td>23%</td>
</tr>
<tr>
<td>St Err</td>
<td>0.155</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td><strong>Current Efficiency</strong></td>
<td>0.458</td>
<td>0.60</td>
<td>30%</td>
</tr>
<tr>
<td>St Err</td>
<td>0.043</td>
<td>0.12</td>
<td></td>
</tr>
</tbody>
</table>
VITA
Saloumeh Kolahchyan

Education
2017 - 2018  M.S. in Chemical Engineering, University of Mississippi, MS, USA
2009 - 2014  B.S. in Polymer Engineering, Tehran’s Science and Research University, Tehran, Iran

Academic Appointments
2017-Present Research and Teaching Assistant. Department of Chemical Engineering, University of Mississippi, Oxford, MS

• Research Project: Design and synthesize of Imidazolium and Phosphonium-based ionic liquid composite thin-films for selective ion separations in electrodialysis for water treatment applications.

• TA Courses: Process Fluid Dynamics and Heat Transfer-Plant Design

Work Experience

• Did research on raw material formulation and conducted laboratory tests on roofing membranes.

• Analyzed tests results for cost saving developments.
Sep 2014-Dec 2016  **R&D Polymer Engineer.** Shahin Plastic Company, Tehran, Iran.

- Did research on raw material formulations and new products designs with PVC and PU
- Troubleshot and resolved production-related issues in PVC plant (Spread coating, Calendar, Extruder)
- Developed a novel 3 layer PVC foam for sport floorings
- Supervised product testing and quality control


- Provided technical support to new application.
- Recommended new technologies and materials to increase productivity of the plant.

Jun 2013-Sep 2013  **Polymer Engineering Intern.** Shahin Plastic Company, Tehran, Iran.

- Provided technical support to process optimization

**Skills**

**Instruments**

- Spread Coating Machine
- Polymer Calendaring Machine
- Plastic Extruders
- Electrodialysis System
- Contact Angle
- Fourier Transform Infrared (FTIR)
- Tensile Strength Test Instrument
• Nuclear Magnetic Resonance (NMR)
• Scanning Electron Microscope (SEM)
• Atomic Force Microscopic (AFM)
• Differential Scanning Calorimetry (DSC)
• Thermal Gravimetric Analysis (TGA)

Programming
• Python, Mathcad, Microsoft Office, State-ease

Conference Presentations


**Publication**

  DOI: [10.1016/j.cej.2018.08.086](https://doi.org/10.1016/j.cej.2018.08.086)

**Honors and Activities**

- Won the First Prize in the STEM poster session at the 8th Annual Research Symposium organized by the UM Graduate Student Council, University of Mississippi, Oxford, MS, USA. March 21-(2018).
- Scholarship for graduate studies, University of Mississippi, Oxford, Mississippi, USA (Jan 2017-Present).
- Treasurer of the Iranian Student Association of the University of Mississippi (Apr 2017-Apr 2018).
- The President of Polymer Engineering Association, Tehran’s Science and Research University, (2011-2014).
- Scored 100/100 in Chemistry in University Entrance Exam.
- High GPA in High School Diploma in Physics and Mathematics. GPA: 4/4