Macedonian Journal of Chemistry and Chemical Engineering, Vol. **39**, No. 1, pp. 101–108 (2020)

MJCCA9 – 798

ISSN 1857-5552
e-ISSN 1857-5625
DOI: 10.20450/mjcce.2020.1721
Original scientific paper

Received: February 25, 2019
Accepted: March 18, 2020

CO_2/N_2 SEPARATION BY SUPPORTED IONIC LIQUID MEMBRANES BASED ON TUBULAR CERAMIC SUPPORT IMPREGNATED WITH SELECTED IONIC LIQUID

Zenon Ziobrowski[*], **Adam Rotkegel**

Institute of Chemical Engineering, Polish Academy of Sciences, Gliwice, Poland
zenz@iich.gliwice.pl

The separation of CO_2/N_2 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 CO_2/N_2 selectivity. The obtained results present an inexpensive alternative in selective CO_2/N_2 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: CO_2/N_2 separation; supported ionic liquid membranes (SILMs); PDMS

РАЗДЕЛУВАЊЕ НА CO_2/N_2 СО ЈОНСКИ ТЕЧНИ МЕМБРАНИ НА ПОДЛОГА ОД ЦЕВЧЕСТА КЕРАМИКА ИМПРЕГНИРАНА СО СЕЛЕКТИРАНА ЈОНСКА ТЕЧНОСТ

Опишано е разделувањето на CO_2/N_2 со јонски течни мембрани на носачи (SILMs). SILMs беа подготвени со импрегнација на керамички подлоги со нанопори на комерцијални PDMS (полидиметилсилоксански) мембрани (произведени од Pervatech BV) и комерцијални мембрани за микрофилтрирање (произведени од Inopor) со 1-етил-3-метилимидазолиниум ацетат ([Emim][Ac]). Споредбата на ефикасноста на разделувањето на SILMs приготвени од исти керамички носачи покажува дека SILMs на основа на PDMS-мембрани покажува добра стабилност и многу висока селективност на CO_2/N_2. Добиените резултати претставуваат евтина алтернатива на селективноста на разделувањето на CO_2/N_2 со SILMs, особено кога изборот на селективноста е приоритет. Споредбата со корелација на горните граница на Robeson и литературните податоци покажува дека примената на јонски течности и соодветен метод на импреганција на PDMS-мембраните резултира во значително подобрување на способноста на разделување.

Клучни зборови: разделување на CO_2/N_2; јонски течни мембрани на носач (SILMs); PDMS

1. INTRODUCTION

The continuously growing consumption of fossil fuels and increase in CO_2 emissions is stimulating the development of new technologies for efficient removal of large quantities of CO_2 [1, 2]. CO_2 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 CO_2 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 CO_2 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. Jindaratsamee 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 ([Vbtma][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_2O_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_2O_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).

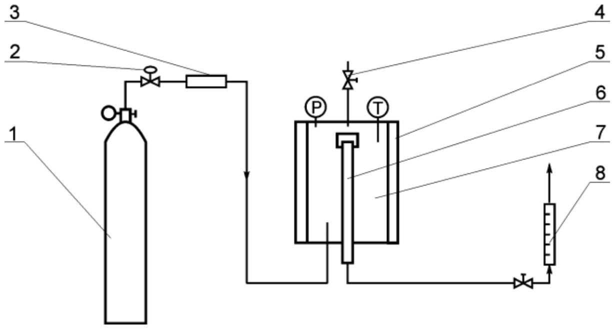

Fig. 1. Experimental setup. 1 – gas cylinder, 2 – pressure valve, 3 – molecolar sieve, 4 – exhaust valve, 5 – heating jacket, 6 – membrane, 7 – membrane module, 8 – flowmeter

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.

2.2. *SILM preparation*

The SILMs were prepared based on PDMS membrane made by Pervatech BV and micro-filtration 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-Al_2O_3 with an average pore size of 100 nm. The active layers of the microfiltration and PDMS membranes were composed of 100 nm TiO_2 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 CO_2/N_2 selectivity was calculated as a ratio of the permeabilities of pure CO_2 and N_2 gases, measured under similar pressure:

$$\alpha_{CO2/N2} = \frac{P_{CO2}}{P_{N2}} . \tag{1}$$

Membrane molar flux can be calculated as follows:

$$j_i = \frac{D_i s_i}{\delta} \Delta P = \frac{P_i}{\delta} \Delta P . \tag{2}$$

The pure CO_2 and N_2 gas permeabilites (P) were calculated according to the formula:

$$P_i = \frac{j_i \, \delta}{A \, \Delta P_i} . \tag{3}$$

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

$$\alpha_{CO2/N2} = \frac{\dfrac{j_{CO2} \, \delta}{A \, \Delta P_{CO2}}}{\dfrac{j_{N2} \, \delta}{A \, \Delta P_{N2}}} = \frac{j_{CO2}}{j_{N2}} \frac{\Delta P_{N2}}{\Delta P_{CO2}} . \tag{4}$$

When transmembrane pressure ΔP is the same, equation (4) simplifies to:

$$\alpha_{CO2/N2} = \frac{j_{CO2}}{j_{N2}} \cong \frac{V_{Co2}}{V_{N2}} . \tag{5}$$

The measurements were carried out for pure gases CO_2 and N_2 (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, CO_2 and N_2 permeabilities for the PDMS membrane on a ceramic support before impregnation with IL increased with increasing feed temperature and pressure difference. N_2 permeabilities were low in comparison with O_2 permeabilities.

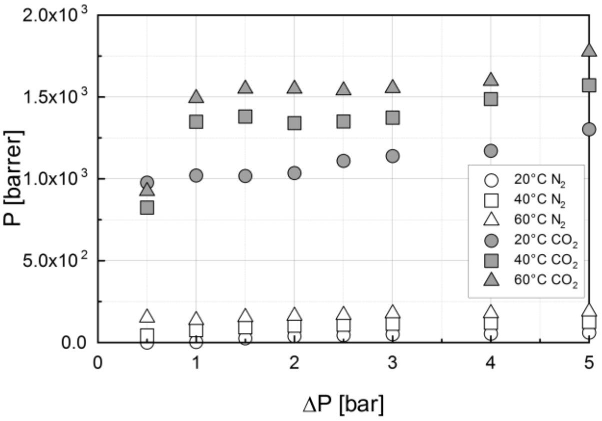

Fig. 2. Effect of feed temperature and pressure difference on CO_2 and N_2 mass flux for a PDMS membrane

The ideal CO_2/N_2 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).

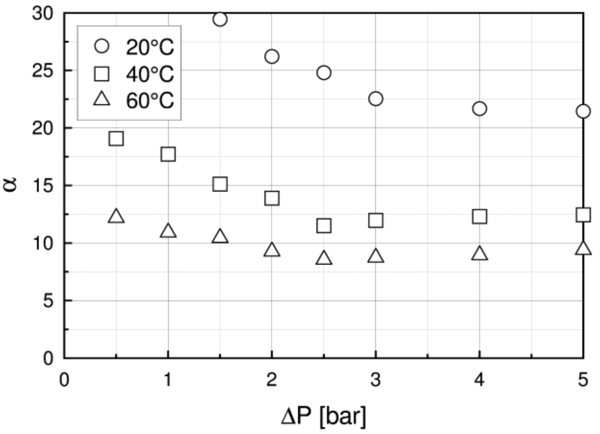

Fig. 3. Effect of feed temperature and pressure difference on ideal CO_2/N_2 selectivity for a PDMS membrane

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 CO_2/N_2. 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 CO_2/N_2 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).

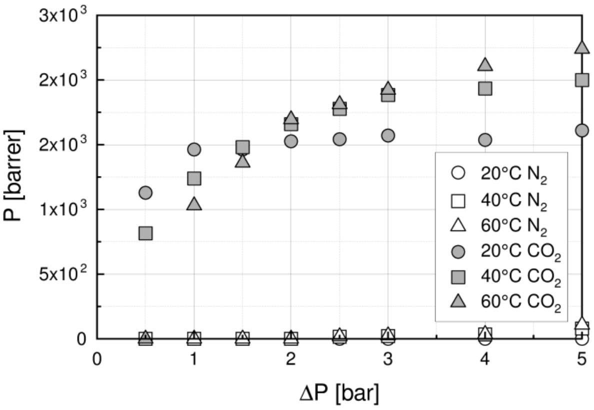

Fig. 4. Effect of feed temperature and pressure difference on CO_2 and N_2 permeabilties for a PDMS membrane impregnated by coating the outer side of the tube with [Emim][Ac]

The CO_2/N_2 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 CO_2 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.

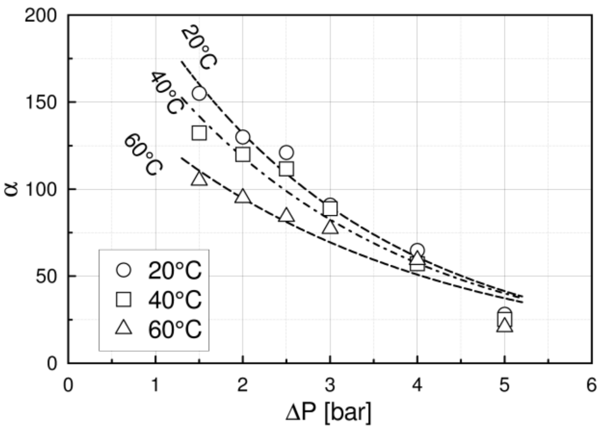

Fig. 5. Effect of feed temperature and pressure difference on ideal CO_2/N_2 selectivity for a PDMS membrane impregnated by coating the outer side of the tube with [Emim][Ac]

For the SILM prepared by soaking the outer side of the PDMS membrane in [Emim][Ac], CO_2 and N_2 permeabilities increased with increasing feed temperature and pressure difference (Fig. 6). The SILM prepared this way showed smaller CO_2 permeabilities than those obtained from the coating method.

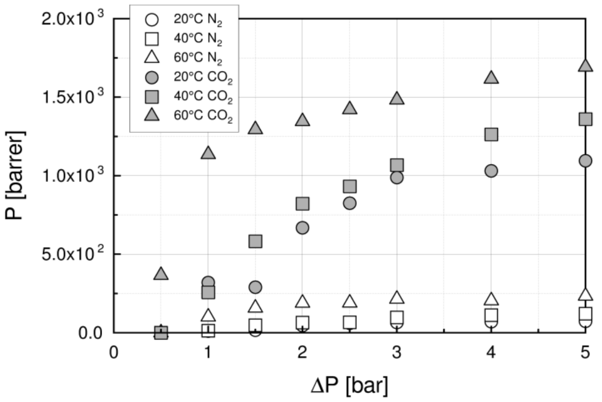

Fig. 6. Effect of feed temperature and pressure difference on CO_2 and N_2 permeability for a PDMS membrane impregnated by soaking the outer side of the tube with [Emim][Ac]

For the SILM prepared by soaking the outer side of the PDMS membrane in IL, the ideal CO_2/N_2 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.

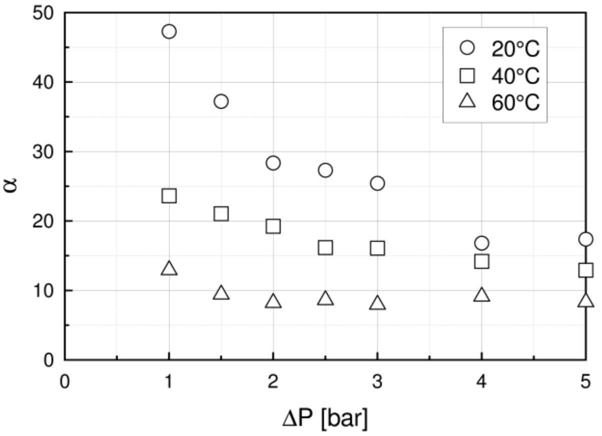

Fig. 7. Effect of feed temperature and pressure difference on ideal CO_2/N_2 selectivity for a PDMS membrane impregnated by soaking the outer side of the tube with [Emim][Ac]

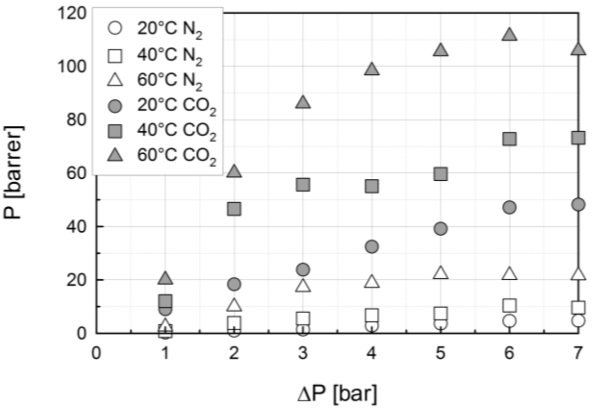

Fig. 8. Effect of feed temperature and pressure difference on CO_2, N_2 permeability for a microfiltration membrane impregnated by coating the outer side of the tube with [Emim][Ac]

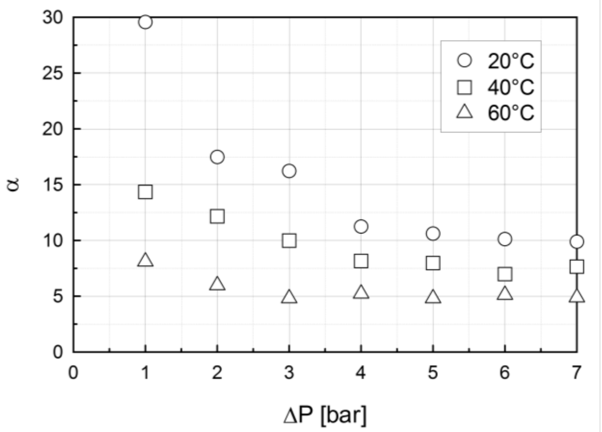

Fig. 9. Effect of feed temperature and pressure difference on ideal CO_2/N_2 selectivity for a microfiltration membrane impregnated by coating the outer side of the tube with [Emim][Ac]

Comparison of the results presented in Figures 4–7 and Figures 8–9 showed that for the SILM prepared by impregnation of a microfiltration 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.

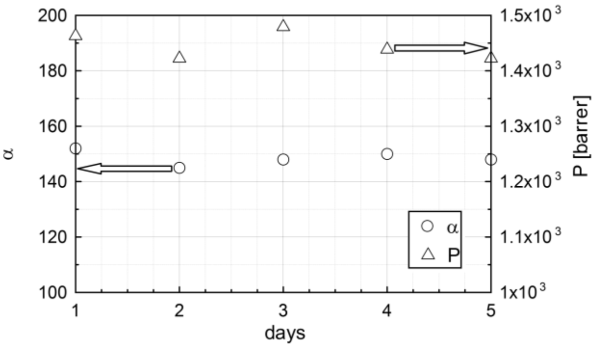

Fig. 10. Long-term stability of the prepared SILMs at a pressure of 1.5 bar and temperature of 20 °C.

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 CO_2 and N_2 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 CO_2/N_2 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.

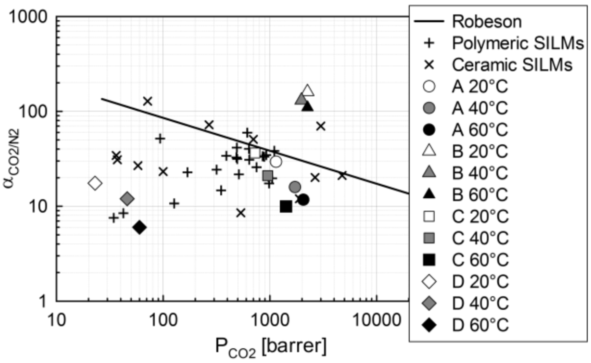

Fig.11. The separation performance comparison of developed SILMs with literature data (A – PDMS not impregnated, B – PDMS impregnated by coating, C – PDMS impregnated by soaking, D – microfiltration membrane impregnated by coating).

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 CO_2 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 permselectivity 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_2O_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^2s^{-1}
j – mass flux, kg $m^{-2}s^{-1}$
P – permeability, Barrer (1 Barrer = 2.99×10^{15} kmol m m^{-2} s^{-1} kPa^{-1})
ΔP – pressure difference on both membrane sides, bar
s – sorption coefficient
V – volumetric flow rate, m^3s^{-1}

Greek letters

$\alpha_{CO2/N2}$ – ideal membrane selectivity
δ – membrane thickness, m

Subscripts

CO_2 – carbon dioxide
i – CO_2, N_2
N_2 – nitrogen

REFERENCES

[1] W. M. Budzianowski, Single solvents, solvent blends, and advanced solvent systems in CO_2 capture by absorption: a review, *Int. J. Glob. Warm.*, **7**(2), 184–225 (2015).

[2] Y. Zhang, X. Ji, Y. Xie, X. Lu, Screening of conventional ionic liquids for carbon dioxide capture and separation, *Applied Energ*y, **162**, 1160–1170 (2016.

[3] P. Luis, Use of monoethanolamine (MEA) for CO_2 capture in a global scenario: Consequences and alternatives, *Desalination*; **380**, 93–99 (2016).

[4] J. E. Bara, Ionic liquids for post combustion CO_2 capture, in: *Absorption based post-combustion capture of carbon dioxide*, P. H. M. Feron (Ed.), Woodhed Publishing, Duxford, 2016.

[5] M. Hasib-ur-Rahmana, M. Siaj, F. Larachia, Ionic liquids for CO_2 capture – Development and Progress, *Chemical Engineering and Processing*, **49,** 313–322 (2010).

[6] B. Zhao, Y. Sun, Y. Yuan, J. Gao, S. Wang, Y. Zhuo, C. Chen, Study on corrosion in CO_2 chemical absorption process using amine solution, *Energy Proced.*, **4**, 93–100 (2011).

[7] *IPCC Special Report on Carbon Dioxide Capture and Storage*, Prepared by Working Group III of the Intergovernmental Panel on Climate Change. B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer (Eds.), Cambridge University Press, New York, 2005.

[8] B. Schäfer, A. E. Mather, K. N. Marsh, Enthalpies of solution of carbon dioxide in mixed solvents, *Fluid Phase Equilib.*, **194**, 929–935 (2002).

[9] R. E. Baltus *et al.*, Examination of the potential of ionic liquids for gas separations, *Sep. Sci. Technol.*, **40**(1–3), 525–541 (2005).

[10] J. Blatha, N. Deublerb, T. Hirtha, T. Schiestelb, Chemisorption of carbon dioxide in imidazolium based ionic liquids with carboxylic anions, *Chemical Engineering Journal*, **181**–**182**, 152–158 (2012).

[11] Y. Xie, Y. Zhang, X. Lu, X. Ji, Energy consumption analysis for CO_2 separation using imidazolium-based ionic liquids, *Applied Energy*, **136**, 325–335 (2014).

[12] M. B. Shiflett, D. W. Drew, R. A. Cantini, A. Yokozeki, Carbon dioxide capture using ionic liquid 1-butyl-3-methylimidazolium Acetate. *Energy Fuels*, **24**, 578–579 (2010).

[13] A. Yokozeki, M. B. Shiflett, L .M. Grieco, T. Foo, Physical and chemical absorptions of carbon dioxide in room-temperature ionic liquids, *J. Phys. Chem.B.*, **112**, 16654–16663 (2008).

[14] P. Scovazzo, J. Kieft, D. A. Finan, C. Koval, D. Du Bois, R. Noble, Gas separations using non-hexafluorophosphate $[PF_6]^-$ anion supported ionic liquid membranes, *J. Membr. Sci.*, **238**, 57–63, (2004).

[15] J. E. Bara, T. K. Carlisle, C. J. Gabriel, D. Camper, A. Finotello, D. L. Gin, R. D. Noble, Guide to CO_2 separations in imidazolium-based room-temperature ionic liquids, *Ind. Eng. Chem. Res.*, **48,** 2739–2751 (2009).

[16] P. Cserjési, N. Nemestóthy, K. Bélafi-Bakó, Gas separation properties of supported liquid membranes prepared with unconventional ionic liquids, *J. Membr. Sci.*, **349**, 6–11, (2010).

[17] L. A. Neves, J. G. Crespo, I. M. Coelhoso, Gas permeation studies in supported ionic liquid membranes, *J. Membr. Sci.*, **357**, 160–170 (2010).

[18] P. Jindaratsamee, Y. Shimoyama, H. Morizaki, A. Ito, Effects of temperature and anion species on CO_2 permeability and CO_2/N_2 separation coefficient through ionic liquid membranes, *J. Chem. Thermodyn.*, **43**, 311–314 (2011).

[19] E. Santos, J. Albo, A. Irabien, Acetate based supported ionic liquid membranes (SILMs) for CO_2 separation: Influence of the temperature, *J. Membr. Sci.*, **452**, 277–283 (2014).

[20] J. Albo, T. Yoshioka, T. Tsuru, Porous Al_2O_3/TiO_2 tubes in combination with 1-ethyl-3-methylimidazolium acetate ionic liquid for CO_2/N_2 separation, *Separation and Purification Technology*, **122**, 440–448 (2014).

[21] C. E. Sánchez Fuentes, D. Guzmán-Lucero, M. Torres-Rodriguez, N. V. Likhanova, J. Navarrete Bolaños, O. Olivares-Xometl, I. V. Lijanova, CO_2/N_2 separation using alumina supported membranes based on new functionalized ionic liquids, *Separation and Purification Technology*, **182**, 59–68 (2017).

[22] Y. F. Liu, Q. Q. Xu, P. Cai, M. Y. Zhen, X. Y. Wang, J. Z. Yin, Effects of operating parameters and ionic liquid properties on fabrication of supported ionic liquid membranes based on mesoporous γ-Al_2O_3 supports, *J. Membr. Sci.*, **545**, 176–184 (2018).

[23] D. S. Karousos, A. I. Labropoulos, A. Sapalidis, N. K. Kanellopoulos, B. Iliev, T. J. S. Schubert, G. E. Romanos, Nanoporous ceramic supported ionic liquid membranes for CO_2 and SO_2 removal from flue gas, *Chemical Engineering Journal*, **313**, 777–790 (2017).

[24] Y. F. Liu, Q. Q Xu, X. Y. Wang, M. Y. Zhen, J. Z. Yin, Preparation of supported ionic liquid membranes using supercritical fluid deposition based on γ-alumina membrane and imidazolium ionic liquids, *The Journal of Supercritical Fluids*, **139**, 88–96 (2018).

[25] D. S. Karousos, A. I. Labropoulos, O. Tzialla, K. Papadokostaki, M. Gjoka, K. L. Stefanopoulos, K. G. Beltsios, B. Iliev, T. J. S. Schubert, G. E. Romanos, Effect of a cyclic heating process on the CO_2/N_2 separation performance and structure of a ceramic nanoporous membrane supporting the ionic liquid 1-methyl-3-octylimidazolium tricyanomethanide, *Separation and Purification Tech.*, **200**, 11–22, (2018).

[26] M. B. Shiflett, D. J. Kasprzak, A. Yokozeki, Phase behavior of Carbon dioxide - [bmim][Ac] mixtures, *J. Chem. Thermodyn.*, **40**, 25–31 (2008).

[27] M. B. Shiflett, A. Yokozeki, Phase behavior of carbon dioxide in ionic liquids: [Emim][Acetate], [Emim] [Trifluoroacetate], and [Emim][Acetate] [Emim][Trifluoroacetate] mixtures, *J. Chem. Eng. Data*, **54**, 108–114 (2009).

[28] M. B. Shiflett, B. A. Elliott, A. M. S. Niehaus, A. Yokozeki, Separation of N_2O and CO_2 using room-temperature ionic liquid [Bmim][Ac], *Sep.Sci.Technol.*, **47**, 411–421 (2012).

[29] M. B. Shiflett, A. M. S. Niehaus, B. A. Elliott, A. Yokozeki, Phase behavior of N_2O and CO_2 in room-temperature ionic liquids [bmim][Tf_2N], [bmim][BF_4], [bmim][$N(CN)_2$], [bmim][Ac], [eam][NO_3], and [bmim][SCN], *Int.J.Thermo-phys.*, **33,** 412–436 (2012).

[30] P. Luis, L. A. Neves, C. A. M. Afonso, I. M. Coelhoso, J. G. Crespo, A. Garea, A. Irabien, Facilitated transport of CO_2 and SO_2 through supported ionic liquid membranes (SILMs), *Desalination*, **245**, 485–493, (2009).

[31] M. G. Freire, A. R. R. Teles, M. A. A. Rocha, B. Schroder, C. M. S. S Neves, P. J. Carvalho, D. V. Evtuguin, L. M. N. B. F. Santos, J. A. P. Coutinho, Thermophysical characterization of ionic liquids able to dissolve biomass, *J. Chem. Eng. Data*, **56**, 4813–4822 (2011).

[32] R. E. Baltus, R. M. Counce, B. H. Culbertson, H. Luo, D. W. Depaoli, S. Dai, D. C. Duckworth, Examination of the potential of ionic liquids for gas separations, *Sep. Sci. Technol.*, **40**, 525–541 (2005).

[33] S. H. Barghi, M. Adibi, D. Rashtchian, An experimental study on permeability, diffusivity, and selectivity of CO_2 and CH_4 through [bmim][PF_6] ionic liquid supported on an alumina membrane: investigation of temperature fluctuations effects, *J. Membr. Sci.*, **362**, 346–352 (2010).

[34] R. Kreiter, J. P. Overbeek, L. A. Correia, J. F. Vente, Pressure resistance of thin ionic liquid membranes using tailored ceramic supports, *J. Membr. Sci.*, **370**, 175–178, (2011).

[35] J. J. Close, K. Farmer, S. S. Moganty, R. E. Baltus, CO_2/N_2 separations using nanoporous alumina-supported ionic liquid membranes: effect of the support on separation performance, *J. Membr. Sci.*, **390–391**, 201–210, (2012).

[36] L. M. Robeson, The upper bound revisited, *J. Membr. Sci.*, **320**, 390–400, (2008).