CO₂/N₂ SEPARATION BY SUPPORTED IONIC LIQUID MEMBRANES BASED ON TUBULAR CERAMIC SUPPORT IMPREGNATED WITH SELECTED IONIC LIQUID

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The separation of CO₂/N₂ by supported ionic liquid membranes (SILMs) is presented. SILMs have been developed through impregnation of the ceramic support nanopores of commercial PDMS (polidimethylosiloxane) membranes (made by Pervatech BV) and commercial microfiltration membranes (made by Inopor) with 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]). Comparison of the separation efficiency of SILMs prepared on the same ceramic supports shows that SILMs based on PDMS membranes show good stability and very high CO₂/N₂ selectivity. The obtained results present an inexpensive alternative in selective CO₂/N₂ separation by SILMs, especially when the choice of selectivity is the first priority. Comparison with Robeson upper bound correlation and literature data shows that applying the ionic liquid and appropriate impregnation method to PDMS membranes results in a significant improvement in separation performance.

Keywords: CO₂/N₂ separation; supported ionic liquid membranes (SILMs); PDMS

1. INTRODUCTION

The continuously growing consumption of fossil fuels and increase in CO₂ emissions is stimulating the development of new technologies for efficient removal of large quantities of CO₂ [1, 2]. CO₂ separation from post combustion gases can be achieved by adsorption, absorption, low temperature condensation or membrane separation. The most popular techniques used in industry for CO₂ capture from flue gases are amine scrubbing processes [3, 4]. Reported obstacles include: degradation and poor thermal stability of amines; high solvent losses caused by evaporation; and equipment corrosion [5, 6]. In addition, the total operating costs of the process may increase in the regeneration step because of the high heat of the reaction between CO₂ and amines [7, 8].
In recent years, supported ionic liquid membranes (SILMs) have been found to be promising tools for selective gas separation. In the SILM, ionic liquid (IL) is embedded in the porous structure of a polymer or inorganic support. The application of ILs as solvents for CO$_2$ absorption avoids the disadvantages of amine based methods for CO$_2$ removal from flue gases [9, 10]. IL properties include high CO$_2$ solubility, negligible vapor pressure, thermal stability and more environmentally friendly character, making them effective liquid CO$_2$ absorbents. The usage of ILs in the process of CO$_2$ absorption may lead to a significant reduction in investment and operation costs [11–13]. An important disadvantage of ILs, however, is their high viscosity and price.

CO$_2$/N$_2$ separation by SILMs was studied on polymeric and inorganic supports impregnated with different ILs. Scovazzo et al. [14] studied gas separation on a porous hydrophilic polyethersulfone (PES) support impregnated with different room temperature ionic liquids (RTILs) at a temperature of 30 °C. They found the CO$_2$ permeability in the range of 350–920 barrers and the CO$_2$/N$_2$ ideal selectivity in the range of 15–61. Bara et al. [15] used imidazolium based RTILs and measured CO$_2$ permeability between 210 and 320 barrers and CO$_2$/N$_2$ separation factor in the range of 16–26. Cserjési et al. [16] investigated SILMs based on a hydrophilic polyvinylidene fluoride (PVDF) support and 12 different RTILs. The CO$_2$ permeabilities were in the range of 94–750 barrers and the CO$_2$/N$_2$ ideal selectivities were in the range of 10.9–52.6. Neves et al. [17] investigated the effect of the length of alkyl cation chains on gas separation. They found that the CO$_2$ permeability and CO$_2$/N$_2$ ideal selectivity increased with alkyl cation chain length. Jindarat-samee et al. [18] used a PVDF porous support impregnated with imidazolium based IL to study the CO$_2$ permeability in the temperature range of 30–70 °C. The CO$_2$ permeabilities were in the range of 120–445 barrers and the ideal CO$_2$/N$_2$ selectivities were in the range of 42–86. Santos et al. [19] prepared SILMs by impregnating PVDF porous membranes with the following ILs: 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]); 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]); and vinylbenzyltrimethylammonium acetate ([Vbma][Ac]) for CO$_2$ selective separation from N$_2$. Experiments were carried out in the temperature range of 25–60 °C. The permeability increased and selectivity decreased with rising temperature for all studied ILs. The CO$_2$ permeabilities were between 852 and 2114 barrers and the CO$_2$/N$_2$ ideal selectivities were between 26.4–39.

Albo et al. [20] investigated SILMs based on porous Al$_2$O$_3$/TiO$_2$ tubes impregnated with [Emim][Ac]. They obtained a CO$_2$ permeability of 780 barrer and a CO$_2$/N$_2$ ideal selectivity of 35.4. Sánchez Fuentes et al. [21] found that NH$_2$-functionalised ceramic SILMs, with the amine group at the anionic part of the IL, showed a high permeability of 3000 barrer and a CO$_2$/N$_2$ ideal selectivity of 70.

To date, ILs have been immobilized in macropores and nanopores of polymeric and ceramic supports. The impregnation of nanopores can significantly improve the stability of the IL phase in a SILM by the reduction of IL displacement from the porous structure of the support [22–25].

This work presents a comparison study of CO$_2$/N$_2$ separation by SILMs, developed through the impregnation of the ceramic supports of microfiltration and PDMS membranes with [Emim][Ac]. The ceramic supports of both the investigated commercial membranes were made out of α-Al$_2$O$_3$, with an average pore size of 100 nm. Two methods of impregnation were used: coating and soaking. [Emim][Ac] was used due to its high predictable CO$_2$ absorption capacities, chemical absorption mechanism, moderate cost and known properties. Imidazolium based ILs with an acetate anion show strong CO$_2$ absorption. Shifflet et al. [26–29] studied the CO$_2$ phase behavior in [Bmim][Ac] and [Emim][Ac] in temperatures of 10–75 °C and pressures up to 2 MPa. Applying ILs with a dominant physical absorption mechanism leads to low loading capacities in comparison with MEA (monoethanolamine) solutions. The CO$_2$ chemical absorption in imidazolium-based ILs can be an alternative to commonly used amine scrubbing processes.

Our target was to determine the CO$_2$/N$_2$ separation efficiency of the prepared SILMs, as well as the stability obtained by impregnation of the microfiltration and PDMS membranes with [Emim][Ac]. The effects of SILM layer thickness, feed temperature, pressure differences and impregnation methods on the performance of the developed SILMs were investigated.

2. EXPERIMENTAL

2.1. Setup

The experimental setup is shown in Figure 1. The main part of the setup was a stainless steel membrane module (7) with a fitted membrane (6).
CO₂/N₂ separation by supported ionic liquid membranes based on tubular ceramic support impregnated with selected ionic liquids

The feed gas from cylinder (1) through valve (2) was brought to a molecular sieve trap (3), where trace amounts of moisture were removed. Dried gas flowed to the membrane module (7). The feed gas pressure was measured by a manometer in the range of 0–5 bar with accuracy 0.1 bar. The permeate was at atmospheric pressure. The feed temperature was maintained at 20, 40 and 60 °C using a temperature control system with accuracy ±0.2 °C. The gas flow rate was measured by a Varian digital flowmeter with 3 % accuracy.

![Fig. 1. Experimental setup. 1 – gas cylinder, 2 – pressure valve, 3 – molecular sieve, 4 – exhaust valve, 5 – heating jacket, 6 – membrane, 7 – membrane module, 8 – flowmeter](image)

2.2. SILM preparation

The SILMs were prepared based on PDMS membrane made by Pervatech BV and microfiltration membrane made by Inopor. For both commercial tubular ceramic membranes the outer diameter was 0.01 m, the inner diameter 0.007 m and the length was 0.25 m. The ceramic support of both membranes was made out of α-Al₂O₃ with an average pore size of 100 nm. The active layers of the microfiltration and PDMS membranes were composed of 100 nm TiO₂ and PDMS respectively. Active layers were placed inside the ceramic tubes.

The ceramic supports of both membranes were impregnated with [Emim][Ac] (97.8 %), purchased from Sigma-Aldrich. The IL was used after vacuum purification (about 24 h).

In our experiments, coating and soaking methods of impregnation were used to introduce the IL into the porous structure of the ceramic supports. The coating method was achieved by applying three layers of [Emim][Ac] to the outer surface of the ceramic tube. The IL was applied with a brush to uniformly distribute the IL in the ceramic support, and each layer was allowed to dry at room temperature (under vacuum). The soaking method consisted of submerging the outer surface of the ceramic tube in IL at room temperature and under vacuum for 24 h. The tube was then pulled out of the IL and dried with tissue paper. The mass of the membrane was measured before and after impregnation to determine the amount of IL used for impregnation.

2.3. Gas separation measurements

Ideal CO₂/N₂ selectivity was calculated as a ratio of the permeabilities of pure CO₂ and N₂ gases, measured under similar pressure:

\[ \alpha_{\text{CO}_2/\text{N}_2} = \frac{\frac{P_{\text{CO}_2}}{P_{\text{N}_2}}}{\frac{\Delta P_{\text{CO}_2}}{\Delta P_{\text{N}_2}}} \]  \hspace{1cm} (1)

Membrane molar flux can be calculated as follows:

\[ j_i = \frac{D_i S_i}{\delta} \frac{\Delta P}{\delta} = \frac{P_i}{\Delta P} \ \text{(2)} \]

The pure CO₂ and N₂ gas permeabilities (P) were calculated according to the formula:

\[ P_i = \frac{j_i \delta}{\Delta P} \]  \hspace{1cm} (3)

Thus, for the same membrane, selectivity can be expressed as follows:

\[ \alpha_{\text{CO}_2/\text{N}_2} = \frac{\frac{j_{\text{CO}_2}}{j_{\text{N}_2}} \delta}{\frac{\Delta P_{\text{CO}_2}}{\Delta P_{\text{N}_2}}} = \frac{\frac{\Delta P_{\text{CO}_2}}{\Delta P_{\text{N}_2}}}{\frac{\Delta P_{\text{CO}_2}}{\Delta P_{\text{N}_2}}} \]  \hspace{1cm} (4)

When transmembrane pressure \( \Delta P \) is the same, equation (4) simplifies to:

\[ \alpha_{\text{CO}_2/\text{N}_2} = \frac{j_{\text{CO}_2}}{j_{\text{N}_2}} \approx \frac{V_{\text{CO}_2}}{V_{\text{N}_2}} \]  \hspace{1cm} (5)

The measurements were carried out for pure gases CO₂ and N₂ (purity 99.99 %). Membranes were outgassed under vacuum before the measurement, and then the membrane module was flushed with the investigated gas and heated to a given temperature (20–60 °C). When the setup was preheated to the required temperature, the feed gas pressure was increased to 0.5 bar. After the flow through the membrane was stabilised, the gas flux was measured by a Varian digital flowmeter, and then the feed pressure was increased by 0.5 bar up to 7 bar and the measuring cycle was repeated. After reaching the maximum pressure (7 bar), the feed gas was changed, the setup was flushed and the measurements were repeated.
3. RESULTS AND DISCUSSION

The gas separation results obtained for the investigated membranes and for the SILMs prepared by impregnation of the ceramic supports of microfiltration membrane and PDMS membrane with [Emim][Ac] are presented in Figures 2–9.

As shown in Figure 2, CO₂ and N₂ permeabilities for the PDMS membrane on a ceramic support before impregnation with IL increased with increasing feed temperature and pressure difference. N₂ permeabilities were low in comparison with O₂ permeabilities.

![Fig. 2. Effect of feed temperature and pressure difference on CO₂ and N₂ mass flux for a PDMS membrane](image)

The ideal CO₂/N₂ selectivities for the PDMS membrane on a ceramic support before impregnating with IL ranged from 9 to 30, and they decreased with increased pressure difference and feed temperature (Fig. 3).

![Fig. 3. Effect of feed temperature and pressure difference on ideal CO₂/N₂ selectivity for a PDMS membrane](image)

The separation data for the ceramic microfiltration membrane before impregnation with IL are not presented. The pore size of 100 nm was not an effective barrier to separate CO₂/N₂. The selectivities were about 1, meaning that the membrane had no selective properties.

For the developed SILMs, the effects of feed temperature, pressure difference and impregnation method on CO₂/N₂ separation were investigated. Two methods of impregnation were used to develop the SILMs based on a tubular ceramic microfiltration membrane and a polymeric PDMS membrane with a ceramic support: coating and soaking.

For the SILM prepared by coating the outer surface of a PDMS membrane with [Emim][Ac], permeabilities increased with increasing feed temperature and pressure difference (Fig. 4).

![Fig. 4. Effect of feed temperature and pressure difference on CO₂ and N₂ permeabilities for a PDMS membrane impregnated by coating the outer side of the tube with [Emim][Ac]](image)

The CO₂/N₂ selectivities decreased with increasing feed temperature and pressure difference (Fig. 5). High selectivities were obtained from the SILM prepared by coating the ceramic support of a PDMS membrane: up to 152, compared to 30 for the PDMS membrane before impregnation with IL.

It should be noted that the measured CO₂ mass fluxes were much smaller than for the PDMS membrane before impregnation with IL; this may limit the application of the membrane. The cost and stability of SILMs prepared this way, however, may be advantageous, particularly in comparison with other SILMs made of advanced materials and expensive functionalised ILs.
For the SILM prepared by soaking the outer side of the PDMS membrane in [Emim][Ac], CO₂ and N₂ permeabilities increased with increasing feed temperature and pressure difference (Fig. 6). The SILM prepared this way showed smaller CO₂ permeabilities than those obtained from the coating method.

For the SILM prepared by soaking the outer side of the PDMS membrane in IL, the ideal CO₂/N₂ selectivities decreased with increasing temperature and pressure difference (Fig. 7). The measured selectivities were slightly better than those obtained from the PDMS membrane before impregnation with IL.

In Figures 8–9, the results for the SILM based on a ceramic microfiltration membrane impregnated by coating the outer side of the tube with [Emim][Ac] are presented.

Comparison of the results presented in Figures 4–7 and Figures 8–9 showed that for the SILM prepared by impregnation of a micro-
filtration membrane, the measured permeabilities and selectivities were much lower than those obtained from the SILM based on a PDMS membrane. This suggests that not all surfaces were correctly covered with IL in the case of the microfiltration membrane, or that the separating IL layer was destroyed and removed from the pores of the microfiltration membrane support.

3.1. Long-term stability and SILM thickness

The SILMs based on PDMS membranes prepared by coating and soaking the outer surfaces of the tubes with [Emim][Ac] showed good stability. In Figure 10, experimental data for the SILM prepared by coating the outer surface of the PDMS membrane with [Emim][Ac] are presented. Long-term experiments were carried out over a period of five days at a temperature of 20 °C and pressure of 1.5 bar. The time of continuous work of the SILM was about 5 h per day. Between experiments, the membrane was kept in the experimental setup in a nitrogen atmosphere. Permeabilities and selectivities decreased slightly at the beginning and then stabilized in subsequent experiments. The mass of IL in the SILM was controlled after each experimental series. The observed loss of mass of embedded IL within a five day period was about 1.5 %. Similar results were obtained for the SILM prepared by soaking.

![Fig. 10. Long-term stability of the prepared SILMs at a pressure of 1.5 bar and temperature of 20 °C.](image)

The SILM based on a PDMS membrane may be considered as a composite membrane consisting of two active layers. The first layer is the polymeric material (PDMS), with a thickness of 30 μm. The second layer is the IL in the pores of the ceramic support. The thickness of this layer was estimated based on the weight of the membrane before and after impregnation with [Emim][Ac]. Assuming that the IL was evenly distributed in the ceramic support of the prepared SILM, it was found that the IL layer thickness was 210 μm for coating the outer surface of the tube and 450 μm for soaking the outer side of the tube. The CO₂ and N₂ permeabilities decreased significantly with growing thickness of the IL layer from 210 μm to 450 μm (Figs. 4 and 6).

The SILM based on a microfiltration membrane prepared by coating was not stable. It lost its separation properties after one or two days of continuous work. The mass of embedded IL decreased with time. The IL layer inside the SILM was gradually removed from the nanopores of the ceramic support, and eventually the SILM lost its separation properties.

3.2. SILM performance comparison

The CO₂/N₂ separation efficiency of the investigated SILMs was compared with several polymeric SILMs [16–19, 30–31], as well as ceramic SILMs [20–21, 32–35] (Fig. 11). An upper bound correlation for polymeric membranes defined by Robeson [36] was included for comparison. Any separation results above this correlation represent an improvement to the currently reported state of research.

![Fig. 11. The separation performance comparison of developed SILMs with literature data (A – PDMS not impregnated, B – PDMS impregnated by coating, C – PDMS impregnated by soaking, D – microfiltration membrane impregnated by coating).](image)

As can be seen in Figure 11, the best results were obtained with the SILM prepared by coating the outer surface of the ceramic support of a PDMS membrane with [Emim][Ac]. The obtained results exceed the upper bound defined by Robeson and the literature data for ceramic and polymeric SILMs. These results may present an interesting alternative in the selective removal of CO₂ by SILMs, especially when the choice of selectivity is the first priority.
The results for the SILMs prepared by soaking the outer side of a PDMS membrane or a microfiltration membrane in [Emim][Ac] lie below the upper bound correlation given by Robeson and are comparable with CO$_2$/N$_2$ permeselectivity data found in the literature for polymeric and ceramic materials. The results obtained in these cases are only slightly better than those obtained for a PDMS membrane without IL.

4. CONCLUSIONS

Inexpensive SILMs were prepared by impregnation of ceramic supports of commercial tubular PDMS and microfiltration membranes with IL [Emim][Ac]. The same ceramic support, Al$_2$O$_3$, with an average pore size of 100 nm, was used to compare the CO$_2$/N$_2$ separation efficiency of the ceramic and polymeric materials.

For the developed SILMs, CO$_2$ and N$_2$ permeabilities increased and CO$_2$/N$_2$ ideal selectivities decreased with increasing feed temperature and pressure difference (Figs. 4–9). Two impregnating methods were used to develop SILMs based on PDMS membranes: coating and soaking. The best results were obtained by coating the ceramic support of a PDMS membrane with IL (Figs. 4–5). The developed SILM showed good long-term stability and very high CO$_2$/N$_2$ selectivities up to 152 (Fig. 5), compared to 30 for a PDMS membrane without IL (Fig. 3). Although the measured CO$_2$ and N$_2$ permeabilities were very small, the results may be of importance in instances where the choice of selectivity is the first priority.

For the SILM prepared by soaking the outer side of a PDMS membrane in [Emim][Ac], the ideal CO$_2$/N$_2$ selectivities ranged from 9 to 47 and were slightly higher than those obtained for a PDMS membrane without IL (Fig. 7). The CO$_2$ and N$_2$ permeabilities measured in this case were the lowest (Fig. 6). The permeabilities decreased significantly with the growing thickness of the IL layer in SILMs (Figs. 4 and 6).

For the SILM prepared by coating the outer surface of a microfiltration membrane with [Emim][Ac], the ideal CO$_2$/N$_2$ selectivities ranged from 5 to 30 and were smaller than those obtained for SILMs based on PDMS membranes (Fig. 9). Permeabilities of microfiltration membranes were significantly smaller than PDMS membranes (Fig. 8).

Comparison with literature data showed that the results for the SILM prepared by coating the outer surface of a PDMS membrane with [Emim][Ac] were above the upper bound correlation given by Robeson for polymeric membranes and also above the available literature data for ceramic and polymeric SILMs (Fig. 11). For the SILMs based on microfiltration membranes, the separation results were significantly below the upper bound defined by Robeson.

Applying an appropriate impregnation method to the ceramic support of a PDMS or microfiltration membrane may result in a significant improvement of the separation performance of the membrane. The low cost of a commonly used polymeric material (PDMS) and IL ([Emim][Ac]), as well as a simple method of IL immobilisation in a ceramic support, allows preparation of stable and highly selective SILMs.

NOMENCLATURE

\[ A \] – membrane area, m$^2$
\[ D \] – membrane diffusion coefficient, m$^2$s$^{-1}$
\[ j \] – mass flux, kg m$^{-2}$s$^{-1}$
\[ P \] – permeability, Barrer (1 Barrer = 2.99 $\times$ 10$^{10}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$)
\[ \Delta P \] – pressure difference on both membrane sides, bar
\[ s \] – sorption coefficient
\[ V \] – volumetric flow rate, m$^3$s$^{-1}$

Greek letters
\[ \alpha_{CO2/N2} \] – ideal membrane selectivity
\[ \delta \] – membrane thickness, m

Subscripts
\[ CO2 \] – carbon dioxide
\[ N2 \] – nitrogen

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