REVERSE-SELECTIVE BEHAVIOR OF THE
ROOM TEMPERATURE IONIC LIQUID BASED MEMBRANES

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ABSTRACT

This experimental study explore the reverse-selective potential of RTIL based membranes by lowering the solubility of the non-condensing gases like \( \text{N}_2 \) and \( \text{CH}_4 \). It explored reverse-selectivity by measuring the permeance of carbon dioxide, nitrogen, methane, propylene, propane, 1-butene, and butane in supported ionic liquid membranes (SILM). Particular attention was given to the reverse-selective behavior in the propane/methane and propane/nitrogen separations. For this purpose, a series of experiments were conducted in a batch gas permeance system. The permeance of the above-mentioned gases was obtained using polyvinylidene fluoride (PVDF) as the support and \([\text{emim}][\text{Tf}_2\text{N}]\), \([\text{emim}][\text{BF}_4]\), \([\text{emim}][\text{TfO}]\), \([\text{emim}][\text{DCA}]\), \([\text{emim}][\text{SCN}]\), and \([\text{bmim}][\text{NO}_3]\) as immobilized room temperature ionic liquid (RTIL). The results showed that permeance of carbon dioxide was the highest in \([\text{emim}][\text{Tf}_2\text{N}]\), while it was the lowest in \([\text{bmim}][\text{NO}_3]\). Moreover, permeance of the tested gases increased in the following order of anions: \([\text{Tf}_2\text{N}] > [\text{TfO}] > [\text{BF}_4] > [\text{SCN}] > [\text{DCA}] > [\text{NO}_3]\). In addition, the molar volume of the tested RTIL has a positive effect on the permeance of the tested gases. However, for the viscosity less than 30 cP, an increase in the viscosity of the tested RTILs leads to an increase in the permeance. In contrast, for the viscosity larger than 30 cP, the permeance decreases with an escalation in the viscosity. Furthermore, the permeance of \( \text{CH}_4 \) and \( \text{N}_2 \) was investigated in terms of hydrogen bond accepting ability of the RTIL, as an indication of the gas/ionic liquid solution nonideality. The results showed that an increase in the nonideality of the solution leads to a decrease in the permeance of \( \text{CH}_4 \) and \( \text{N}_2 \), which is in agreement with results reported by Carvalho for \( \text{CH}_4 \) [1].
Moreover, correlations were derived for the prediction of the permeance of CO\textsubscript{2}, N\textsubscript{2}, and CH\textsubscript{4} as well as for the prediction of CO\textsubscript{2}/N\textsubscript{2}, CO\textsubscript{2}/CH\textsubscript{4}, C\textsubscript{3}H\textsubscript{8}/CH\textsubscript{4}, and C\textsubscript{3}H\textsubscript{8}/N\textsubscript{2} separations. The R-squared and mean relative error were determined for the derived correlations showing good conformity with the experimental data. In addition, the reverse-selective behavior of C\textsubscript{3}H\textsubscript{8}/CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8}/N\textsubscript{2} separations was investigated using prepared SILMs. The results showed that reverse-selectivity decreases with an increase in the viscosity of the RTILs which is may be due to a shift in the transmission mechanism from solubility to diffusion.

Keywords: RTIL, SILM, permeance, selectivity, reverse-selectivity, solubility, diffusivity.
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CHAPTER 1

INTRODUCTION

1.1. Hypothesis

The purpose herein is to explore the reverse-selective potential of RTIL based membranes by lowering the solubility of the non-condensing gases like N$_2$ and CH$_4$. This solubility is one characteristic of reverse-selective membranes affecting membrane selectivity. Figure 1.1 shows the difference between size-selective and reverse-selective membranes. To our best knowledge, the reverse-selective behavior of the RTIL based membranes has not been explored previously.

The C$_3$H$_8$/N$_2$ separation is a prime indicator for the reverse selectivity [2]. Therefore, the main objective of this work is to examine the reverse-selective potential of RTIL based membranes for C$_x$H$_y$/CH$_4$ separations as well as C$_3$H$_8$/N$_2$ separation in order to prove, or disprove, reverse-selectivity. One of the potential applications of the reverse-selective membranes discussed by Freeman and Pinnau [3] is the separation of larger molecules like C$_3$H$_8$ from CH$_4$.

Furthermore, another objective of this study is to increase the CO$_2$/N$_2$ separation selectivity by exploring the reverse-selective potential of RTIL based membranes. However, improving CO$_2$/N$_2$ selectivity by reducing the flux of N$_2$ is insufficient to prove that we have created reverse-selective membranes; because of their molecule size. Since the kinetic diameter of CO$_2$ (3.3 Å) is less than that for N$_2$ (3.64 Å), and CH$_4$ (3.8 Å), the successful separation of CO$_2$/N$_2$ and CO$_2$/CH$_4$
is not sufficient to prove reverse-selectivity, because the separation can be due to size-selectivity rather than reverse-selectivity [5].

Moreover, for the CO$_2$/N$_2$ separation using membranes, maximizing the selectivity by minimizing the solubility of the N$_2$ is also a novel component. There is only one example in literature for increasing selectivity by decreasing the solubility of the slower gas corresponding to the absorption separation of CO$_2$/CH$_4$ and H$_2$S/CH$_4$ [1].
1.2. Relevant Membrane Background

Membranes have emerged as viable gas-separation systems due to their lower energy consumption, higher reliability, and lower initial cost requirements [6,7]. Membrane technology for separation of gas mixtures has progressed considerably over the past decades [8]. Gas separation using membranes for industrial applications are mainly for the separation of simple gases; such as, H₂, O₂, N₂, CH₄, CO₂, or vapor recovery from gas mixtures [9]. Efforts to improve membrane performance have been directed at the membrane material synthesis and fabrication methods. Although most polymeric membranes are low-priced, easy to make, and easy to scale up, their gas separation performance does not always meet the required separation and efficiency [8]. One method to intensify permeability through solution/diffusion membranes is the fabrication of membranes in a liquid state instead of solid state. Higher liquid phase diffusivities, as well as higher solubilities in the liquid phase, allow substantial improvements to be realized in the liquid-state membrane permeability over most solid-state counterparts [10].

Room temperature ionic liquids (RTIL) are salts that are liquid at room temperature [11]. RTILs have drawn great attention in recent years for the fabrication of novel and effective materials for special tasks such as carbon dioxide capture [12]. RTILs are environmental friendly solvents with special properties such as negligible vapor pressure, chemical and thermal stability, recyclability, and non-flammability [13]. Many investigations have shown that CO₂ is highly soluble in most RTILs when expressed in mole/mole units. CO₂ solubility is affected by both anion and cation components of the RTIL [14]. The integration of ionic liquids and membranes is predicted to play an important role in providing cost-effective and energy efficient CO₂ separation technologies to replace traditional methods [15]. Supported ionic liquid membranes (SILM) are
porous membranes in which ionic liquid is immobilized inside the pores of a polymeric or inorganic support [16,17].

1.3. Permeability and selectivity for CO$_2$/N$_2$, CO$_2$/CH$_4$, and C$_3$H$_8$/CH$_4$ separations

1.3.1. Supported ionic liquid membranes

The potential applications of SILMs in gas separations reported in literature are CO$_2$ separation from permanent gases, natural gas upgrading, and gas dehumidification [14,18–25]. Uchytil et al. [14] collected the names, abbreviations, and applications of the regularly used RTILs in membrane separation processes for gas and vapor separation. The permeability and selectivity data are available for commonly studied RTILs in different supports. Until now, the highest reported CO$_2$ permeability for SILMs with RTILs was around 2000 Barrers with a CO$_2$/N$_2$ selectivity of about 40 at room temperature [26]. However, Dai et al. [26] reported that selectivity in the SILMs with RTILs can be higher than 60 with permeabilities larger than 1000 Barrers.

Scovazzo [19–21] determined and summarized pure gas permeability of CO$_2$, N$_2$, CH$_4$, and O$_2$ and determined the corresponding ideal selectivities through a porous hydrophilic glass-fiber support with different immobilized RTILs. Close et al. determined CO$_2$ and N$_2$ permeabilities using alumina based SILM for different RTILs [22]. In another research, Grunauer et al. investigated CO$_2$ and N$_2$ permeabilities and selectivities for isoporous membrane using [emim][DCA], [emim][Tf$_2$N], and [bmim][Ac] as liquid carrier [23]. Also, reviews by Krull et al. [24] and Lozano et al. [25] provides detailed information about the development of novel liquid membranes and SILMs for gas and vapor separations. After evaluating the data and representing
the data obtained in a Robeson-plot, the authors concluded that SILMs are competitive or even better in comparison to other membrane materials [19–22].

To our best knowledge, there are no reported data or work in literature for the C₃H₈/CH₄ separation using SILMs with RTILs. The C₃H₈/CH₄ separation using these membranes is a novel concept, whose investigation is reported below.

1.3.2. Polymers

Separation of higher hydrocarbons such as propane and butane is a typical stage in the natural gas treatment. Natural gas is treated to eliminate water, CO₂, sulfur components, mercury vapors, and higher hydrocarbons [27]. Usually, the natural gas treatment and removal of higher hydrocarbons is done by pressure distillation or cooling the condensable components [27,28]. The separation of higher hydrocarbons using membranes is an interesting alternative and economic analyses show feasibility with short payback periods [27,29]. Glassy polymers such as polyacetylenes, functionalized polysulfones, and thermally-rearranged cardocopolybenzoxazoles show excellent gas transport properties and reverse selectivity for the separation of condensable hydrocarbons or CO₂ from permanent gases [4]. The favored separation of condensable hydrocarbons from permanent gases is done by competitive sorption. Therefore, the recent studies have mainly focused on the reverse selectivity in new glassy materials and some reverse-selective glassy nanocomposites [4].

Arruebo et al. [27] determined permeability and selectivity for C₂+ hydrocarbons from CH₄ using silicalite membranes. Their reported selectivity for the C₃H₈ and CH₄ separation was approximately 6 at 1 bar and 28°C [27]. In a similar work, Javaid et al. [2] examined Membralox® membranes for the C₃H₈/CH₄ and C₃H₈/N₂ separations and determined a selectivity of less than 2
for both gases. In another research, Pinnau et al. [30] used rubbery polydimethylsiloxane for hydrocarbon/CH$_4$ and hydrocarbon/hydrogen separations. Pinnau’s group [30] reported similar results to Arruebo’s group [27]. Their calculated selectivity for the C$_3$H$_8$/CH$_4$ separation was around 6 at 35 $^\circ$C. Khosravi et al. [29] has summarized the permeability and selectivity data for the C$_2$H$_6$/CH$_4$ and C$_3$H$_8$/CH$_4$ separations.

The separation of CO$_2$ from N$_2$ using polymeric membranes has extensively been investigated [28,31–34]. Current industrial applications of gas separation using membranes are CO$_2$ capture from natural gas and hydrogen purification in refinery operations [31]. Dense film polymeric membranes separate gases by the solution-diffusion mechanism and their performance are usually limited by a tradeoff between permeability and selectivity [31,32]. Present efforts to develop new membranes are mainly focused on the design of new high-performance polymers or the design of mixed-matrix systems including a molecular sieve discontinuous phase dispersed in a continuous polymer host matrix [31].

1.4. Selectivities of RTIL-based membranes

Reverse-selectivity in RTIL-membranes comes from their solubility selectivity. The RTIL-membrane selectivities are dominated by solubility selectivity; therefore, characterization of reverse-selectivity in RTIL-membranes dictates a review of solubility theories. Regular solution theory is widely used to determine the solubility of a gas in RTILs. Furthermore, there is a recent theory which relates the solubility of a gas in RTILs to the polarity of RTILs.
1.4.1. Regular solution: Selectivity as a function of RTIL molar volume

The main assumption for the regular solution theory (RST) is that the excess entropy of mixing disappears and solute/solvent interactions are negligible. The columbic forces of the RTIL solvent/solvent interactions are much greater than all of the other interactions. Therefore, the assumption of negligible solute/solvent interactions is reasonable for RTIL solutions [35].

RST states that gas solubilities or Henry’s Law Constants can be obtained from solubility parameters. The following equation shows the relationship between Henry’s constant and solubility parameter [36,37]:

\[
\ln(H_{2,1}(atm)) = a + b(\delta_1 - \delta_2)^2
\]  

(1.1)

where \(H_{2,1}(atm)\) is the Henry’s constant in which 1 is RTIL and 2 is gas, \(\delta\) is the solubility parameter, and \(a\) and \(b\) are empirically determined constants for a specific temperature and pressure.

To obtain the solubility behavior of gases in different RTILs, the solubility parameter [36–39] is predicted using the vaporization energy. The accurate determination of vaporization energy for RTILs is difficult, because RTILs are nonvolatile; however, the modified Kapustinskii equation can calculate the vaporization energy in the following method first proposed by Camper et al [38,39]:

\[
E_{vap} = 2.56 \times 10^6 \left( \frac{J}{mol} \right) \left( \frac{z_1 z_2 (cm^3/mol)^{1/3}}{V_{RTIL}^{1/3}} \right) \left( 1 - \frac{0.367 (cm^3/mol)^{1/3}}{V_{RTIL}^{1/3}} \right)
\]  

(1.2)
where $E_{\text{vap}}$ is the vaporization energy from saturated liquid to the ideal gas state, $V_{\text{RTIL}}$ is the liquid molar volume, and $z_1$ and $z_2$ are the cation and anion charges, respectively.

The solubility parameter for a molecule is expressed as the square root of its vaporization energy density [36–39]:

$$
\delta = \left( \frac{E_{\text{vap}}}{V_{\text{RTIL}}} \right)^{1/2} \tag{1.3}
$$

Equations 1.2 and 1.3 are combined to estimate the solubility parameter of the RTILs [36–39].

$$
\delta = \left( \frac{E_{\text{vap}}}{V_{\text{RTIL}}} \right)^{1/2} = \left( 2.56 \times 10^6 \left( \frac{J}{\text{mol}} \right) \left( \frac{z_1 z_2 \text{ cm}^3}{\text{mol} \cdot \text{V}_{\text{RTIL}}^3} \right)^{1/3} \left( 1 - \frac{0.367 \text{ cm}^3}{\text{V}_{\text{RTIL}}^{1/3}} \right) \right)^{1/2} \tag{1.4}
$$

Eq. 1.4 shows that the solubility parameter is inversely proportional to the RTIL molar volume [36–39].

$$
\delta \propto \left( \frac{1}{V_{\text{RTIL}}^{3/4}} \right)^{1/2} \tag{1.5}
$$

Modified versions of the RST model lump the solubility parameter of the gas into the constant in Eq. 1.1 [37]:

$$\ln \left( H_{2,1} (\text{atm}) \right) = \alpha + \beta (\delta_4)^2 \tag{1.6}$$

The combination of Eqs. 1.5 and 1.6 yield to a model, in which the molar volume of the RTIL is the only required parameter to calculate the solubility parameter[37,40]:
\[ \ln(H_{2,1}(atm)) = \alpha + \left( \frac{\beta^*}{V_{RTIL}^{1/3}} \right) \]  

(1.7)

where \( \alpha, \beta, \) and \( \beta^* \) are experimentally obtained constants related to the temperature and gas species.

In the above equations, only molar volume of the RTIL is needed to obtain solubility and selectivity. The selection of an RTIL with desired properties is done using the regular solution based models. In addition, the prediction of the RTIL performance is possible in the case where no experimental data exists [37,40].

Scovazzo [19] determined correlations to estimate selectivity for \( \text{CO}_2/\text{N}_2 \) and \( \text{CO}_2/\text{CH}_4 \) separations using a wide range of RTILs. He found that separation selectivity for \( \text{CO}_2/\text{N}_2 \) and \( \text{CO}_2/\text{CH}_4 \) mixtures is a weak function of viscosity and it principally depends on the RTIL molar volume [19]:

\[ \alpha(\text{CO}_2/\text{N}_2) = \frac{28.95}{(V_{RTIL})^{0.865}} \]  

(1.8)

\[ \alpha(\text{CO}_2/\text{CH}_4) = \frac{54.83}{(V_{RTIL})^{1.09}} \]  

(1.9)

where \( \alpha \) is the selectivity

1.4.2. Permeability: Permeability as a function of RTIL viscosity

Permeability of a gas in an RTIL mainly depends on the molar volume and viscosity of the RTIL [19]. Scovazzo [19] summarized the permeabilities of permanent gases through SILMs made from different RTILs. He also derived two different models for predicting \( \text{CO}_2 \) permeability based on the RTIL molar volume and viscosity. The first model depends only on the viscosity of the RTIL, while the second one depends on both molar volume and viscosity of the RTIL [19]. Based on the data analysis by Scovazzo [19], \( \text{CO}_2 \) permeability mainly depends on the viscosity of RTIL.
On this basis, Scovazzo [19] suggested the use of the first model, which is only dependent on the viscosity.

1.4.3. CO₂ interaction with the RTIL

One commonly reported theory is that CO₂ solubility in most RTILs is dominated by CO₂-anion interactions [41–44]. If this is true then CO₂ solubility in RTILs cannot be modeled using RST as presented in Equations 1.6 through 1.9. The CO₂-anion interaction theory support comes from correlating increases in the CO₂ mole fraction solubilities with changes in the RTIL anions. For example, the highest reported CO₂ solubility is for the anions containing fluoroalkyl groups when the solubility is stated in the mol/mol unit [45]. An increase in the number of fluoroalkyl groups leads to an increase in the CO₂ solubility (mol/mol unit) [45]. A comprehensive study was performed to determine the anion impact on the CO₂ solubility for the [bmim]⁺ based RTILs at 60°C [45]. The following order was determined: tris(trifluoromethylsulfonyl)imide ([methide]⁺) > bis[(trifluoromethyl)sulfonyl]imide ([Tf₂N]⁻) > trifluoromethanesulfonate ([TfO]⁻) ~ hexafluorophosphate ([PF₆]⁻) ~ dicyanamide ([DCA]⁻) > tetrafluoroborate ([BF₄]⁻) > nitrate ([NO₃]⁻) [45]. Furthermore, no positive effect on the CO₂ solubility has been observed due to the strong Lewis acid-base interactions between the RTILs and the dissolved CO₂ [46]. For example, BF₄ and PF₆ anion based RTILs have stronger interactions in comparison with those of Tf₂N anion based RTILs, while the solubility of the CO₂ in the Tf₂N anion based RTILs is larger than that in BF₄ and PF₆ anion based RTILs [46].

However, other researchers have shown that when CO₂ solubilities are reported in mass/mass units the CO₂ solubility correlation with CO₂-anion interactions is weak except for
anion that chemically bind with the CO$_2$ molecule. Recent work by Carvalho et al. [1,47] showed that by eliminating of the molecular weight effect on the CO$_2$ solubility from the analysis and using molalities for the solubilities, instead of molar fractions, the CO$_2$ solubilities in various chemical systems such as RTILs, alkanes, methyl esters, fatty acids, PEGs, and etc. are the same. Therefore, the CO$_2$ solubility in nonvolatile solvents is essentially solvent independent [1,47]. The results of Carvalho’s work [1,47] shows that research into increasing CO$_2$ physical solubility is fruitless. Consequently, higher separation efficiencies may best be achieved by decreasing the slow permeable gas.

1.4.4. Novel theory based on the polarity effect: Hydrogen bond acceptor parameter (β) vs methane permeability

Since the solubility of the CO$_2$ inversely depends on the RTIL molar volume (Regular Solution Theory), the highest reported CO$_2$ permeability in RTILs by Scovazzo [19] may be the maximum possible permeability for CO$_2$ in RTILs. If this is true then the most promising methods to increase the CO$_2$/CH$_4$ selectivity rely on decreasing the CH$_4$ permeability via decreasing CH$_4$ solubility.

The solubility of the CH$_4$ and its deviation from the ideal solution was studied by Carvalho et al. [1]. For all of the RTILs studied by Carvalho coworkers [1], except that of [P$_{66614}$][Tf$_2$N], solutions present strong positive deviation from the ideal solution behavior resulting from the positive deviations in the residual enthalpic term from the ideal solution behavior [1]. The nonideal solubility behavior of the CH$_4$ in the RTILs results from a delicate balance between the solute-solute, solvent-solvent and solute-solvent interactions [1]. The RTILs with large alkyl chains, such
as phosphonium based RTILs, show a weak solute-solvent interactions for the CH$_4$ in the RTILs leading to an almost ideal solution behavior RTILs with smaller cations present a strong unfavorable solute-solvent interactions [1]. According to Carvalho et al. [1], the nonideal solution behavior of CH$_4$ solution in RTILs is due to the RTILs’ polarity. The higher the polarity, the larger the deviation from the ideal solution behavior [1]. Therefore, in order to decrease the solubility of CH$_4$ in the RTILs, the polarity of the solution should be maximized and as a result, the selectivity of the CO$_2$/CH$_4$ separation will be maximized [1].

Unlike CO$_2$, the interactions between CH$_4$ and RTILs controls the solubility of CH$_4$ in the RTILs. The CO$_2$/CH$_4$ separation selectivities can be correlated well using the hydrogen bond acceptor ability of the solvent [1]. As proposed by Camper and Scovazzo [19,38], the selectivity of the CO$_2$/CH$_4$ separation should only depends on the RTIL molar volume; however, using different RTILs with different polarities than those used by the Scovazzo leads to different results and the “Universal Correlation” proposed by the Scovazzo [1,19] fails to predict selectivity. Therefore, in order to determine a better correlation for CO$_2$/CH$_4$ separation selectivity, the nonideality of the solution as well as the solute-solute, solute-solvent, and solvent-solvent interactions should be considered. The nonideality of the solution can be correlated using the polarity of the RTILs, specifically the ability of the RTIL to accept a hydrogen to form a hydrogen bond.

Polarity of a solvent is a well-accepted concept [48,49], defined as the capacity of a solvent to facilitate intermolecular interactions between the solvent and the solute not including those interactions which would result in chemical reactions. On this basis, the common theory of solvatochromism and other solvent-induced spectral properties, though not considered as exact methods for solvent strength measurements, offer a good measures for general solvent, and can
indicate the similarities and differences between RTILs [48]. The specific variation in the long-wavelength absorption band of selected indicator compounds in terms of the solute-solvent intermolecular interactions is explained by the solvatochromic methods [50].

The Kamlet-Taft solvatochromic parameters, are $\alpha$, $\beta$, and $\pi^*$. They are defined as hydrogen bond acidity, hydrogen bond basicity, and dipolarity/polarizability, respectively [48,51]. The $\beta$ value is a measure of the RTIL’s ability to form a hydrogen bond with [52]. We will use the Kamlet-Taft $\beta$-parameter for correlating Carvalho’s polarity effect on CH$_4$ solubility in RTILs. Details on Kamlet-Taft parameters and how to measure them are in Appendix A.
CHAPTER 2

EXPERIMENTAL

2.1. Materials

To achieve the goals of this thesis, we determined pure gas permeabilities through six different RTILs. All of the RTILs have the same cation, [emim], except for [bmim][NO₃] because of the solid state of [emim][NO₃] at room temperature. Moreover, anions were selected according to their hydrogen bond acceptor ability in the range of 0.4-0.75, in order to examine the polarity effect on selectivity as proposed by Carvalho (see section 1.3.3).

The following RTILs were purchased from IOLITEC Inc. (Tuscaloosa, Alabama): 1-Ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([emim][Tf₂N]), 1-ethyl-3-methylimidazolium thiocyanate ([emim][SCN]), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][TfO]), 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]), and 1-butyl-3-methylimidazolium tetrafluoroborate ([emim][BF₄]). Moreover, 1-butyl-3-methylimidazolium nitrate ([bmim][NO₃]) was prepared in the lab. A comprehensive procedure for the synthesis of [bmim][NO₃] can be found in Appendix C. Table 2.1 contains the relevant properties of the RTILs [51,53–70]. The β values depend mostly on the anion of the RTILs rather than the cation. We examined how using these values will affect our calculations and found that an increase in the cation alkyl chain length leads to a change of less than an average of 5% in the β values. Therefore, using estimated β values reported in Table 2.1 is reasonable.
Ultrahigh purity carbon dioxide, nitrogen, methane, and propene were purchased from NexAir (Memphis, Tennessee). Also, propane, 1-butene, and butane were obtained from Conley Gas (LA Porte, Texas). The porous hydrophilic polyvinylidene fluoride (PVDF) (obtained from Millipore Corporation) and porous hydrophobic polytetrafluoroethylene (PTFE) (obtained from Pall Corporation) were used for membrane fabrications as stabilizing supports. The characteristics of the supports used in this work are given in Table 2.2.

Table 2.2. Characteristics of the PVDF and PTFE supports used in this study

<table>
<thead>
<tr>
<th>Polymer support</th>
<th>Diameter (mm)</th>
<th>Thickness (µm)</th>
<th>Porosity</th>
<th>Tortuosity</th>
<th>Nominal pore size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>47</td>
<td>125</td>
<td>0.70</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>PTFE</td>
<td>47</td>
<td>178</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 2.1. Physical properties of the used RTILs

<table>
<thead>
<tr>
<th>RTIL</th>
<th>Chemical formula</th>
<th>Melting point °C</th>
<th>Molar volume (m³/mol)×10⁴</th>
<th>Viscosity at 30°C (cP)</th>
<th>Hydrogen bond accepting ability (β)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[emim][Tf[N]</td>
<td>C₈H₁₇F₃N₅O₄S₂</td>
<td>-16</td>
<td>2.59</td>
<td>26.28</td>
<td>0.42</td>
<td>[51,54–56,62]</td>
</tr>
<tr>
<td>[bmim][NO₃]</td>
<td>C₆H₁₃N₃O₃</td>
<td>-</td>
<td>1.75</td>
<td>144.00</td>
<td>0.74</td>
<td>[51,53,57]</td>
</tr>
<tr>
<td>[emim][SCN]</td>
<td>C₆H₁₃N₃S</td>
<td>-</td>
<td>1.52</td>
<td>20.79</td>
<td>0.71</td>
<td>[51,58–61]</td>
</tr>
<tr>
<td>[emim][TFO]</td>
<td>C₆H₁₃F₃N₂O₂S</td>
<td>-10.92</td>
<td>1.79</td>
<td>35.98</td>
<td>0.57</td>
<td>[51,58,63,64]</td>
</tr>
<tr>
<td>[emim][DCA]</td>
<td>C₆H₁₇N₅</td>
<td>-4.85</td>
<td>1.61</td>
<td>14.78</td>
<td>0.64</td>
<td>[51,65–67]</td>
</tr>
<tr>
<td>[emim][BF₄]</td>
<td>C₆H₁₇BF₃N₂</td>
<td>14.85</td>
<td>1.55</td>
<td>23.35</td>
<td>0.55</td>
<td>[51,68–70]</td>
</tr>
</tbody>
</table>
2.2. Apparatus

Figure 2.1 is a schematic diagram of the experimental apparatus. A detailed description of the experimental apparatus appears in Morgan et al., the following is a brief summary. The apparatus consists of two stainless steel chambers as feed and permeate chambers, a vacuum pump (Fisher Scientific Maxima C Plus, Model M8C with an ultimate pressure rating of $10^{-4}$ Torr), a 0-5-psia pressure transducer (Omega PX811-005AV), and a PC for recording data. Furthermore, the unit is in an insulated box with a temperature controller. There is a septum port to inject test gases to the feed chamber using a syringe. In this work, two Viton O-rings were used to hold vacuum.

The volumes of upper (feed) and lower (permeate) chambers were determined by measuring the resulting pressure from a known amount of air at fixed temperature. These volumes were determined to be 97 and 81 mL, respectively. The active area of the membrane is 11.064 cm$^2$.

*Figure 2.1. Schematic diagram of the diffusion cell [55]*
2.3. Methods

2.3.1. SILM fabrication

The SILMs were prepared by impregnating the polymer supports with 1 mL of RTIL. First 0.5 ml of the RTIL was spread on a watch glass using a syringe. Then, the polymer support was placed on it to absorb the RTIL. This process minimized the amount of trapped air during immobilization of the RTIL. In addition to minimize the trapped air in the back of the active side of the support, the active side was placed on top of the liquid. Upon completion of the membrane wetting, the remaining 0.5 mL of the RTIL was spread over the membrane until it was completely soaked with the RTIL. The prepared membrane was degassed and dehydrated by a vacuum desiccator overnight, after which, the excess of the RTIL was removed from the surface of the membrane using a filter paper before mounting in the apparatus.

2.3.2. Mounting and testing the prepared membrane

Before mounting the newly prepared membrane, the old one was removed from the apparatus plus the feed and permeate chambers cleaned using ethanol and Kimwipes. To prevent the displacement of liquid from pores under pressure, a layer of the hydrophobic Polytetrafluoroethylene (PTFE) was placed beneath the prepared membrane before mounting it inside the cell. The PTFE prevents the RTIL from being displaced from the support under pressure. The hydrophobic nature of the PTFE support prevents its wetting with the RTIL. After mounting the membrane inside the cell, the system was put under vacuum (< 4 Pa) overnight for degassing. Different volumes of the test gases were injected into the cell using a syringe. For fast permeating gases (carbon dioxide, propene, 1-butene, and butane), a gas volume of 5 ml was injected into the
cell while for slow permeating gases (nitrogen, methane, and propane) the injection volume was 10 ml. We decided to use 10 ml of the slower permeating gases to increase the driving force (pressure difference across the membrane), because the leakage rate of the cell was higher than the gas permeance at 5 ml injections. The pressure at the permeate chamber was measured continuously for 5 hours using a pressure transducer. After each experiment, vacuum was pulled to remove the remaining gases and to degas the RTIL for 45 minutes. Next, a new sample was injected into the cell. All experiments were performed at least three times to test the reproducibility and repeatability of tests. Furthermore, experiments were carried out using a new support for each RTIL to ensure that variability due to support was accounted for in the tests.
CHAPTER 3

RESULTS AND DISCUSSION

3.1. Permeance results

In this study, the experimental permeances were determined based on the assumption that gas transport is completely through the RTIL and the effect of the PVDF support on the gas permeance is negligible due to very low PVDF permeance for the test gases. The permeabilities for PVDF support is 2.7 and 0.4 Barrers for CO$_2$ and N$_2$, respectively [17]. The lowest determined permeability of CO$_2$ for the prepared SILMs is 117 Barrers in which the permeability of the CO$_2$ in the support is only 2.3% of the lowest determined permeability for CO$_2$. Furthermore, similar comparison for N$_2$ showed that the N$_2$ permeability of the support is less than 14% of the lowest obtained permeability (2.9 Barrers) for N$_2$. Therefore, the assumption that gas transport is completely through the RTIL is adequate. Furthermore, the leakage rate for the cell adds approximately 0.012 GPUs to any measurement with the lowest reported permeance being 0.023 GPUs. The leakage rate is almost 50% of the detected permeance, consequently, the determined selectivity is highly affected by the leakage rate especially for low permeance gases.

The following RTILs were selected according to their hydrogen bond accepting ability: [emim][Tf$_2$N], [emim][BF$_4$], [emim][TfO], [emim][DCA], [emim][SCN], and [emim][NO$_3$]. The pressure versus time data were fitted to Eq. B.7 in appendix B and permeances were determined using the steady state region of data. The pure gas permeances for CO$_2$, N$_2$, CH$_4$, C$_3$H$_6$, C$_3$H$_8$, H$_2$, and N$_2$.
C₄H₈, and C₄H₁₀ were determined in the initial pressure range of 0.76 to 1.51 psi at 30°C and are presented in Table 3.1. The gas permeances range from 2.9±0.1 GPUs (CO₂) to 0.023±0.006 GPUs (N₂) for the tested RTILs and the leakage rate is 0.012 GPUs which is almost 53% of the lowest reported N₂ permeance. The permeances of N₂; therefore, have a systematic error of approximately 50%. Based on the reported data in literature, the effect of the cation on the gas permeance is negligible compared to that of the anion [17,71,72]. Therefore we did not vary the cation but kept it as an experimental constant. In this work, all of the cations are [emim] except for [bmim][NO₃], since [emim][NO₃] is solid at room temperature. The permeance of CO₂ increases in the following order of anions: [Tf₂N] > [TfO] > [BF₄] > [SCN] > [DCA] > [NO₃]. The permeances of the N₂ and CH₄ is the lowest for [bmim][NO₃], while the highest permeances value is for [emim][Tf₂N]. Similar trends were observed for the rest of the gases. The permeance of gases in the RTILs is mostly affected by the gas solubility in the RTILs.

According to Scovazzo [19], the viscosity and molar volume of the RTILs have a positive relationship. As it was mentioned in the introduction section, the solubility of many gases in RTILs depends on the RTIL molar volume. Diffusivity, a component of permeability, is related to the RTIL viscosity. Therefore, the permeance may be affected by both viscosity and molar volume of the RTILs in which permeance is the product of diffusivity and solubility. However, for the reverse-selective membranes, the solubility is dominant. Therefore, the permeance is a strong function of the RTIL molar volume. Furthermore, the solubility of the non-condensing gases such as N₂ and CH₄ may also depend on the RTIL polarity which is investigated in the next section. The effects of viscosity and molar volume of the RTILs on the CO₂ permeance are presented in Figures 3.1 and 3.2. There appears to be two regions for the CO₂ permeance dependence on the RTIL viscosity. In the first region (viscosity < 30 cP), the CO₂ permeance increases with an increase in
the viscosity of RTIL (Figure 3.1). In contrast, for the second region (viscosity > 30 cP), viscosity of the RTIL has a negative effect on the CO\textsubscript{2} permeance in which an increase in the RTIL viscosity leads to a reduction in the CO\textsubscript{2} permeance (Figure 3.1). Similar trends were observed for the rest of the test gases. The RTIL molar volume has a positive impact in which an increase in the RTIL molar volume leads to an increase in the CO\textsubscript{2} permeance (Figure 3.2).

\textit{Table 3.1. Experimental gas permeances at 30°C}

<table>
<thead>
<tr>
<th>Gas</th>
<th>[emim][Tf\textsubscript{2}N]</th>
<th>[emim][BF\textsubscript{4}]</th>
<th>[emim][TfO]</th>
<th>[emim][DCA]</th>
<th>[emim][SCN]</th>
<th>[bmim][NO\textsubscript{3}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>2.9±0.1</td>
<td>1.78±0.08</td>
<td>2.6±0.1</td>
<td>1.43±0.07</td>
<td>1.73±0.08</td>
<td>0.94±0.05</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>0.142±0.006</td>
<td>0.042±0.002</td>
<td>0.074±0.004</td>
<td>0.030±0.005</td>
<td>0.048±0.008</td>
<td>0.023±0.006</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>0.26±0.01</td>
<td>0.078±0.003</td>
<td>0.17±0.02</td>
<td>0.151±0.006</td>
<td>0.096±0.009</td>
<td>0.070±0.006</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}</td>
<td>1.71±0.09</td>
<td>0.63±0.03</td>
<td>1.0±0.2</td>
<td>1.27±0.05</td>
<td>1.55±0.06</td>
<td>0.40±0.08</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>0.67±0.03</td>
<td>0.14±0.01</td>
<td>0.34±0.02</td>
<td>0.41±0.02</td>
<td>0.64±0.08</td>
<td>0.130±0.008</td>
</tr>
<tr>
<td>C\textsubscript{4}H\textsubscript{8}</td>
<td>2.03±0.09</td>
<td>0.62±0.03</td>
<td>1.4±0.1</td>
<td>1.39±0.06</td>
<td>1.9±0.2</td>
<td>0.10±0.06</td>
</tr>
<tr>
<td>C\textsubscript{4}H\textsubscript{10}</td>
<td>1.19±0.06</td>
<td>0.73±0.03</td>
<td>0.74±0.04</td>
<td>0.73±0.04</td>
<td>1.5±0.1</td>
<td>0.22±0.05</td>
</tr>
</tbody>
</table>
Figure 3.1. The CO$_2$ permeance vs viscosity of the tested RTILs vs at 30°C. The CO$_2$ permeance increases with an increase in the RTIL viscosity for viscosities less than 30cP and it decreases for viscosities larger than 30cP.

Figure 3.2. The CO$_2$ permeance vs molar volume of the tested RTILs vs at 30°C. The RTILs molar volume has a positive impact on the CO$_2$ permeance.

3.2. CH$_4$ and N$_2$ permeances based on the hydrogen bond acceptor property

The nonideal solubility of CH$_4$, studied by Carvalho et al. [1], can be attributed to the polarity of the RTILs, which can be determined using Kamlet-Taft parameters. The hydrogen bond accepting ability ($\beta$) was determined for the tested RTILs by Lungwitz’s work [51] using dyes.
showed in Figure A.2 in appendix A. The values of β are reported in Table 2.1. Some of the values in this table are estimated, because the values reported by Lungwitz are for [bmim] cation.

Figure 3.3 shows the CH₄ and N₂ permeances versus β values. The plotted data are consistent with β values except for [emim][BF₄], in which it seems that the interactions of CH₄ with the RTIL is different from the other RTILs. [emim][BF₄] shows different behavior and it breaks down at room temperature in the presence of water. The R-squared values for the fitted lines when neglecting [emim][BF₄] are 0.99 and 0.92 for CH₄ and N₂, respectively. Moreover, when [emim][BF₄] are considered, the R-squared values were decreased to 0.66 and 0.74 CH₄ and N₂, respectively. The nonideal behavior of CH₄ in the RTILs, unlike CO₂, is due to the strong solute-solvent interactions, which leads to a positive deviation from the ideal solutions. The permeance of CH₄, as it was proposed by Carvalho and Coutinho [1], decreases with an increase in the hydrogen bond accepting ability of the RTILs; higher β values leads to more deviation from the ideal solution. The nonideal behavior of the CH₄ solubility in the RTILs confirms Carvalho’s hypothesis [1]. In Figure 3.3, N₂ shows similar behavior with respect to the β values except for [emim][BF₄]. Therefore, as before, the N₂ solubility can be attributed to the interactions between N₂ and the RTILs. Furthermore, the permeance and nonideal solubility of N₂ in the RTILs can be correlated by hydrogen bond accepting ability of the tested RTILs.
3.3. Selectivity results

The ideal selectivity, $\alpha_{ij}$, was determined by dividing the permeance of the faster permeating gas $i$ with the permeance of the slower permeating gas $j$. Table 3.3 shows the selectivities for $\text{CO}_2/\text{N}_2$, $\text{CO}_2/\text{CH}_4$, $\text{C}_3\text{H}_6/\text{CH}_4$, $\text{C}_3\text{H}_8/\text{CH}_4$, $\text{C}_4\text{H}_8/\text{CH}_4$, and $\text{C}_4\text{H}_{10}/\text{CH}_4$ separations at 30°C. The $\text{CO}_2$ permeances for these membranes are in the order of 2.9-0.94 GPUs. Moreover, perm-selectivity ranges for different gas pairs separations are:

- $\text{CO}_2/\text{N}_2$: 20 to 42
- $\text{CO}_2/\text{CH}_4$: 10 to 23
- $\text{C}_3\text{H}_6/\text{CH}_4$: 6 to 17
- $\text{C}_3\text{H}_8/\text{CH}_4$: 2 to 7
- $\text{C}_4\text{H}_8/\text{CH}_4$: 1 to 21
- $\text{C}_4\text{H}_{10}/\text{CH}_4$: 3 to 17

Figure 3.3. The experimentally determined $\text{N}_2$ and $\text{CH}_4$ permeances versus $\beta$ values at 30°C. The hydrogen bond accepting ability of the RTIL has negative impact on the $\text{N}_2$ and $\text{CH}_4$ permeances and an increase in the hydrogen bond accepting ability of the RTIL leads to a decrease in the $\text{N}_2$ and $\text{CH}_4$ permeances.
C₃H₈/N₂: 3 to 14

For the CO₂/N₂ separation, the highest selectivity is for [emim][BF₄] with a value of 42, while the lowest selectivity is for [emim][Tf₂N] with a value of 20. Furthermore, the highest and the lowest selectivity values for the CO₂/CH₄ separation are 23 and 10 for [emim][BF₄] and [emim][DCA], respectively. Moreover, the highest reported selectivity values for the CO₂/N₂ and CO₂/CH₄ separations in literature are 56 and 23 for [emim][DCA] [19]. A regular order was not observed for the gas pair separations. For example, for the CO₂/N₂ separation, [emim][Tf₂N] has the lowest selectivity, while for the CO₂/CH₄ separation, [emim][DCA] has the lowest.

The comparison of the information given in Table 3.2 and literature shows that the results are in good agreement with the literature except for [emim][DCA]. The determined selectivities for [emim][DCA] are almost 84% of the literature values which it can be due to the different membrane preparation methods or system error. The highest reported selectivities for the C₃H₈/CH₄, C₃H₈/N₂, and C₄H₁₀/CH₄ in literature for polymer membranes are 5.7, 7.5, and 14, respectively [6,27,29]; compared to respective highest in this study of 7, 14, and 17 (for [emim][SCN]). The comparison of the RTIL-membranes and polymeric membranes shows that RTIL-membranes are better than the polymeric membranes for the separation of C₃H₈/CH₄, C₃H₈/N₂, and C₄H₁₀/CH₄. Moreover, RTIL-membranes showed better performance when compared to the polymeric membranes.

Even a very small leak in the permeate chamber leads to the overestimation of the permeance of slower permeating gases such as N₂, CH₄, and C₃H₈, especially in the RTILs with high viscosity such as [bmim][NO₃]. Therefore, the experimentally reported selectivity could be lower than obtained from ideal test equipment with no leaks. For example, the lowest determined
Table 3.1. Experimental gas selectivities at 30°C

<table>
<thead>
<tr>
<th>Gas</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[emim][Tf₂N]</td>
</tr>
<tr>
<td>CO₂/N₂</td>
<td>20±2</td>
</tr>
<tr>
<td>CO₂/CH₄</td>
<td>10.9±0.8</td>
</tr>
<tr>
<td>C₃H₆/CH₄</td>
<td>6.6±0.6</td>
</tr>
<tr>
<td>C₄H₁₀/CH₄</td>
<td>2.6±0.2</td>
</tr>
<tr>
<td>C₃H₈/N₂</td>
<td>4.8±0.4</td>
</tr>
</tbody>
</table>

<sup>a</sup> All data are determined from [19].
permeance is 0.023 for N\textsubscript{2} permeance in [bmim][NO\textsubscript{3}] showing that N\textsubscript{2} permeance in [bmim][NO\textsubscript{3}].

In Figures 3.4 through 3.6 investigate the effect of molar volume on the selectivity of the above-mentioned gas pairs. The selectivities of the CO\textsubscript{2} gas pairs depend inversely on the molar volume of the tested RTILs, which is approximately in the agreement with the Camper’s model [38]. Similar results have been reported by Scovazzo [19] for the CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} separations. The selectivities for the alkane gas pairs do not have an obvious dependence on RTIL molar volumes (fig. 3.5 and 3.6) For this study, a regular trend was not observed for the dependence of the RTIL viscosity on the selectivity of gas pair separations (figures not shown). All of this confirms that the separation mechanism in the RTILs is solubility rather than diffusion.

![Figure 3.4. The experimentally determined selectivities for CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} separations vs molar volume at 30\textdegree C. The selectivity depends on the RTIL molar volume with a power law function which close to Camper’s model exponent for the CO\textsubscript{2}/N\textsubscript{2} separation.](image)
Figure 3.5. The experimentally determined selectivities for C$_3$H$_6$/CH$_4$, C$_3$H$_8$/CH$_4$, and C$_3$H$_8$/N$_2$ separations vs molar volume at 30°C. The selectivities depend on the inverse of RTIL molar volume for the gas pairs.

Figure 3.6. The experimentally determined selectivities for C$_4$H$_8$/CH$_4$ and C$_4$H$_{10}$/CH$_4$ separations vs molar volume at 30°C. The selectivities depend on the inverse of RTIL molar volume for the gas pairs.

3.4. Correlations for CO$_2$, N$_2$, and CH$_4$ permeance prediction

Since the permeance and selectivity results for [bmim][NO$_3$] is strongly affected by leakage rate, the permeances and selectivities of [bmim][NO$_3$] are not considered for the
correlations. Semi-empirical models were proposed for the prediction of CO$_2$, N$_2$, and CH$_4$ permeance:

$$P = A\mu^B \beta^C$$  \hspace{1cm} (3.1)

where $P$ is the permeance in GPUs, $A$, $B$, and $C$ are correlation parameters, $\mu$ is the RTIL viscosity in cP, and $\beta$ is the hydrogen bond accepting ability of the RTIL. Three types of models are considered: viscosity dependence only ($B=0$), hydrogen bond dependence only ($C=0$), and correlations with both viscosity and hydrogen bond dependency.

The parameters of all correlations were determined by the least square method using Eviews ® software version 3.1 [73]. In this software, analyzing and fitting data were carried out as follows:

1. R-squared ($R^2$): this statistic measures the success of the regressed model in predicting the values of the dependent variable within the sample. The value of this statistic is equal to one if the regressed model fits the data perfectly.

2. Durbin-Watson (D.W.) Test: this test gives another parameter, which considers the difference between the actual and model predicted value in every data point, known as residual. In fact, this parameter determines the relationship between the residual data.

In addition to $R^2$ and D.W., the mean relative percent error (MRPE) was utilized in order to choose the best fitting model. Furthermore, MRPE was used to compare the predicted results with the experimental data. MRPE was calculated from the following formula:

$$MRPE = \frac{1}{N}\sum_{i=1}^{N} \left| \frac{(P \text{ or } \alpha)_{\text{expi}} - (P \text{ or } \alpha)_{\text{calci}}}{(P \text{ or } \alpha)_{\text{expi}}} \right| \times 100$$  \hspace{1cm} (3.2)
where $N$ is the number of data points and $P$ and $\alpha$ are permeance and selectivity, taken from the experiments or calculated using the correlation.

Table 3.3 shows the calculated correlation constants, $R^2$, D.W. test results, and MRPE values for the permeance of $\text{CO}_2$, $\text{N}_2$, and $\text{CH}_4$.

Table 3.3. Fitting results for the $\text{CO}_2$, $\text{N}_2$, and $\text{CH}_4$ permeances at 30°C

<table>
<thead>
<tr>
<th></th>
<th>$A^a$</th>
<th>$B^a$</th>
<th>$C^a$</th>
<th>$R^2^b$</th>
<th>D.W. $^c$</th>
<th>MRPE $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2$</td>
<td>0.28</td>
<td>0.63</td>
<td>0.00</td>
<td>0.59</td>
<td>1.73</td>
<td>11.22</td>
</tr>
<tr>
<td></td>
<td>1.12</td>
<td>0.00</td>
<td>-1.06</td>
<td>0.61</td>
<td>3.53</td>
<td>13.55</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.51</td>
<td>-0.81</td>
<td>0.91</td>
<td>2.23</td>
<td>6.50</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>0.008</td>
<td>0.69</td>
<td>0.00</td>
<td>0.16</td>
<td>1.57</td>
<td>36.03</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.00</td>
<td>-2.70</td>
<td>0.86</td>
<td>2.81</td>
<td>22.19</td>
</tr>
<tr>
<td></td>
<td>0.004</td>
<td>0.40</td>
<td>-2.57</td>
<td>0.87</td>
<td>1.89</td>
<td>20.73</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>0.04</td>
<td>0.44</td>
<td>0.00</td>
<td>0.08</td>
<td>2.17</td>
<td>41.91</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.00</td>
<td>-1.97</td>
<td>0.68</td>
<td>2.47</td>
<td>26.53</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>0.05</td>
<td>-1.95</td>
<td>0.68</td>
<td>2.42</td>
<td>26.51</td>
</tr>
</tbody>
</table>

$^a$ Correlation parameters  
$^b$ R-squared  
$^c$ Durbin-Watson test  
$^d$ Mean relative percent error
Based on the information given in Table 3.3, the best correlations for the prediction of CO$_2$, N$_2$, and CH$_4$ permeances are:

\[
P_{CO_2} = 0.25 \mu^{0.51} \beta^{-0.81} \tag{3.3}
\]

\[
P_{N_2} = 0.004 \mu^{0.40} \beta^{-2.57} \tag{3.4}
\]

\[
P_{CH_4} = 0.05 \beta^{-1.97} \tag{3.5}
\]

Table 3.3 shows that R$^2$ values for the CH$_4$ permeance correlation is the smallest, while the correlation for CO$_2$ permeance has the best R$^2$ value. Furthermore, the D.W. test results for all of the correlations are more than one showing good fitting quality. The CO$_2$ correlation has the lowest MRPE value, which means it has the best fitting quality. Furthermore, Table 3.4 shows that addition of the hydrogen bond accepting ability of RTIL to the correlations has a large impact on the correlation performance which proves Carvalho’s hypothesis for the gas solubility in RTILs [1].

Figures 3.7 and 3.8 examine the effect of hydrogen bond accepting ability of the RTILs on the permeance of CO$_2$, N$_2$, and CH$_4$. The β parameter has a negative effect on the selectivity of the CO$_2$, N$_2$, and CH$_4$ and an increase in the β value leads to a decrease in the permeances. However, most of RTILs with high hydrogen bond accepting ability are viscous fluids (viscosity > 60 cP) which makes them difficult to determine gas separation properties. Figures 3.7 and 3.8 show that the hydrogen bond accepting ability of RTILs have potential to correlate the selectivity of gas pairs. Furthermore, the lines represent Eqs. 3.3 to 3.5 which shows the proposed correlations are in a good agreement with the experimental data.
Figure 3.7. The effect of the hydrogen bond accepting ability of the tested RTILs on the permeance of CO$_2$ at 30°C. The line is determined using proposed correlations. The permeance of CO$_2$ is well correlated using the hydrogen bond accepting ability of RTIL.

Figure 3.8. The effect of the hydrogen bond accepting ability of the tested RTILs on the permeances of N$_2$ and CH$_4$ at 30°C. The lines are determined using proposed correlations. The permeances are well correlated using the hydrogen bond accepting ability.

Figures 3.9 and 3.10 compare the experimentally determined gas permeances and calculated permeances for CO$_2$, N$_2$, and CH$_4$, respectively. Dashed lines in in Figures 3.9 and 3.10...
are 25% percent error margins. As seen in Figures 3.9 and 3.10, the calculated permeances are in a good agreement with the experimental data except for CH₄ correlation.

Figure 3.9. Comparison of the calculated and measured CO₂ permeance which shows that calculated values are in good agreement with the experimentally determined values.

Figure 3.10. Comparison of the calculated and measured permeance of N₂ and CH₄ which shows that calculated values are almost in good agreement with the experimentally determined values.
3.5. Correlations for the CO$_2$/N$_2$, CO$_2$/CH$_4$, C$_3$H$_8$/CH$_4$, and C$_3$H$_8$/N$_2$ selectivity prediction

Semi-empirical correlations were proposed to determine the selectivities of CO$_2$/N$_2$, CO$_2$/CH$_4$, C$_3$H$_8$/CH$_4$, and C$_3$H$_8$/N$_2$ separations. The following equation was used to correlate the above-mentioned gas pair separations:

$$\alpha_{ij} = AV_{RTIL}^B \beta^C + D$$  \hspace{1cm} (3.6)$$

where $\alpha_{ij}$ is the selectivity of the more permeable gas i and less permeable gas j and D is a correlation parameter. Similar to permeance correlations three cases are considered. At first, only the RTIL molar volume, and then, the RTIL hydrogen bond accepting ability, and in the end, both are considered.

The calculations results for the correlation constants, R$^2$, D.W. test results, and MRPE values for the selectivities of CO$_2$/N$_2$, CO$_2$/CH$_4$, C$_3$H$_8$/CH$_4$, and C$_3$H$_8$/N$_2$ separations are summarized in Table 3.4.

Based on the information given in Table 3.5, the best correlations for the prediction of CO$_2$, N$_2$, and CH$_4$ are:

$$\alpha(CO_2/N_2) = 1585.88V_{RTIL}^{-0.66} \beta^{0.10} - 19.17$$  \hspace{1cm} (3.7)$$

$$\alpha(CO_2/CH_4) = 182.72\beta^{0.06} - 161.25$$  \hspace{1cm} (3.8)$$

$$\alpha(C_3H_8/CH_4) = 1820.75\beta^{17.23} + 2.14$$  \hspace{1cm} (3.9)$$

$$\alpha(C_3H_8/N_2) = 375406.5V_{RTIL}^{-1.47} \beta^{8.41} + 3.61$$  \hspace{1cm} (3.10)$$
In Table 3.5, R² values for the C₃H₈/CH₄ correlation is the highest, while the correlation for CO₂/CH₄ selectivity has the lowest R² value. Furthermore, the D.W. test results for all of the correlations are more than one, which indicates a good quality of fitting. Moreover, the MRPE

Table 3.4. Fitting results for the selectivities of CO₂/N₂, CO₂/CH₄, C₃H₈/CH₄, and C₃H₈/N₂ separations at 30°C

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>R²,b</th>
<th>D.W.</th>
<th>MRPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂/N₂</td>
<td>681.72</td>
<td>-0.08</td>
<td>0.00</td>
<td>-425.9</td>
<td>0.76</td>
<td>2.55</td>
<td>8.50</td>
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<tr>
<td></td>
<td>595.70</td>
<td>0.00</td>
<td>0.05</td>
<td>-544.56</td>
<td>0.53</td>
<td>2.15</td>
<td>12.64</td>
</tr>
<tr>
<td></td>
<td>1585.88</td>
<td>-0.66</td>
<td>0.10</td>
<td>-19.17</td>
<td>0.75</td>
<td>2.46</td>
<td>8.59</td>
</tr>
<tr>
<td>CO₂/CH₄</td>
<td>325.40</td>
<td>-0.04</td>
<td>0.00</td>
<td>-247.72</td>
<td>0.18</td>
<td>2.43</td>
<td>23.67</td>
</tr>
<tr>
<td></td>
<td>182.72</td>
<td>0.00</td>
<td>0.06</td>
<td>-161.25</td>
<td>0.14</td>
<td>2.33</td>
<td>22.44</td>
</tr>
<tr>
<td></td>
<td>149.34</td>
<td>-0.09</td>
<td>0.04</td>
<td>-75.89</td>
<td>0.18</td>
<td>2.36</td>
<td>22.43</td>
</tr>
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<td></td>
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<td></td>
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<td>2.64×10⁻⁴</td>
<td>2.22</td>
<td>3.07</td>
<td>14.85</td>
</tr>
<tr>
<td>C₃H₈/CH₄</td>
<td>22.19</td>
<td>-0.03</td>
<td>0.00</td>
<td>-15.63</td>
<td>0.01</td>
<td>1.12</td>
<td>48.27</td>
</tr>
<tr>
<td></td>
<td>1820.75</td>
<td>0.00</td>
<td>17.23</td>
<td>2.14</td>
<td>0.98</td>
<td>2.25</td>
<td>11.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.64×10⁻⁴</td>
<td>2.22</td>
<td>3.07</td>
</tr>
<tr>
<td>C₃H₈/N₂</td>
<td>90.12</td>
<td>-0.09</td>
<td>0.00</td>
<td>-50.19</td>
<td>0.05</td>
<td>0.90</td>
<td>52.24</td>
</tr>
<tr>
<td></td>
<td>167.75</td>
<td>0.00</td>
<td>8.03</td>
<td>3.64</td>
<td>0.90</td>
<td>2.38</td>
<td>22.86</td>
</tr>
<tr>
<td></td>
<td>375406.5</td>
<td>-1.47</td>
<td>8.41</td>
<td>3.61</td>
<td>0.91</td>
<td>2.40</td>
<td>21.47</td>
</tr>
</tbody>
</table>

a Correlation parameters

b R-squared

c Durbin-Watson test

d Mean relative percent error
values vary from 8 to 52% and the correlation for the CO$_2$/N$_2$ separation has the lowest MRPE value, which indicates it has the best quality of fitting. Furthermore, C$_3$H$_8$ involving models are strongly affected by introduction of the RTIL hydrogen bond ability. For the slow permeable gases such as C$_3$H$_8$, CH$_4$, and N$_2$, the Carvalho’s theory is well-confirmed. Figures 3.11 and 3.12 investigate the effect of hydrogen bond accepting ability of the RTILs on the selectivity of CO$_2$/N$_2$, CO$_2$/CH$_4$, C$_3$H$_8$/CH$_4$, and C$_3$H$_8$/N$_2$. The $\beta$ parameter has a positive effect on the selectivity of the CO$_2$/CH$_4$, C$_3$H$_8$/CH$_4$, and C$_3$H$_8$/N$_2$ separations and an increase in the $\beta$ value leads to an increase in the selectivities. However, most of RTILs with high hydrogen bond accepting ability are viscous fluids (viscosity > 60 cP) which makes them difficult to determine gas separation properties. Furthermore, the hydrogen bond accepting ability of RTIL has more impact on the C$_x$H$_y$/CH$_4$ separations. Figures 3.11 and 3.12 show that the hydrogen bond accepting ability of RTILs have potential to correlate the selectivity of gas pairs. Furthermore, the lines represent Eqs. 3.7 through 3.10 which shows the proposed correlations are in a good agreement with the experimental data.

![Figure 3.11](image_url)

*Figure 3.11. The effect of the hydrogen bond accepting ability of the tested RTILs on the selectivity of CO$_2$/N$_2$ separation at 30°C. The lines are determined using proposed correlations. The selectivity of the gas pairs are well correlated using the hydrogen bond accepting ability of RTIL. Eq. 3.7 correlates selectivity based on the molar volume and hydrogen bond accepting ability of RTIL.*
Figure 3.12. The effect of the hydrogen bond accepting ability of the tested RTILs on the selectivities of $\text{C}_3\text{H}_8/\text{CH}_4$ and $\text{C}_3\text{H}_8/\text{N}_2$ separations at 30°C. The lines are determined using proposed correlations. The selectivity of the gas pairs are well correlated using the hydrogen bond accepting ability of RTIL.

In Figures 3.13 and 3.14, the calculated and experimentally determined selectivities for the $\text{CO}_2/\text{N}_2$, $\text{CO}_2/\text{CH}_4$, $\text{C}_3\text{H}_8/\text{CH}_4$, and $\text{C}_3\text{H}_8/\text{N}_2$ separations are displayed. In these figures, dashed lines are 25% error margins. As seen in these figures, the calculated selectivities are in a good agreement with the experimental data except for $\text{CO}_2/\text{CH}_4$ correlation.

Figure 3.13. Comparison of the calculated and measured selectivities of the $\text{CO}_2/\text{N}_2$ and $\text{CO}_2/\text{CH}_4$ separations which shows that calculated values are almost in good agreement with the experimentally determined values.
3.6. Reverse-selective behavior of the C$_3$H$_8$/CH$_4$ and C$_3$H$_8$/N$_2$ separations

Reverse-selective membranes permeate larger molecules faster than the smaller ones; as shown by our reported selectivities of C$_3$H$_8$ and C$_4$H$_{10}$ over CH$_4$ and N$_2$. These membranes are getting more attention due to their efficiency in the separation of volatile hydrocarbons from permanent gases [4]. The favorable separation of condensable gases or vapors over permanent gases can be achieved by the competitive gas sorption or solubility. The first attempt to investigate the reverse-selective behavior of SILMs was done by Yokozeki et al. [4]. They tried to separate CO$_2$ from hydrogen [4]. However, to our best knowledge, the reverse-selective ability of SILMs for the separation of volatile hydrocarbon gas pairs has not been investigated. In this section, the reverse-selective behavior of C$_3$H$_8$/CH$_4$ and C$_3$H$_8$/N$_2$ separations using SILMs is investigated. Table 3.5 shows the kinetic diameters for the test gases.
Table 3.5. Kinetic diameters for the test gases

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>C₃H₆</th>
<th>C₃H₈</th>
<th>C₄H₈</th>
<th>C₄H₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic diameter (Å)</td>
<td>3.30</td>
<td>3.64</td>
<td>3.80</td>
<td>4.50</td>
<td>4.30</td>
<td>4.50</td>
<td>4.30</td>
</tr>
</tbody>
</table>

The kinetic diameter of C₃H₈ is larger than those of CH₄ and N₂; therefore, for the diffusion mechanism based membranes, CH₄ and N₂ should permeate faster than C₃H₈. However, for the reverse-selective membranes, C₃H₈ should have higher permeance. Figure 3.15 shows the permeance of C₃H₈, CH₄, and N₂ against kinetic diameter of the gases. The selected RTILs are [emim][Te₂N], [emim][DCA], [emim][SCN], and [bmim][NO₃]. As seen in this figure, the permeance difference for the C₃H₈, CH₄, and N₂ varies considerably for the less viscous (viscosity <60 cP) RTILs confirming reverse-selective behavior of the C₃H₈/CH₄ and C₃H₈/N₂ separations. The difference between gas permeances decreases with an increase in the viscosity of the RTILs. As the viscosity increases, the permeance differences for C₃H₈, CH₄, and N₂ decrease, which may indicate a change from solubility dominated transport to the dominance of a gas diffusion mechanism for the gas transmission. The higher solubility of C₃H₈ compared to CH₄ and N₂ in the tested RTILs is responsible for the reverse-selectivity behavior.

The effect of the hydrogen bond accepting ability of the RTILs on the selectivity of C₃H₈/CH₄ and C₃H₈/N₂ are presented in the section 3.5 (Figure 3.12). The β parameter has a positive effect on the selectivity of the C₃H₈/CH₄ and C₃H₈/N₂ separations and an increase in the β value leads to an increase in the selectivities. However, RTILs with large β values have larger viscosity. Therefore, there is a tradeoff between choosing a large β and a high selectivity because of a change in the transport mechanism. In Figure 3.12, [bmim][NO₃] is not considered because
its viscosity is one order of magnitude higher than the other tested RTILs and the permeances are not quantifiable. CH$_4$ and N$_2$ are slow permeable gases and according to the Carvalho’s hypothesis [1], to decrease the CH$_4$ solubility in the RTILs, the nonideality of the solution should increase. Our data and results confirm the Carvalho’s theory [1] with great accuracy. N$_2$ showed a similar behavior to CH$_4$ and its permeance change can be explained by a change in the β value.

**Figure 3.15.** The permeances of C$_3$H$_8$, CH$_4$, and N$_2$ versus kinetic diameter at 30°C. The lines are provided to show trends and behavior of RTILs. The lines are drawn to show the trend. The permeance difference decreases with an increase in the RTIL viscosity.
CHAPTER 4

CONCLUSIONS

This work measured the permeance of selected gases in RTIL based membranes using PVDF support. Following RTILs were examined: [emim][Tf$_2$N], [emim][BF$_4$], [emim][TfO], [emim][DCA], [emim][SCN] and [emim][NO$_3$]. The permeance of CO$_2$ increases in the following order of anions: [Tf$_2$N] > [TfO] > [BF$_4$] > [SCN] > [DCA] > [NO$_3$]. The permeance of the N$_2$ and CH$_4$ is the lowest for [bmim][NO$_3$]. The permeances of the N$_2$ and CH$_4$ are decreasing according to the hydrogen bond accepting ability confirming Carvalho’s hypothesis [1]. Furthermore, selectivities of the selected gas pairs were obtained in which the maximum determined values for the selectivity of CO$_2$/N$_2$ and CO$_2$/CH$_4$ separations are 42 and 23, respectively. Semi-empirical correlations were achieved based on the viscosity, molar volume, and hydrogen bond accepting ability of the RTILs. The most of resulting correlations are in good agreement with the experimental data. In addition, the reverse-selective behavior of the C$_3$H$_8$/CH$_4$ and C$_3$H$_8$/N$_2$ separations were examined. The higher permeance of C$_3$H$_8$ in comparison with those of CH$_4$ and N$_2$ is due to solution mechanism of permeance in the RTILs. However, the selectivities were decreased for the viscous RTILs which may be due to an increasing dominance of diffusion mechanism for the permeance.
CHAPTER 5

FUTURE WORKS

We stopped gathering data using glass-fiber support because the slow permeance of the RTILs with higher viscosities gave results that were too close the detection limit of the lag-time apparatus. Because of the failure of the glass-fiber support, we recommend that future work use Bucky Paper to prepare RTIL based membranes. Also, we need to test more RTILs and take additional data to prove our hypothesis. We should test more RTILs with a wider range of viscosity.

The synthesis of an RTIL with competitive selectivity would remain only a laboratory success story unless a means to easily and continuously cast RTILs onto a membrane is found. The lack of viable casting technique for large scale industrial fabrication is a hindrance to industrial deployment of the RTIL-membranes. To this end, we started to look at the fundamental science to create a casting solution that would result in a SILM after exposure to a polar solvent such as water or an alcohol. Biphasic membranes such as cellulose acetate (CA) based membrane have a potential for CO$_2$ separation from the permanent gases should also be investigated. To that end, we have obtained preliminary phase diagram data for the CA, [emim][SCN], and isopropanol systems (Appendix D).
LIST OF REFERENCES


A. Khosravi, M. Sadeghi, Separation performance of poly(urethane–urea) membranes in


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APPENDIX D: TERNARY DIAGRAMS FOR CELLULOSE ACETATE/[emim][SCN]/ISOPROPANOL SYSTEM
APPENDIX A: KAMLET-TAFT PARAMETERS
A.1. Kamlet-Taft parameters

Polarity of a solvent is a well-accepted concept [48,49], defined as the capacity of a solvent to facilitate intermolecular interactions between the solvent and the solute not including those interactions which would result in chemical reactions. On this basis, the common theory of solvatochromism and other solvent-induced spectral properties, though not considered as exact methods for solvent strength measurements, offer a good measures for general solvent, and can indicate the similarities and differences between RTILs and conventional solvents [48]. The specific variation in the long-wavelength absorption band of selected indicator compounds in terms of the solute-solvent intermolecular interactions is explained by the solvatochromic methods [50].

Reichardt et al. [51] presented the first dye to measure solvatochromic parameters and Chiappe and Pieraccini [74] determined the first set of the solvatochromic parameters for a number of the RTILs. Determination of the solvent and surface polarity using solvatochromic dyes is convenient since only a small concentration of the corresponding probe is required. Furthermore, this method is relatively sensitive and gives reproducible results [49]. In the last decades, Kamlet-Taft solvent parameters, as well as Reichardt's solvent parameter, have been established for liquids as well as RTILs [51]. The solvatochromic parameters, known as Kamlet-Taft parameters, are $\alpha$, $\beta$, and $\pi^*$. They are defined as hydrogen bond acidity, hydrogen bond basicity, and
dipolarity/polarizability, respectively [48,51]. In practice, the Kamlet-Taft equation can be simplified to the following equation:

$$\tilde{\nu}_{max} = \tilde{\nu}_{max,0} + a\alpha + b\beta + s\pi^*$$ \hspace{1cm} (A.1)

where a, b, and s are the solvent-independent coefficients representing the solvent effect contributions to the UV/vis absorption shift $\tilde{\nu}_{max}$. $\tilde{\nu}_{max,0}$ is the value of a solvent reference such as the nonpolar medium cyclohexane [49].

Different dyes have been used to determine Kamlet-Taft parameters. With the Reichardt's dyes being the most famous ones. These dyes are N,N-dimethyl-p-nitroaniline, 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridino)phenolate (known as Reichardt’s betaine dye), and 4-nitroaniline. They are used to obtain $\alpha$, $\beta$, and $\pi^*$ [75]. In Figure 1.2, the dye structure for $\alpha$ and $\beta$ indicators is shown.

![Figure A.1. Molecular structures of Reichardt's dyes: a) betaine dye b) N,N-Dimethyl-p-nitroaniline c) 4-nitroaniline [75]](image_url)
In a comprehensive survey by Chiappe et al. [76] and Rani et al. [77] the Kamlet-Taft parameters for most of the commonly studied RTILs have been summarized. An investigation of the Kamlet-Taft parameter sets shows that the linear relationship between different solvatochromic dyes (Reichardt's dye, 1-pyrenealdehyde, Nile red, dansyl amide) may give different values for the polarity parameters (See Eq. 1.10) [51]. The difference in these values are explained on the basis of additional effects, such as viscosity and polarizability or specific hydrogen bonds [51].

The hydrogen bond donating ability of the RTILs, α, can be ascribed to the hydrogen atom of the cation (position 2 between the two nitrogens) and to the polar α-CH bond of the alkyl groups bound at the positively charged nitrogen atom of the cation [78]. Furthermore, α values can be affected by the ring and the anion interactions [78]. Reichardt's dye has mainly been used to determine α values because of its sensitivity to the hydrogen bond donating sites [78]. The α values are affected by the water content due to the formation of stoichiometric 1:1 water–dye complexes. This is due to the potential interactions of the Reichardt’s dye and other hydrogen bond donating sensitive dyes with water [78]. Since the very low concentrations of water cannot be measured, another solution or dye, which measures the α values as independently as possible from the other effects of the solvent, is required to overcome this problem. The Fe(phen)2(CN)2 is a known α indicator, but, unfortunately, it is completely insoluble in dry RTILs [79]. It was found that [Fe(phen)2(CN)2]ClO4 as a dye is suitable, because it is adequately soluble in the RTILs [79].

The hydrogen bond acceptor parameter, β, was introduced to quantify the anionic nature of the RTILs. The β value is a measure of the ability of an anion to form a hydrogen bond with the CH, OH, or NH acidic sites of organic molecules [52]. The solvatochromic probes containing acidic NH or OH groups can be used to determine β value by interacting with an external base. The NH and anion interactions typically makes a bathochromic shift of the UV/vis absorption band
of the chromophore [52]. The response of the UV/vis dye is sensitive not only to the hydrogen bond accepting ability, but also to the dipolarity/polarizability. The separation of the dipolarity/polarizability contribution from the total shift of the UV/vis dye is rarely achieved [52]. Therefore, a dye is required in which its UV/vis dye is significantly affected by the nature of the anion. This allows the accurate measurement of the β value for the RTILs. The 3-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-b:4,5-b0]-difuran-2,6-di-one dye has been introduced by the Lungwitz et al. [52].

The dipolarity/polarizability ability, $\pi^*$, is a measure of the dipolarity/polarizability behavior of the solvents. To measure $\pi^*$, a dye is required that would show a significant UV/Vis shift to only one of the Kamlet–Taft parameters [78]. The dipolarity/polarizability of the solvent should not be affected by the hydrogen bond accepting ability of the solvent and the $\nu_{\text{max}}$ of the solvatochromic dye for the measurement of the $\pi^*$ should be independent of $\alpha$ and $\beta$ [78]. Oehlke vet al. [78] used 4-tert-butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]-Δ3-thiazoline, which is equally possess both dipolarity and polarisability, to determine $\pi^*$ values. Figure 1.3 shows the structure of the dyes used to measure $\alpha$, $\beta$, and $\pi^*$.

![Figure A.2. The structure of the dyes for a) α indicator b) β indicator c) $\pi^*$ indicator [51]](image)

Figure A.2. The structure of the dyes for a) α indicator b) β indicator c) $\pi^*$ indicator [51]
APPENDIX B: DATA ANALYSIS
B.1. Data analysis

The main assumption for this work is that the transport through an immobilized RTIL membrane occurs by a solution-diffusion mechanism [55,80]. Furthermore, it is assumed that boundary layer resistance at the membrane interface is not the rate-limiting step for the mass transfer. This assumption is valid, because the rate limiting step for the mass transfer is the gas diffusion through the RTIL membrane [55]. The liquid convection was eliminated by the immobilization of the RTIL in a porous support. In this case, as described for low Rayleigh numbers, the mass transport is limited to the molecular diffusion [55]. The concentration profile in the immobilized RTIL membrane can be determined using the Fick’s second law for a porous medium [55]:

\[
\frac{\partial c_i}{\partial t} = \frac{D_i}{\tau^2} \frac{\partial^2 c_i}{\partial z^2}
\]

where \( c_i \) is the concentration of the species \( i \), \( D_i \) is its diffusivity, \( t \) is time, \( \tau \) is the tortuosity of the membrane, and \( z \) is the distance. At first, it is assumed that the membrane is free from the permeating gas. Moreover, the feed chamber was charged with a gas to a pressure of \( P_{io} \) at time zero assuming the pressure will remain constant during experiment, while the permeate chamber pressure will remain near to zero [55]. The following boundary conditions are resulted from the above-mentioned assumptions:

\[
t = 0 \quad 0 \leq z \leq L \quad c_i = 0
\]
\[ t > 0 \quad z = 0 \quad c_i = c_{i0} = P_{i0}S_i \]  
\[ (B.3) \]

\[ t > 0 \quad z = L \quad c_i \approx 0 \]  
\[ (B.4) \]

where \( S_i \) is the solubility of the species \( i \) in the immobilized RTIL membrane and \( L \) is the membrane thickness [55]. The concentration profile is given by [55]:

\[
\frac{c_{i0} - c_i}{c_{i0}} = \frac{z}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( n\pi \frac{z}{L} \right) \exp \left( -n^2 \pi^2 \frac{D_i t}{L^2 \tau^2} \right) 
\]  
\[ (B.5) \]

The flux is obtained at the membrane-permeate chamber interface in order to determine the pressure distribution with time [55].

\[
\frac{V_P}{RT} \frac{dP_{iL}}{dt} = \phi A \frac{D_i}{\tau} \left( \frac{dc_i}{dz} \right)_{z=L} 
\]  
\[ (B.6) \]

where \( V_P \) is the permeate chamber volume, \( A \) is the nominal membrane area, and \( \phi \) is the membrane porosity. The simplification of Eq. B.6 combined with Eq. 2.3 results in a relation for the pressure of the permeate chamber with time [55]:

\[
P_{iL} = \frac{\phi}{\tau} \frac{D_i ART}{LV_P} P_{i0}S_i \left( t - \frac{L^2 \tau^2}{6D_i} \right) 
\]  
\[ (B.7) \]

The term of \( L^2 \tau^2/6D_i \) is defined as lag-time which is determined by a linear regression. In addition to the lag-time, both solubility and diffusivity can be obtained by using Eq. B.7 in combination with linear regression [55].
APPENDIX C: [bmim][NO₃] PREPARATION IN ACETONE AND CHLOROFORM BASED ON IN-HOUSE PROCEDURE
C.1. [bmim][NO₃] Preparation in acetone and chloroform based on in-house procedure

The synthesis of [bmim][NO₃] from [bmim][Cl] and AgNO₃ is a one-to-one by mole basis double displacement reaction. Due to the light sensitivity of silver compounds and to prevent side reactions, the entire reaction was conducted in the dark with the beakers wrapped in aluminum foil. First, [bmim][Cl] was dissolved in acetone and gently stirred for an hour. Then AgNO₃ was added, and the mixture was sealed and stirred for 24 hours at room temperature. After a 30 minute settling time and vacuum filtration, the filtrate was dried under vacuum (10 Torr) at 100°C overnight to remove the acetone. The resulting RTIL phase was washed with chloroform, stirred for 1-hour, and again filtered after a 30-min. settling time. Finally the filtrate was dried overnight under vacuum (10 Torr) at 100°C to ensure high purity of the product. The result was a light yellow liquid.
D.1. Ternary diagrams for cellulose acetate/[emim][SCN]/isopropanol system

The ternary phase diagrams were determined for the cellulose acetate/[emim][SCN]/isopropanol system in which two molecular weights of cellulose acetate were used. The cloud point method was used to determine ternary phase diagrams by slightly titrating IP into the CA/RTIL mixture. Figures 3.19 and 3.20 show the ternary phase diagrams for the tested systems at 30°C. For both molecular weights, the equilibrium points are close to RTIL/IP axis because of low solubility of CA in the RTIL. Furthermore, there is a critical concentration for the CA/RTIL/IP system in which with any initial concentration of CA/RTIL, the final equilibrium point is almost the same for initial concentration of CA in the RTIL higher than 6%. This proposes that there is an upper bond for the CA/[emim][SCN]/IP solutions in which the solution is one phase. The determined equilibrium points are biphasic regions which implies coexistence of an excess RTIL rich phase and another phase that RTIL solubilizes an appropriate amount of CA. Xing et al. reported similar results [13,81].
Figure D.1. Ternary phase diagram for CA(MW=30000)/RTIL/IP system at 30°C
Figure D.2. Ternary phase diagram for CA(MW=50000)/RTIL/IP system at 30°C
VITAE

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