Synthesis, Characterization, and Impregnation of Some Ionic Liquids on Polymer Membrane for Separation of Carbon Dioxide from its Mixture with Methane

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Keywords: ionic liquid, CO₂/CH₄ separation, membrane, supported ionic liquid membrane

doi: 10.15255/CABEQ.2017.1193

Introduction

Much of the natural gas produced worldwide requires significant treatment because in some natural gas wells the content of CO₂ up to 70 % of the total gas volume can be observed. CO₂ separation is of critical economical importance because CO₂ causes pipeline corrosion and decreases the calorific value of natural gas. The current US pipeline specifications require CO₂ content to be below 2 % by volume. The most frequently used methods in the CO₂ separation technology include adsorption using solid adsorbents (carbon) or absorption and stripping using physical or chemical solvents (aqueous amines), separation using membrane, molecular sieve.

Membrane separation is an emerging technology and has numerous advantages over adsorption and absorption methods, such as ease of operation, low operating and installation cost, small size, low weight, and low environmental impact. Some kinds of membranes for CO₂ separation have been currently commercialized, such as cellulose acetate, polyimide, polysulfone, polycarbonate, polyethersulfone... However, membrane technology still has some disadvantages, since long-term stability of the flux and the membrane material is still not proved to be reliable and there is a trade-off between permeability and selectivity, in most cases polymers have high permeability with relatively low selectivity values.

The application of supported liquid membranes (SLMs) for gas/vapor separations has been widely investigated over the last 20 years. In a SLM, the membrane pores are impregnated with a selected solvent, and permeation of the gas/vapor molecules occurs according to a solution-diffusion mass trans-
carrier mechanism. The gas separation using SLM combines the advantages of permeation and extraction; the selectivity of those membranes is higher than that of non-impregnated liquid membranes (conventional membranes) if appropriate solvents are selected.\(^9\) The permeability across supported liquid membranes is higher than when using solid membranes, because the diffusion of species in liquids is faster compared to the diffusion in solids. Even though SLMs are considered attractive for gas separations, their application in industry is still limited, mainly due to problems in their stability and long-term performance.

Ionic liquids (ILs) are organic salts that are liquid at room temperature, thermally stable and non-flammable, and have a negligible vapor pressure, and these properties make them ideal candidates as the separation medium for liquid membranes.\(^{10–14}\) Supported ionic liquid membranes (SLMs) are a new type of membrane system composed of ionic liquids (ILs) impregnated onto polymeric or inorganic supports. Their advantages in gas separation include the high solubility of CO\(_2\) in selected ILs, they are environmentally friendly and can effectively treat gases consisting of a wide range of CO\(_2\) amounts, and they can eliminate the problem of solvent evaporation and leaching that typically occur in SLMs due to the negligible vapor pressure and moderate high viscosity of ionic liquids, allowing for obtaining liquid membranes with high stability.\(^{15–23}\) Different types of ionic liquids were used to prepare SILPs and membranes were tested under a variety of conditions. Membrane separation performance was evaluated based on gas permeability and selectivity. He/CO\(_2\) permeability and selectivity of SILPs based on hexyl methyl imidazolium and methylimidazolium based ionic liquids from 25 °C to 75 °C, the selectivity increased from 7.33 to 9.\(^{25}\) The permeability of groups of gases (CO\(_2\), SO\(_2\)) and (N\(_2\), O\(_2\), CO\(_2\), CH\(_4\)) has been investigated using different SILMs.\(^{26–31}\) The results showed that selectivity of CO\(_2\)/air, SO\(_2\)/air, CO\(_2\)/N\(_2\), CO\(_2\)/CH\(_4\), and O\(_2\)/N\(_2\) reached 86–87 %, 73–81 %, 86–88 %, 82–86 %, and 57–73 %, respectively. In order to increase membrane stability and selectivity, several kinds of composite membranes have been recently prepared from polymers and ionic liquids, and used for CO\(_2\) separation from hydrocarbon gases.\(^{32–37}\)

Promising results encourage further research in this field. This work attempts to focus on some aspects: synthesis and structural characterization of some ionic liquids, immobilization of synthesized ILs onto preselected polymer membranes, calculation of the amount of ionic liquid impregnated, evaluation of the filling extent of ionic liquids in the pores of membranes, determination of the change of the structural surface of SLMs after immobilization of ILs, effect of pressure on the working stability of SLMs, evaluation of permeability of the single gases and of mixed gas (CO\(_2\) and CH\(_4\)), selectivity of CO\(_2\)/CH\(_4\) mixture, and the influence of ionic liquid structure and type of polymer membranes on properties of SILPs.

### Experimental

#### Materials

**Polymeric porous membranes**

The supported ionic liquid membranes were prepared using three different polymeric porous membranes as supporting materials, with a similar pore size but with different chemical nature, made of polyvinylidene fluoride (PVDF), polyethersulfone (PES) and cellulose acetate (CA), provided by Sterlitech Company, USA. These membranes play the role of supporting material of ionic liquids, and are characterized by their high chemical resistance. The pore size, porosity, thickness, dimension of these membranes are summarized in Table 1.

**Chemicals**

Methyl imidazole 99.5 %, \(n\)-butyl chloride 99.95 %, sodium tetrafluoroborate (NaBF\(_4\)) were provided by Merk Schuchardt OHG, Germany. Ethyl acetate 99.5 %, acetonitrile 99.55 %, methanol 99 %, ethanol 99 %, dichloromethane 99.5 %, ammonium acetate 99 % were provided by Guangdong Guanghua, China. They were used without further purification.

Pure gases CO\(_2\), CH\(_4\), N\(_2\), and CO\(_2\)/CH\(_4\) mixture (50:50 volume ratio, purity of 99.99 %) were provided by Cryotech Company, Vietnam.

#### Synthesis of ionic liquids

Synthesis of ionic liquids 1-\(n\)-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF\(_4\)]), 1-\(n\)-butyl-3-methyl imidazolium acetate

<table>
<thead>
<tr>
<th>Table 1 – Properties of membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Membrane</strong></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>PVDF</td>
</tr>
<tr>
<td>PES</td>
</tr>
<tr>
<td>CA</td>
</tr>
</tbody>
</table>

### References

([BMIM][CH₃COO]), and 1-n-octyl-3-methyl imidazolium acetate ([OMIM][CH₃COO]) was performed in two steps.

In the first step, 1-methyl imidazolium and butyl chloride (or octyl chloride) were stirred at 70–75 °C for 100 h to form 1-butyl methyl imidazolium chloride ([BMIM]Cl) or 1-octyl methyl imidazolium chloride ([OMIM]Cl). The reaction mixture was extracted with ethyl acetate to remove unconverted reagents (yield = 98 %).

In the second step, ionic liquids [BMIM][CH₃COO] ([OMIM][CH₃COO]) and [BMIM][BF₄] were synthesized through the exchange reactions of [BMIM]Cl ([OMIM]Cl) with NH₄CH₃COO or NaBF₄ in acetone, stirred at room temperature for 48 h. After the reaction was finished, inorganic salts and solvents were removed to obtain pure ionic liquids (yield = 90 – 93 %).

**Preparation of supported ionic liquid membranes (SILMs)**

The polymer membranes were placed to dry in a desiccator for several days and the original weights were determined. These membranes were then immersed in corresponding ionic liquids for 48 h to allow ionic liquids to penetrate and stabilize in the membranes. The excess ionic liquids on the membrane surface was cleaned with paper tissue. The amount of ILs immobilized in the membrane was determined gravimetrically by the difference in weights of the membrane before and after IL impregnation.

**Characterization of ionic liquids and membrane surface**

Infrared spectra (IR) of the prepared ionic liquids were measured using an IMPAC 410 spectrometer (Nicolet, USA). Mass spectra (MS) were measured by a LC/MS/MS-Xevo, API-ESI spectrometer in MeOH. Nuclear magnetic resonance spectra ¹H-NMR were measured using Bruker Advance in DMSO (for [BMIM][BF₄] and [BMIM][CH₃COO]), and in D₂O (for [OMIM][CH₃COO]) solutions. The surface characteristics of polymer membranes and SILPs were measured by a scanning electron microscope (SEM) S4800-NIHE 10 kV.

**Selection of suitable pressure difference between feed and permeate compartments**

The experiments were performed using a system as shown in Fig. 1. The stainless steel chamber consisted of feed and permeation compartments, which were separated by the supported ionic liquid membrane. The effective membrane area was 14.5 cm². Firstly, the stability of supported ionic liquid membranes (SILMs) was investigated by gradually increasing the difference in pressure between the feed and permeation compartments. The supported ionic liquid membrane SILP to be investigated (9 kinds of SILPs) was installed within the two chamber compartments. The different amounts of N₂ gas were filled in each compartment to form the pressure differences between them. The pressure difference increased from 0.4 to 1.9 bar. The pressures in both compartments were detected using two pressure gauges (Extech, USA) in order to evaluate the stability of SILMs by following the sudden change in pressure difference of the two compartments.

**Gas permeation experiments**

**Single gas permeability**

The permeability of pure gases (CH₄ and CO₂) through the supported ionic liquid membranes was determined using the experimental apparatus (Fig. 1). The apparatus consisted of one feed compartment and one permeate compartment. Those two compartments were separated by the investigated membrane. The permeation cell was vacuumed and filled with investigated gas several times to ensure that only the investigated gas was filled in the system. The pure gas was introduced into the two compartments from bottle 1. The initial transmembrane pressures (initial difference in pressure between the feed and the permeate compartments) were established at around 1 bar. The pressure change in both compartments over time was measured by two pressure gauges (Extech, USA).

**Gas mixture permeability**

The experimental procedure was similar to that used for measuring the single gas permeability. CO₂/CH₄ binary mixture (50/50 by volume) was ad-
mitted into both compartments of the permeation cell. The gas mixture was pressurized into the feed and permeate compartments (an initial transmembrane pressure of around 1 bar), and the pressure change in both compartments over time was detected using two pressure gauges. Samples from the feed and permeate compartments were collected and analyzed by online GC (CHROMPACK) at the beginning and end of the experiment.

**Calculation methods**

Pore volume of polymer membranes is calculated according to eq. 1.

\[ V_{\text{por}} = V_{\text{memb}} \times P_{\text{memb}} = \pi d^2 l \times P_{\text{memb}} \]  

(1)

where, \( V_{\text{por}} \) is pore volume of membrane, \( V_{\text{memb}} \) is membrane porous volume, \( P_{\text{memb}} \) is porosity of membrane, \( d \) and \( l \) are diameter (cm), and thickness (cm) of the membranes, respectively. Ionic liquid volume immobilized on polymer membranes is given by eq. 2.

\[ V_{\text{IL/memb}} = \frac{m}{d} \]  

(2)

where \( m \) and \( d \) are immobilized ionic liquid weight (g), and density (g cm\(^{-3}\)), respectively.

The permeability of a pure gas through a membrane is calculated according to the following equation:

\[ \frac{1}{\beta} \ln \left( \frac{P_{\text{feed}} - P_{\text{perm}}}{P_{\text{feed}} - P_{\text{perm}}} \right) = \frac{1}{\beta} \ln \left( \frac{\Delta P_0}{\Delta P} \right) = P \frac{t}{l} \]  

(3)

where \( P_{\text{feed}} \) and \( P_{\text{perm}} \) are the pressures in the feed and permeate compartments (Pa), respectively, \( P \) is membrane permeability (m\(^2\) s\(^{-1}\)), \( t \) is time (s), and \( l \) is membrane thickness (m). The geometric parameter \( \beta \) (m\(^{-1}\)) is characteristic of the geometry of the cell shown in Fig. 1, and is given by

\[ \beta = A \left( \frac{1}{V_{\text{feed}}} + \frac{1}{V_{\text{perm}}} \right) \]  

(4)

where \( A \) is membrane area (m\(^2\)), and \( V_{\text{feed}} \) and \( V_{\text{perm}} \) are the volumes of the feed and permeate compartments (m\(^3\)), respectively. The ideal selectivity (\( \alpha_{A:B} \)) can be determined by dividing the permeabilities of two different pure gases (A and B) (5).

\[ \alpha_{A:B} = \frac{P_A}{P_B} \]  

(5)

In the gas mixture experiments, the selectivity (\( \alpha_{A:B} \)) is given by the equation:

\[ \alpha_{A:B} = \frac{y_A / x_A}{y_B / x_B} \]  

(6)

where \( y_A \) and \( y_B \) are mole fractions of gases A and B in the permeate compartment, respectively, and \( x_A \) and \( x_B \) are mole fractions of gases A and B in the feed compartment, respectively. The yield separation of gas A from a mixture with gas B is given by the eq. (7):

\[ H = \frac{\alpha_{A:B}}{\alpha_{A:B} + 1} \]  

(7)

where \( \alpha_{A:B} \) is selectivity.

**Results and discussion**

**Characterization of synthesized ionic liquids**

Ionic liquids were characterized by FT-IR, \(^1\)H-NMR, \(^{13}\)C-NMR and mass spectra. Structures of synthesized ionic liquids are given in Fig. 2.

**FTIR spectroscopy**

Bands of wave number 2905 cm\(^{-1}\) and 2869 cm\(^{-1}\) are the aliphatic asymmetric and symmetric (C–H) stretching vibrations. The bands of wave number of 1193 and 1112.93 cm\(^{-1}\) are due to the bending vibrations of methyl groups. The broad band in the range of 3124.68 – 3200.97 cm\(^{-1}\) is due to quaternary amine salt formation. The bands in the range 3157 – 3147 cm\(^{-1}\) come from C=H bond in imidazolium ring. C=C and C–C stretching vibrations are shown by wave numbers 1640 – 1680 cm\(^{-1}\) and 1558 – 1577 cm\(^{-1}\), respectively.

The band at wave numbers 832 – 886 cm\(^{-1}\) is due to the C–N stretching vibration. The band in range 1100 – 1000 cm\(^{-1}\) in FT-IR spectra of [BMIM] [BF\(_4\)] is due to the presence of B–F bond. The bands in the range of 1700 – 1730 cm\(^{-1}\) in FT-IR spectra of [BMIM][CH\(_3\)COO] and [OMIM][CH\(_3\)COO] have been assigned the C=O stretching vibrations in ester groups.

\(^1\)H-NMR and \(^{13}\)C-NMR spectra

Examples of numbering carbon and corresponding hydrogen atoms in ionic liquids are shown in Fig. 2.

\(^1\)H-NMR data in ppm (δ) from the internal standard (TMT, 0.0 ppm), chemical shift (multiplicity, integration), and \(^{13}\)C-NMR data in ppm (δ) from the internal standard (TMS, 0.0 ppm) were reported. The results of FT-IR and \(^1\)H-NMR analysis of [BMIM][BF\(_4\)], [BMIM][CH\(_3\)COO], and [OMIM][CH\(_3\)COO] have been assigned the C=O stretching vibrations in ester groups.

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1-n-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF\(_4\)]

\[ \text{IR (KBr) } \nu/cm^{-1} 3628, 3164, 2965, 2879, 1574, 1484, 1062, 484; \]

\[ \text{\(^1\)H-NMR (500 MHz, DMSO-d) } \delta (ppm): 8.99 (s, 1H, CH), 7.70 (s,
The results of FT-IR and 1H-NMR analysis of [BMIM][BF₄], [BMIM][CH₃COO], and 1H-NMR data in ppm (δ ppm): 9.68 (s, 1H, CH), 7.63 (s, 1H, CH), 4.16 (t, 2H, CH₂), 0.89 (t, 3H, CH₃). Some properties of ILs at 25 °C are:

- **1-n-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄]**:
  - IR (KBr) ν/cm⁻¹: 3628, 3164, 1440, 1403, 1318, 1265, 1170, 1120, 951, 726.
  - 1H-NMR (500 MHz, DMSO-d) δ ppm: 9.68 (s, 1H, CH), 7.63 (s, 1H, CH), 4.16 (t, 2H, CH₂), 0.89 (t, 3H, CH₃).

- **1-n-octyl-3-methylimidazolium acetate [OMIM][CH₃COO]**:
  - IR (KBr) ν/cm⁻¹: 3423, 3081, 2960, 1712, 1646, 1384, 1170, 518, 458.
  - 1H-NMR (500 MHz, DMSO-d) δ ppm: 7.36 (s, 1H, CH), 7.02 (s, 1H, CH), 6.92 (s, 1H, CH), 4.08 (t, J 14, 7.0, CH₃).

**Table 2 – Some properties of ILs at 25 °C**

<table>
<thead>
<tr>
<th>Property</th>
<th>[BMIM][BF₄]</th>
<th>[BMIM][CH₃COO]</th>
<th>[OMIM][CH₃COO]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass (g mol⁻¹)</td>
<td>226</td>
<td>198</td>
<td>255</td>
</tr>
<tr>
<td>Density (g cm⁻³, 25 °C)</td>
<td>1.17</td>
<td>1.02</td>
<td>1.05</td>
</tr>
<tr>
<td>Viscosity (N s m⁻², 25 °C)</td>
<td>0.1538</td>
<td>0.440</td>
<td>0.5451</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>−71</td>
<td>&lt;−20</td>
<td>−13</td>
</tr>
</tbody>
</table>

Based on FT-IR and NMR, it was observed that synthesized ILs are [BMIM][BF₄], [BMIM][CH₃COO], and [OMIM][CH₃COO]. Some properties of the three ionic liquids are given in Table 2.

### Impregnation of ionic liquids on porous polymer membranes

To evaluate the impregnation of ionic liquids on the pores of polymer membranes, their weight was determined gravimetrically before and after IL impregnation. The volume of immobilized ionic liquids was then determined and compared to the volume of pore of polymer membranes.

**Table 3 – Determination of ionic liquids weight immobilized on polymer membranes**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ionic liquid</th>
<th>Original membrane weight (g)</th>
<th>Weight of SILMs (g)</th>
<th>IL weight immobilized on membrane (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>[BMIM][BF₄]</td>
<td>0.1353</td>
<td>0.3669</td>
<td>0.2316</td>
</tr>
<tr>
<td></td>
<td>[OMIM][CH₃COO]</td>
<td>0.3601</td>
<td>0.2224</td>
<td></td>
</tr>
<tr>
<td>PES</td>
<td>[BMIM][BF₄]</td>
<td>0.2727</td>
<td>0.2183</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[OMIM][CH₃COO]</td>
<td>0.2818</td>
<td>0.2128</td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>[BMIM][BF₄]</td>
<td>0.2913</td>
<td>0.2123</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[OMIM][CH₃COO]</td>
<td>0.2854</td>
<td>0.2064</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4 – Pore volume of membrane and volume of ionic liquids immobilized on polymer membranes**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ionic liquid</th>
<th>Pore volume of membrane, ( V_{pore} ) (m³)</th>
<th>Ionic liquids volume immobilized on membrane, ( V_{imm} ) (m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>[BMIM][BF₄]</td>
<td>0.195 · 10⁻¹</td>
<td>0.198 · 10⁻¹</td>
</tr>
<tr>
<td></td>
<td>[OMIM][CH₃COO]</td>
<td>0.211 · 10⁻¹</td>
<td></td>
</tr>
<tr>
<td>PES</td>
<td>[BMIM][BF₄]</td>
<td>0.202 · 10⁻¹</td>
<td>0.186 · 10⁻¹</td>
</tr>
<tr>
<td></td>
<td>[OMIM][CH₃COO]</td>
<td>0.203 · 10⁻¹</td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>[BMIM][BF₄]</td>
<td>0.185 · 10⁻¹</td>
<td>0.195 · 10⁻¹</td>
</tr>
<tr>
<td></td>
<td>[OMIM][CH₃COO]</td>
<td>0.197 · 10⁻¹</td>
<td></td>
</tr>
</tbody>
</table>
It can be seen from Tables 3 and 4 that the volumes of ionic liquids immobilized on polymer membrane are higher than the volume of membrane pores. This shows that all the pores of polymer membrane were filled with ionic liquids, while a part of ionic liquids covered the surface of membrane. In all the experiments, the volumes of immobilized tetrafluoroborate ionic liquid were lower than those of acetate ionic liquids. This can be explained by the difference in viscosity of the three ILs, the viscosity of $[\text{BMIM}][\text{BF}_4]$ (0.1538 N s m$^{-2}$) is lower than that of $[\text{BMIM}][\text{CH}_3\text{COO}]$ (0.440 N s m$^{-2}$) and of $[\text{OMIM}][\text{CH}_3\text{COO}]$ (0.5451 N s m$^{-2}$) at 25°C.

**SEM results of original polymer membranes and SILMs**

Surface properties of membranes and SILMs were characterized by a Scanning Electron Microscope (SEM) – S-4800, Hitachi High-Tech., Japan. The SEM images are shown in Figs. 3 – 5. The appearance and mechanical stability of PVDF and PES membranes had not changed after impregnation with ionic liquids. The porous and uniform surfaces of membranes were covered in ionic liquids (Figs. 3 – 5).

SEM images of cellulose acetate membranes before and after soaking in ionic liquids given in Fig. 5, show that the surface of membranes was destroyed. The mechanical stability of the membranes decreased dramatically and the membranes became much softer, which could also be observed by the naked eye. These results show that cellulose acetate membranes are not suitable for immobilizing ionic liquids because some ILs can dissolve the biomass-based polymers. This is consistent with the results of experimental work carried out by Hou et al.$^{38}$ Some ionic liquids can dissolve lignin and cellulose, and many researchers focus on using them as solvents for pretreating biomass to produce bioethanol.

The instability of cellulose acetate membrane was clearly observed during investigation of the influence of pressure difference between feed and permeate compartments on the stability of SILPs (see the next section).

**Appropriate pressure difference between feed and permeate compartments**

Different ILs within nine SILMs made from three distinct polymeric
membranes and three ionic liquids were tested in order to select the best membrane support and the best range of pressure difference between the two compartments of the system.

The stability of investigated SILPs as a function of initial transmembrane pressure is shown in Table 5. When the initial transmembrane pressure increased, the stability of SILMs deceased; the membranes can even be broken when the initial transmembrane pressure is high enough. The PVDF based SILMs have the highest stability, while the cellulose acetate membranes showed the lowest stabilities. These results and the obtained SEM results demonstrated that cellulose acetate membranes are not stable in contact with [BMIM][BF4], [BMIM][CH3COO], and [OMIM][CH3COO] ionic liquids. SILMs from PES and PVDF membranes with high stability were used for experiments of measuring permeability of gases and membrane selectivity. The pressure difference in the range of 0.7 – 1.3 atm was selected for gas permeability and selectivity measurements to ensure the stability of SILMs.

Single gas permeation results

The effect of ILs structure (different alkyl chain length and distinct anions) and of polymer membranes on the membrane permeability and selectivity was studied for the pure gases CH4 and CO2.

All the permeability, selectivity and separation yield values were calculated according to Eqs. 5 – 7. Table 6 shows permeability of pure CO2 and CH4 gases through the supported ionic liquids membrane. CO2 permeability was higher than CH4 permeability for all the SILMs. There is a small difference in molecular size between these two gases (3.69 ⋅ 10–10 m for CO2 and 3.76 ⋅ 10–10 m for CH4), therefore, the difference in permeability is due to the higher polarity of CO2 compared to that of CH4.

Influence of the IL cation

The CO2 and CH4 permeability of the SILMs prepared with two hydrophilic supports and two different ILs was measured for the different alkyl chain length of the 1-alkyl side chain of cations. The influence of the alkyl chain length of the 1-alkyl side chain of cations for the anions [CH3COO]–

<table>
<thead>
<tr>
<th>Entries</th>
<th>Supported ionic liquid membranes</th>
<th>Permeability of a pure gas ·10–11 (m2·s–1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO2</td>
</tr>
<tr>
<td>1</td>
<td>[BMIM][BF4]/PES</td>
<td>41.90±0.51</td>
</tr>
<tr>
<td>2</td>
<td>[BMIM][CH3COO]/PES</td>
<td>32.90±0.50</td>
</tr>
<tr>
<td>3</td>
<td>[OMIM][CH3COO]/PES</td>
<td>59.50±0.55</td>
</tr>
<tr>
<td>4</td>
<td>[BMIM][BF4]/PVDF</td>
<td>46.60±0.45</td>
</tr>
<tr>
<td>5</td>
<td>[BMIM][CH3COO]/PVDF</td>
<td>38.30±0.35</td>
</tr>
<tr>
<td>6</td>
<td>[OMIM][CH3COO]/PVDF</td>
<td>65.98±0.65</td>
</tr>
</tbody>
</table>

Table 5 – Differential pressure between feed compartment and permeate compartment

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>0.4</th>
<th>0.7</th>
<th>1.0</th>
<th>1.3</th>
<th>1.5</th>
<th>1.7</th>
<th>1.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][BF4]/PES</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>[BMIM][CH3COO]/PES</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>[OMIM][CH3COO]/PES</td>
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<td>✓</td>
<td>✓</td>
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<tr>
<td>[BMIM][BF4]/PVDF</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>[BMIM][CH3COO]/PVDF</td>
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<td>[BMIM][BF4]/CA</td>
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<tr>
<td>[BMIM][CH3COO]/CA</td>
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<tr>
<td>[OMIM][CH3COO]/CA</td>
<td>✓</td>
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<td>✓</td>
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<td>✓</td>
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</tbody>
</table>
✓ : stable
✗ : unstable/break

Fig. 5 – Surface of cellulose acetate membrane before and after impregnation with different ILs (a: original, b: after impregnation with [OMIM][CH3COO], c: after impregnation with [BMIM][CH3COO], d: after impregnation with [BMIM][BF4])
on the permeability of CO$_2$ and CH$_4$ gases of PES and PVDF based SILPs, is presented in Table 6. For easy analysis, the permeability ratios for the pair C$_8$MIM$^+$/C$_4$MIM$^+$ with the respective membranes PVDF and PES, are given in Table 7. From the data in Table 7, CO$_2$ permeability increases approximately 2 times and CH$_4$ permeability increases approximately 1.5 times with an increase in the carbon numbers of the 1-alkyl side chain of cation for both PVDF and PES membranes. In addition, the diffusion of gases through respective SILPs should decrease due to higher viscosity of [OMIM][CH$_3$COO] compared with [BMIM][CH$_3$COO]. Therefore, the resulting estimated permeability must increase by a higher factor. These results show that solubility of gases in ionic liquids significantly affects the transport of gases through ILs with different alkyl chain length of the 1-alkyl side chain of cations. The structure of membrane only slightly affects the permeability of gases, and the permeability of gases through the PVDF membrane is higher than through PES membrane.

**Influence of the IL anion and membrane structure**

The influence of structure of anions on the permeability of SILPs was also investigated. The viscosity has a significant influence on the permeability of CH$_4$ through SILMs. Permeability of gases using SILPs based on [BMIM] and anion [CH$_3$COO]$^-$ is lower than using SILPs that contain the same cation and [BF$_4$]$^-$ anion, which have lower viscosity. The permeability increased from [BMIM][CH$_3$COO] to [OMIM][CH$_3$COO]) for both PVDF and PES membranes even though the viscosity increased correspondingly. However, the permeability of low-interacting gas (CH$_4$) changed only slightly.

In order to evaluate the feasibility of CO$_2$/CH$_4$ separation using SILPs, the CO$_2$/CH$_4$ ideal selectivities for the membranes tested were calculated. The higher permeability of CO$_2$ compared to CH$_4$ points to the possibility of separation of CO$_2$ from its mixture with CH$_4$.

Ideal selectivity and separation yield depend on the type of ionic liquids and carriers (polymer membranes). In this study, the SILP formed from ionic liquid [BMIM][BF$_4$] and PVDF membrane showed the highest selectivity and yield, 23.9 % and 96 %, respectively. The other SILPs also gave high selectivity with ideal yield over 94 %.

**Gas mixture permeation results**

Gas mixture permeation of SILPs was calculated based on the change in composition of gas mixtures in feed and permeate compartments, which was measured using GC–TCD online analysis. The SILPs studied were made from three ILs [BMIM][BF$_4$], [BMIM][CH$_3$COO], and [OMIM][CH$_3$COO], and two kinds of membrane materials – PVDF and PES. The gas mixture (CO$_2$ and CH$_4$ with a 50:50 volume ratio) was injected into feed and permeate compartments with the suitable initial transmembrane pressures which were chosen as already described above. The selectivity and yield were calculated from obtained gas compositions (Table 9).

Similarly to the ideal case, SILMs made of [BMIM][BF$_4$] gave the higher selectivities when compared to those of other ILs. The selectivities of [BMIM][BF$_4$]-based SILMs reached 21.1 for PES membrane and 22.8 for PVDF membrane, and the separation yields reached 95.7 and 95.9, respectively. [OMIM][CH$_3$COO]-based SILPs also lead to rather high selectivities and yields (selectivities of 17.3 and 19.5; separation yields of 94.5 and 95.1, respectively). However, the low cost and stability of [OMIM][CH$_3$COO] ionic liquid towards moisture makes its SILPs more preferable.

**Table 7 – Permeability ratios for the pair C$_8$MIM$^+$/C$_4$MIM$^+$ with the respective membranes PVDF and PES**

| Permeability ratio | Membrane | Gas  |  |  |
|--------------------|----------|-----|  |  |
| C$_8$MIM$^+$/C$_4$MIM$^+$ | PVDF | 1.89 | 1.48 |  |
| C$_8$MIM$^+$/C$_4$MIM$^+$ | PES | 2.02 | 1.47 |  |

**Table 8 – Ideal CO$_2$/CH$_4$ selectivity and performance of SILMs**

<table>
<thead>
<tr>
<th>Supported ionic liquid membranes</th>
<th>Ideal selectivity of CO$_2$/CH$_4$</th>
<th>Ideal separation yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][BF$_4$]/PES</td>
<td>22.41±0.26</td>
<td>95.73±0.03</td>
</tr>
<tr>
<td>[BMIM][CH$_3$COO]/PES</td>
<td>15.45±0.23</td>
<td>93.92±0.05</td>
</tr>
<tr>
<td>[OMIM][CH$_3$COO]/PES</td>
<td>19.01±0.21</td>
<td>95.00±0.04</td>
</tr>
<tr>
<td>[BMIM][BF$_4$]/PVDF</td>
<td>23.90±0.25</td>
<td>95.98±0.03</td>
</tr>
<tr>
<td>[BMIM][CH$_3$COO]/PVDF</td>
<td>17.65±0.31</td>
<td>94.64±0.06</td>
</tr>
<tr>
<td>[OMIM][CH$_3$COO]/PVDF</td>
<td>20.49±0.35</td>
<td>95.35±0.08</td>
</tr>
</tbody>
</table>

**Table 9 – CO$_2$/CH$_4$ selectivity and performance of SILMs in case of gas mixture**

<table>
<thead>
<tr>
<th>Supported ionic liquid membranes</th>
<th>Selectivity of CO$_2$/CH$_4$</th>
<th>Separation yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][BF$_4$]/PES</td>
<td>21.11±0.32</td>
<td>95.48±0.06</td>
</tr>
<tr>
<td>[BMIM][CH$_3$COO]/PES</td>
<td>13.91±0.23</td>
<td>93.29±0.04</td>
</tr>
<tr>
<td>[OMIM][CH$_3$COO]/PES</td>
<td>17.31±0.32</td>
<td>94.54±0.03</td>
</tr>
<tr>
<td>[BMIM][BF$_4$]/PVDF</td>
<td>22.82±0.22</td>
<td>95.80±0.02</td>
</tr>
<tr>
<td>[BMIM][CH$_3$COO]/PVDF</td>
<td>15.84±0.24</td>
<td>94.06±0.03</td>
</tr>
<tr>
<td>[OMIM][CH$_3$COO]/PVDF</td>
<td>19.50±0.31</td>
<td>95.12±0.05</td>
</tr>
</tbody>
</table>
The selectivities measured with gas mixtures are lower than ideal selectivities as calculated by equation (5) by 6 to 8%. This is explained as follows: The permeability of each gas is proportional to its concentration in the mixture. When the permeation takes place, for a while, the concentration of CO₂ decreases whereas that of CH₄ increases because of the higher permeability of CO₂ than that of CH₄. This leads to the decreased selectivity as calculated by eq. (5) with respect to the value calculated by eq. (5). However, the yields only decreased by 0.2 – 0.3% in the gas mixture case.

Conclusions

Ionic liquids [BMIM][BF₄], [BMIM][CH₃COO], and [OMIM][CH₃COO] were successfully synthesized, characterized, and impregnated on PES, PVDF, and CA membranes by direct impregnation method. The calculation results of the amount of ionic liquids immobilized on membranes as well as SEM results showed that ionic liquids filled the pores of the polymer membranes, while a small portion was on surface of the membranes. The amount of ionic liquid [OMIM][CH₃COO] immobilized on the membranes was higher than that on [BMIM][CH₃COO] and [BMIM][BF₄] because of its higher viscosity. Among membranes used, cellulose acetate swelled after impregnation with ionic liquids, therefore, it is not suitable for carrying investigated ionic liquids. This conclusion is also consistent with SEM measurements. The PVDF-based SILPs showed the highest stability and the suitable pressure difference between feed compartment and permeate compartment determined was from 0.7 to 1.5 bar.

The supported ionic liquid membranes in this study showed the selective permeability of CO₂ and high ability of separation of CO₂ from its mixture with CH₄. The CO₂/CH₄ selectivities and corresponding separation yield of SILPs increased with increasing the carbon numbers of the 1-alkyl side chain of cation in IL (from [BMIM to [OMIM]), and with the change in the counterion from [CH₃COO] to [BF₄]. The SILPs prepared from PVDF gave higher CO₂/CH₄ selectivities and separation yields when compared to those from PES. The SILPs prepared from [OMIM][CH₃COO] are preferable because of their stability, absence of halogens, and lower price.

SUPPLEMENTARY INFORMATION

The information of ILs spectra (FT-IR, NMR) are presented in "Supplementary Information” Section.

ACKNOWLEDGEMENTS

Financial support from the Ministry of Science and Technology, Vietnam, is gratefully acknowledged.

Supplementary information

Fig. S1 – of [BMIM][BF₄]
Fig. S2 – FT-IR spectrum of [BMIM][CH$_3$COO]
Fig. S4 – FT-IR spectrum of [BMIM][BF₄]

Fig. S5 – ¹H NMR spectra of [BMIM][CH₃COO]
Abbreviations

CA – cellulose acetate

[BMIM][BF₄] – 1-n-butyl-3-methylimidazolium tetrafluoroborate

[BMIM][CH₃COO] – 1-n-butyl-3-methylimidazolium acetate

FT-IR – Fourier transform infrared spectroscopy

IL – ionic liquid

ILs – ionic liquids

NMR – nuclear magnetic resonance

[OMIM][CH₃COO] – 1-n-octyl-3-methylimidazolium acetate

PES – polyethersulfone

PVDF – polyvinylidene fluoride

SILP – supported ionic liquid membrane

SILMs – supported ionic liquid membranes

SEM – scanning electron microscopy

References


Fig. S6 – ¹H NMR spectra of [OMIM][CH₃COO]


23. Barghi, S. H., Tootis, T. T., Sahimi, M., Solubility and diffusivity of H2 and CO2 in the ionic liquid [bmim][PF6], Int. J. Hydrogen Energy 40 (2015) 8713. doi: https://doi.org/10.1016/j.ijhydene.2015.05.037


34. Ito, A., Yasuda, T., Ma, X., Watanabe, M., Sulfonated polyl-imide/ionic liquid composite membranes for carbon dioxide separation, Polymer J. 49 (2017) 671. doi: https://doi.org/10.1038/pj.2017.31


