

Supported room temperature ionic liquid membranes for CO₂/CH₄ separationD.D. Iarikov^a, P. Hacırlıoğlu^a, S.T. Oyama^{a,b,*}^a Environmental Catalysis and Nanomaterials Laboratory, Department of Chemical Engineering, Virginia Polytechnic Institute & State University, Blacksburg, VA 24061-0211, United States^b Department of Chemical Systems Engineering, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

ARTICLE INFO

Article history:

Received 17 July 2010

Received in revised form

27 September 2010

Accepted 25 October 2010

Keywords:

Room temperature ionic liquids

Carbon dioxide separation

Inorganic membranes

ABSTRACT

Room temperature ionic liquids (RTILs) are organic salts which are liquid at or around room temperature. These compounds exhibit many outstanding physical properties such as great thermal stability and no measurable vapor pressure. In this work supported ionic liquid membranes (SILMs) were prepared by impregnating pores of α -alumina inorganic supports with various ionic liquids. In addition to membranes prepared with pure RTILs we were able to synthesize membranes with RTIL mixtures using 1-aminopyridinium iodide dissolved in 1-butyl-4-methylpyridinium tetrafluoroborate or methyltrioctylammonium bis(trifluoromethylsulfonyl)imide. This combination of an RTIL with an organic salt containing an amine group dramatically improved the membrane separation properties. The SILMs displayed CO₂ permeance on the order of 5×10^{-10} to 5×10^{-9} mol m⁻² s⁻¹ Pa⁻¹ combined with CO₂/CH₄ selectivity of 5–30. Although these values are comparable with the current systems for CO₂ purification, CO₂ permeance is still rather low for these compounds.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Separation of CO₂ from natural gas streams is an area where membranes are expected to play a more significant role in the coming years. Much of the natural gas produced worldwide requires significant treatment [1] because in some natural gas wells up to 70% of the total gas volume can be comprised of CO₂ [2]. Since CO₂ contributes to pipeline corrosion and decreases the calorific value of natural gas [3] its separation is of critical economical importance. The current US pipeline specifications require CO₂ content to be below 2% by volume [1]. Conventional CO₂ separation techniques include pressure swing adsorption using solid adsorbents (carbon) or absorption and stripping using liquids (aqueous amines) [4]. Membrane separation is an emerging technology and has numerous advantages over adsorption and absorption methods, including low energy consumption, ease of operation, and low environmental impact [5].

Supported ionic liquid membranes (SILMs) are a new type of membrane system composed of room temperature ionic liquids (RTILs) impregnated onto polymeric or inorganic supports. RTILs are organic salts that are liquid at room temperature, thermally stable, and non-flammable and nonvolatile [6] and these prop-

erties make them ideal candidates as the separation medium for supported liquid membranes. In contrast aqueous-based solvents experience stability issues under vacuum or pressurized conditions [7] and can dry out, which disrupts membrane performance.

Gas transport in supported liquid membranes can be described using the solution-diffusion mechanism. Gas molecules on the feed side are absorbed into the liquid phase, diffuse across the membrane, and desorb at the permeate side [8]. Membrane systems have also been developed where CO₂ participates in a reversible chemical reaction with a carrier component inside the membrane [9]. In this case separation is governed by facilitated transport of CO₂ as it diffuses through the membrane as a reacted species. Facilitated membranes that utilize amine functional groups experience higher CO₂/CH₄ selectivity compared with non-reactive membranes.

In this work SILMs were prepared by depositing ionic liquids on porous α -alumina. These inorganic supports are attractive because they are stable at high temperatures and resistant to plasticization and chemical attack [10–12]. Different types of ionic liquids were assessed and membranes were tested under a variety of conditions. Membrane separation performance was evaluated based on gas permeance and selectivity.

2. Materials and methods

2.1. Materials

The ionic liquids: 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 1-hexyl-3-methylimidazolium bis(trifluo-

* Corresponding author at: Department of Chemical Systems Engineering, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. Tel.: +81 3 5841 0712; fax: +81 3 5841 0712.

E-mail addresses: ted.oyama@chemsys.t.u-tokyo.ac, oyama@vt.edu (S.T. Oyama).

Table 1
Inorganic support properties.

| Supplier | Type | OD (mm) | ID (mm) | Active layer thickness (μm) | Active layer porosity (%) | Nominal pore size (nm) |
|------------------|---------|---------|---------|--|---------------------------|------------------------|
| PALL Corporation | Tubular | 10 | 7 | 2–6 | <30 | 5 |
| PALL Corporation | Tubular | 10 | 7 | 4–12 | 40–50 | 100 |
| NOK Corporation | Fiber | 2.9 | 2.2 | 40 | 52 [27] | 150 [27] |

romethylsulfonyl)imide, and methyltrioctylammonium bis(trifluoromethylsulfonyl)imide were purchased from EMD Chemicals, 1-butyl-4-methylpyridinium tetrafluoroborate from Alfa Aesar, and 1-aminopyridinium iodide from Sigma–Aldrich. Trihexyltetradecylphosphonium dicyanamide was kindly provided by Cytec Industries Inc.

2.2. Porous support preparation

Two types of inorganic porous supports were used in the current study: tubular α -alumina obtained from the PALL Corporation, and hollow fiber (HF) α -alumina obtained from the NOK Corporation. Porous alumina was cut into 3–5 cm pieces and connected to non-porous alumina tubes with glass glaze (Duncan IN 1001) by heating to 880 °C at the rate of 3.6 °C min⁻¹ and soaking at 880 °C for 40 min. In the case of the hollow fibers the fibers were held in place with epoxy glue, which burned off in the course of the calcinations step. The details for the ceramic support structures are given in Table 1. The tubular support with the nominal pore size of 5 nm was pre-coated with a γ -alumina layer by the manufacturer. The HF support and the 100 nm tubular support had α -alumina as the active layer.

2.3. Supported ionic liquid membrane preparation

Supported ionic liquid membranes were prepared by dissolving the ionic liquids in ethanol (200 Proof, USP grade) at low concentrations (3–4 wt%) and depositing the solution onto outside of the inorganic supports using a pipette. Ethanol was employed because it easily dissolved all the RTILs used in this study, and was useful in the handling of the ionic liquids (allowing the use of solutions rather than pure compounds). Ethanol was then allowed to evaporate leaving the nonvolatile ionic liquid inside the support pores.

Several layers of ionic liquid and ethanol solutions were applied until there was an abrupt drop in membrane permeance as measured by a soap film flowmeter (Hewlett Packard 0101-0113). The amount of the ionic liquid deposited was estimated by weighing the membrane before and after SILM deposition. The thickness of the RTIL layer was approximated to be between 200 and 300 μm although the exact thickness was unknown. The membrane support was then deemed saturated with ionic liquid and single gas permeances were measured. All permeance measurements were repeated at least three times. Total membrane area was used to calculate the permeance values. For low permeating gases and gas mixtures the permeances were determined by using a sweep gas (helium) at a known flowrate and measuring the composition of the permeate stream with a gas chromatograph (SRI 8610C). Hollow fiber ceramic porous supports were visually examined using a field emission scanning electron microscope (Leo 1550) before and after the application of intermediate gamma-alumina layer. Samples were prepared by breaking the membrane tubes after immersing them in liquid nitrogen for 5–10 min and sputter-coating with Au–Pd.

3. Results and discussion

The ionic liquid membranes prepared in this study employed as supports porous tubes and hollow fibers made of α -alumina. Table 1 reports the properties of the supports. The tubular geometry of the membranes is shown in Fig. 1. The central portions (white) are the sections of the tubular membrane or hollow fiber that are attached to the non-porous solid alumina end pieces. This method allows easier preparation of samples and avoids problems of non-uniformity and non-isothermality in the end-regions.

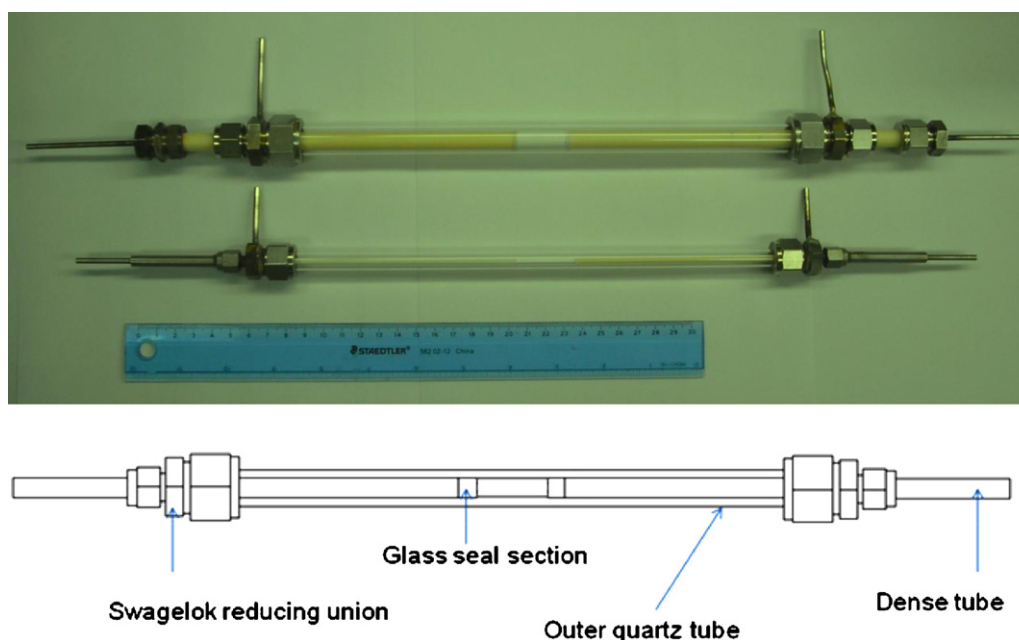
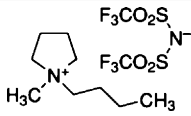
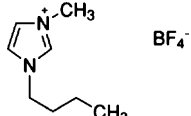
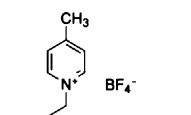
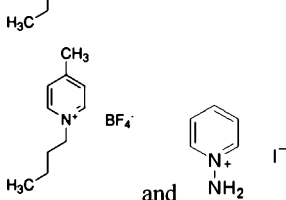
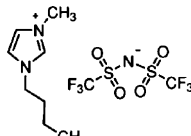
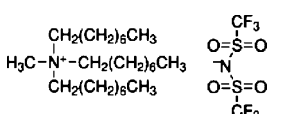
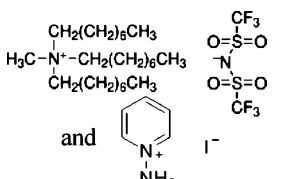
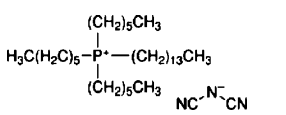


Fig. 1. Tubular and hollow fiber membranes in quartz housings.

Table 2
Properties of different RTIL membranes.

| Ionic Liquid | Chemical structures | Permeance ($\text{mol s}^{-1} \text{m}^{-2} \text{Pa}^{-1}$) | Selectivity CO_2/CH_4 |
|--|--|--|---------------------------------------|
| (1) 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (bmpy) (Tf2N) |  | 1.3×10^{-9} | 6.1 |
| (2) 1-Butyl-3-methylimidazolium tetrafluoroborate (bmim) (BF4) |  | 1.8×10^{-9} | 17 |
| (3) 1-Butyl-4-methylpyridinium tetrafluoroborate * (bmpy) (BF4) |  | 9.9×10^{-10} | 3.7 |
| (4) 1-Butyl-4-methylpyridinium tetrafluoroborate and 1-aminopyridinium iodide * (bmpy) (BF4) + (apir) (I) |  | 2.0×10^{-9} | 52 |
| (5) 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide * (hmim) (Tf2N) |  | 2.3×10^{-8} | 9.0 |
| (6) Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide (mtoa) (Tf2N) |  | 1.0×10^{-9} | 3.5 |
| (7) Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide and 1-aminopyridinium iodide (mtoa) (Tf2N) + (apir) (I) |  | 1.3×10^{-8} | 2.2 |
| (8) Trihexyltetradecylphosphonium dicyanamide |  | 3.1×10^{-8} | 1.2 |

Membranes marked with a star were tested with a sweep gas using GC, the rest were tested using a bubble flow meter.

Table 2 presents a summary of the supported ionic liquid membranes studied in this work, and the permeance and selectivity obtained. It is apparent that most SILMs have CO_2 permeance in the range of 5×10^{-10} to $2 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and CO_2/CH_4 selectivity of 5–25. For SILM preparation tubular supports were deemed more effective than the HF supports based on their separation properties. This can be explained by the fact that the active layer of the HF is several times thicker than the active layer of the tubular support (Table 1).

Fig. 2 gives an overview of membranes prepared in this study from different ionic liquids including the mixtures of ionic liquids. The best membranes are composed of (bmpy) (BF4) + (apir) (I), with a selectivity of 27–30 at a permeance of $2 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. It can be seen that for membranes prepared with the same anion (Tf2N) different cations gave approximately the same permeance but different selectivity in the order (hmim) > (bmpy) > (mtoa). It appears that quaternary ammonium

ions in a ring structure give higher performance than tetrahedrally coordinated ions, possibly because they can sterically interact more easily with CO_2 .

A summary of the properties of different ionic liquid membranes is presented in Table 2 together with the corresponding ionic liquid structures. The CO_2 permeance values for these membranes were in the order of 10^{-10} to $10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and CO_2/CH_4 selectivity ranged between 1.2 and 50. When compared to polymeric membranes, the CO_2 permeance in SILMs is generally higher than the majority of the polymeric membrane systems (10^{-12} to $10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$). The CO_2/CH_4 selectivity is comparable to the selectivity exhibited by the polymeric systems (10–80). The RTIL membranes generally do not exceed the permeance/selectivity trade-off illustrated by the Robeson curve [13].

Supported ionic liquid membranes are most effective at lower pressures. Fig. 3a shows a typical result with 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide showing that the

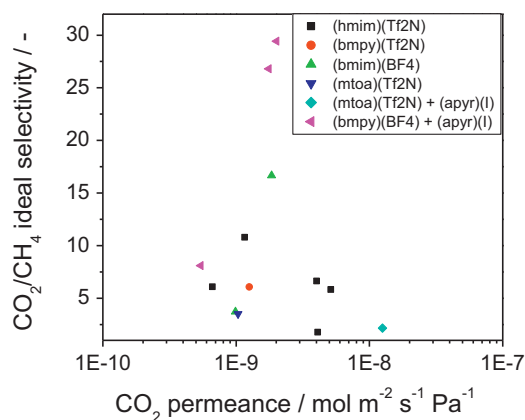


Fig. 2. CO_2/CH_4 ideal selectivity plotted against CO_2 permeance for several of the RTILs used in this work. (hmim) (Tf2N)—1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, (bmpy) (Tf2N)—1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide, (bmim) (BF4)—1-butyl-3-methylimidazolium tetrafluoroborate, (mtoa) (Tf2N)—methyltriocylammonium bis(trifluoromethylsulfonyl)imide, (apir) (I)—1-aminopyridinium iodide.

CO_2/CH_4 selectivity decreased dramatically with increasing total feed pressure for a 50/50 gas mixture. Membranes were tested going up and down in pressure repeatedly to verify that the ionic liquid layer remained intact. Although gas permeance increased rather dramatically at high pressures the integrity of the ionic liquid layer was not compromised which was verified by repeated measurements. Other membranes showed the same behavior. This trend can be understood by examining the dependence of solubility of CO_2 and CH_4 in the ionic liquids with increasing pressure. The solubility of CO_2/CH_4 gas mixtures in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide has been investigated [14]. It was found that although the solubility of pure CO_2 is much higher than that of pure CH_4 , the behavior changed for binary mixtures. In the case of 10/90 and 50/50 CH_4/CO_2 mixtures, the presence of CO_2 actually increased the solubility of CH_4 in the ionic liquid. Since the separation mechanism at work for supported ionic liquid membranes is solution-diffusion, the separation becomes ineffective at relatively mild pressures.

Fig. 3b shows the selectivity for CH_4/CO_2 separation in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide for different inlet compositions. There is no change in the selectivity compared to the pure component selectivity, indicating that there are few interactions between the permeating components, and this could be due to their low solubility.

Increasing temperature increases the rate of diffusion so that permeance increases, but selectivity decreases. Fig. 4 shows this behavior for CO_2 and CH_4 using a 1-butyl-3-methylimidazolium

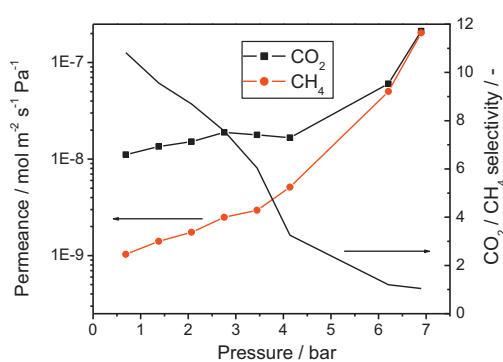


Fig. 3. CO_2/CH_4 selectivity versus feed pressure for a 50/50 mixture. 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide supported on 100 nm Pall α -alumina support, $T=50^\circ\text{C}$.

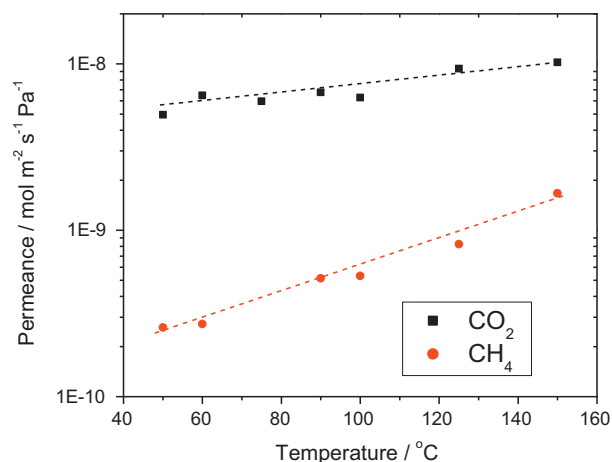


Fig. 4. Permeances of CO_2 and CH_4 for 1-butyl-3-methylimidazolium tetrafluoroborate with 100 nm alumina support (69 kPa trans-membrane pressure).

tetrafluoroborate membrane. It is also evident from the graph that the permeance of CH_4 increases more significantly over this temperature range, which results in lower selectivity at elevated temperatures. The permeance dependence on temperature for CO_2 permeance in this case was 7.5 kJ/mol compared to 20 kJ/mol for CH_4 . This can be explained by examining the CO_2 and CH_4 solubility coefficients at different temperatures. Solubilities of CO_2 and CH_4 in 1-butyl-3-methylimidazolium tetrafluoroborate as functions of temperature between 283 K and 343 K have been determined [15]. It was found that CO_2 solubility in the ionic liquid is much higher than that of other gases, and that CO_2 solubility decreases dramatically with increasing temperature compared to CH_4 . This explains why membranes that use 1-butyl-3-methylimidazolium tetrafluoroborate as the separation medium are not as effective at higher temperatures. In another study by the same research group a similar trend in CO_2 and CH_4 solubilities was observed for 1-butyl-3-methylimidazolium hexafluorophosphate [16]. Gas solubilities in both of these studies were evaluated in limited temperature ranges so it is difficult to generalize the results to higher temperatures, however similar tendencies are expected.

There have been efforts to synthesize RTILs with an amine group incorporated in the molecular structure but the costs associated with the synthesis are prohibitive [21]. The 1-aminopyridinium cation contains an NH_2 group which favors CO_2 permeation as described in the literature. To the best of our knowledge, there has not been any previous work performed using this particular compound for CO_2 removal. While 1-aminopyridinium iodide was stable in the temperature range of this study, it has been reported

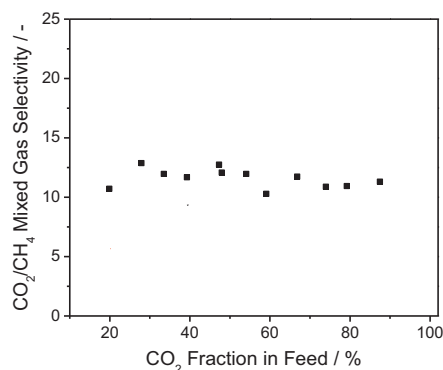


Table 3
Supported ionic liquid membranes for CO₂/CH₄ separation.

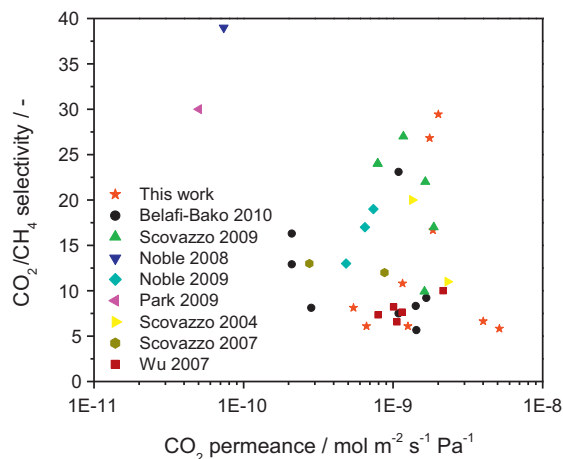
| Membrane type | CO ₂ permeance (barrer) | CO ₂ permeance (mol m ⁻² s ⁻¹ Pa ⁻¹) | α _(CO₂/CH₄) | Ref. |
|---|------------------------------------|---|--|------|
| Imidazolium-based task-specific ionic liquids on porous hydrophilic polytetrafluoroethylene support | 800 | 7.7 × 10 ⁻⁹ | 55 | [21] |
| Imidazolium-based ionic liquids in polysulfone support | 330–740 | 7.3 × 10 ⁻¹⁰ to 1.6 × 10 ⁻⁹ | 4.7–6.0 | [28] |
| Imidazolium-based ionic liquids in polyethersulfone microfiltration support | 360–980 | 8.0 × 10 ⁻¹⁰ to 2.2 × 10 ⁻⁹ | 6.6–10 | [6] |
| Phosphonium-based ionic liquids supported on glass fiber disk filters | 544–1700 | 2.8 × 10 ⁻¹⁰ to 8.8 × 10 ⁻¹⁰ | 12–13 | [27] |
| Supported ionic liquid membranes on poly vinylidene fluorolide support | 94–750 | 2.1 × 10 ⁻¹⁰ to 1.7 × 10 ⁻⁹ | 5.7–23 | [18] |
| Imidazolium-based supported ionic liquid membranes on PES porous disk support | 310–740 | 7.9 × 10 ⁻¹⁰ to 1.9 × 10 ⁻⁹ | 10–27 | [29] |
| Imidazolium-based fluoroalkyl-functionalized supported room-temperature ionic liquid membranes on porous polyethersulfone support | 210–320 | 4.9 × 10 ⁻¹⁰ to 7.4 × 10 ⁻¹⁰ | 13–19 | [22] |
| Supported ionic liquid membranes prepared on polyvinylidene fluorolide support | 6 | 5.0 × 10 ⁻¹¹ | 30 | [30] |
| Imidazolium-based SILMs on porous hydrophilic polyethersulfone | 610–1050 | 1.3 × 10 ⁻⁹ to 2.3 × 10 ⁻⁹ | 11–20 | [8] |

that several aminopyridinium compounds are thermally stable to at least 550 K [17]. The option of dissolving one ionic liquid with a particular functionality in a bulk ionic liquid with well defined physical properties offers another avenue for obtaining membranes suitable for certain separations. This strategy is shown to be successful, with increased performance in both permeance and selectivity as seen in Table 2 by comparing entry (3) with entry (4) and entry (6) with entry (7). Thus for the 1-butyl-4-methylpyridinium tetrafluoroborate RTIL adding 1-aminopyridinium iodide increases permeance from 9.9×10^{-10} to 2.0×10^{-9} mol m⁻² s⁻¹ Pa⁻¹, while simultaneously increasing selectivity from 3.7 to 52. Similarly, for the methyltrioctylammonium bis(trifluoromethylsulfonyl)imide RTIL, adding the amino compound increases permeance tenfold from 1.0×10^{-9} to 1.3×10^{-8} mol m⁻² s⁻¹ Pa⁻¹ while the selectivity falls only slightly from 3.5 to 2.2. The 1-aminopyridinium iodide has an obvious effect on CO₂ permeance and selectivity due to a molecular interaction with the amino moiety. The effect could not be explained by a reversible chemical interaction between the amino group and CO₂ molecules because the experiments were repeated at different partial pressures with no dramatic effect on CO₂ selectivity. Therefore, it is likely that the amino group increases the CO₂ solubility in the bulk ionic liquid. The aminopyridinium salt was added in two different concentrations (7 and 15 wt% in RTIL) with no significant difference in gas separation properties noticed.

The RTIL membranes synthesized in our laboratory were compared with other SILMs reported in the literature (Table 3 and Fig. 5) [18,19]. The supported ionic liquid membranes (SILMs) surveyed in this article (Table 3) displayed permeance com-

parable to those of the polymeric membranes, generally below 2×10^{-9} mol m⁻² s⁻¹ Pa⁻¹ (1000 Barrer). The results that were reported in Barrers were converted into SI units (mol m⁻² s⁻¹ Pa⁻¹) and vice versa for the purpose of comparison. The CO₂/CH₄ selectivity of SILMs reported in the literature was in the range of 5–30 [8]. It is apparent that the best results were obtained using RTILs based on the imidazolium cation. It has been shown in the literature that the relative solubility of CO₂ in imidazolium containing ionic liquids is much higher than that of CH₄ [20]. In one of the studies [21] the ionic liquid was functionalized with an amine group to enable facilitated transport of CO₂. The resultant membrane exhibited CO₂ permeance of 7.7×10^{-9} mol m⁻² s⁻¹ Pa⁻¹ (800 Barrer) and the CO₂/CH₄ selectivity of 55. It is important to note that this result was obtained at extremely low CO₂ partial pressure of 5 kPa. In another study [22] the imidazolium cation was functionalized with fluoroalkyl groups to investigate the increase in gas solubility. The membranes showed CO₂ permeance of 4.9×10^{-10} to 7.4×10^{-10} mol m⁻² s⁻¹ Pa⁻¹ and CO₂/CH₄ selectivity in the range of 13–19.

The question arises whether or not gas permeance in these membranes can be directly correlated with the RTIL viscosity. Looking at the viscosities of the RTILs used in this study (Table 4) it is clear that there is no direct correlation with gas permeance. For example, RTILs with the highest CO₂ permeance (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium tetrafluoroborate) displayed viscosities of around 100 mPa s [23,24]. 1-Butyl-4-methylpyridinium tetrafluoroborate [25] showed similar gas permeance although its viscosity was much higher (203 mPa s). SILM prepared with 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [26] displayed a very high CO₂ permeance which was consistent with a low viscosity of that RTIL (68 mPa s) but on the other hand trihexyltetradecylphosphonium dicyanamide [26] displayed a viscosity that more than three times higher but its gas permeance was

**Fig. 5.** Comparison of performance of supported liquid membranes employing room temperature ionic liquids.**Table 4**
RTIL viscosity data.

| Ionic liquid | Viscosity at 25 °C (mPa s) |
|---|----------------------------|
| 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide | 96 [23] |
| 1-Butyl-3-methylimidazolium tetrafluoroborate | 92 [25] |
| 1-Butyl-4-methylpyridinium tetrafluoroborate ^a | 203 [26] |
| 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | 68 [18] |
| Trihexyltetradecylphosphonium dicyanamide | 213 [27] ^a |

^a Measured at 30 °C.

also 34% higher. It is clear that gas permeance in RTILs is governed by molecular interactions and that bulk liquid properties are not always sufficient to correctly predict membrane behavior.

4. Conclusions

Room temperature ionic liquid membranes with the specific goal of CO₂/CH₄ separation were studied in our laboratory. The RTIL membranes compared favorably with results reported in the literature. The CO₂ permeance of these membranes was on the order of 10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹ with CO₂/CH₄ selectivity ranging between 5 and 30. Although these values compared reasonably well with the current polymeric membrane systems, there were several significant drawbacks inherent to these systems. The RTIL membranes were found to be unsuitable for gas separation at high pressures and their separation performance suffered at high temperatures due to decrease in gas solubility. The properties of the RTIL membranes were found to improve significantly by the addition of an organic salt with an amine group functionality.

References

- [1] R.W. Baker, Membrane Technology and Applications, John Wiley & Sons, Ltd., West Sussex, England, 2004.
- [2] S. Sridhar, R.S. Veerapur, M.B. Patil, K.B. Gudasi, T.M. Aminabhavi, Matrimid polyimide membranes for the separation of carbon dioxide from methane, *J. Appl. Polym. Sci.* 106 (2007) 1585.
- [3] M. Arruebo, R. Mallada, M.P. Pina, in: A.K. Pabby, S.S.H. Rizvi, A.M. Sastre (Eds.), Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications, CRC Press, Boca Raton, FL, 2009, pp. 269–323.
- [4] R. Bounaceur, N. Lape, D. Roizard, C. Vallieres, E. Favre, Membrane processes for post-combustion carbon dioxide capture: a parametric study, *Energy* 31 (2006) 2556.
- [5] S. Sridhar, B. Smitha, T.M. Aminabhavi, Separation of carbon dioxide from natural gas mixtures through polymeric membranes—a review, *Sep. Purif. Rev.* 36 (2007) 113.
- [6] Y.Y. Jiang, Z. Zhou, Z. Jiao, L. Li, Y.T. Wu, Z.B. Zhang, SO₂ gas separation using supported ionic liquid membranes, *J. Phys. Chem. B* 111 (2007) 5058.
- [7] A. Ito, S. Duan, Y. Ikenori, A. Ohkawa, Permeation of wet CO₂/CH₄ mixed gas through a liquid membrane supported on surface of a hydrophobic microporous membrane, *Sep. Purif. Technol.* 24 (2001) 235.
- [8] P. Scovazzo, J. Kieft, D.A. Finan, C. Koval, D. DuBois, R.D. Noble, Gas separations using non-hexafluorophosphate [PF₆]⁻ anion supported ionic liquid membranes, *J. Membr. Sci.* 238 (2004) 57.
- [9] C.A. Scholes, S.E. Kentish, G.W. Stevens, Carbon dioxide separation through polymeric membrane systems for flue gas applications, *Rec. Pat. Chem. Eng.* 1 (2008) 52.
- [10] Y. Gu, S.T. Oyama, Ultra-thin, Hydrogen-selective silica membranes deposited on alumina graded structures prepared from size-controlled boehmite sols, *J. Membr. Sci.* 306 (2007) 216.
- [11] Y. Gu, S.T. Oyama, High molecular permeance in a pore-less ceramic membrane, *Adv. Mater.* 19 (2007) 1636.
- [12] Y. Gu, P. Hacarlioglu, S.T. Oyama, Hydrothermally-stable silica–alumina composite membranes for hydrogen separation, *J. Membr. Sci.* 310 (2008) 28.
- [13] D.D. Iarikov, S.T. Oyama, Review of CO₂/CH₄ separation membranes, in: S.T. Oyama, S.M. Stagg-Williams (Eds.), Correlations in Membrane Science, Elsevier, Amsterdam, 2011.
- [14] D.G. Hert, J.L. Anderson, S.N.V. Aki, J.F. Brennecke, Enhancement of oxygen and methane solubility in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide using carbon dioxide, *Chem. Commun.* (2005) 2603.
- [15] J. Jacquemin, M.F. Costa Gomes, P. Husson, V. Majer, Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric, *J. Chem. Thermodyn.* 38 (2006) 490.
- [16] J. Jacquemin, P. Husson, V. Majer, M.F. Costa Gomes, Low-pressure solubilities and thermodynamics of solvation of eight gases in 1-butyl-3-methylimidazolium hexafluorophosphate, *Fluid Phase Equilib.* 240 (2006) 87.
- [17] J.M. Crosthwaite, M.J. Muldoon, J.K. Dixon, J.L. Anderson, J.F. Brennecke, Phase transition and decomposition temperatures heat capacities and viscosities of pyridinium ionic liquids, *J. Chem. Thermodyn.* 37 (2005) 559.
- [18] P. Cserjesi, N. Nemestothy, K. Belafi-Bako, Gas separation properties of supported liquid membranes prepared with unconventional ionic liquids, *J. Membr. Sci.* 349 (2010) 6.
- [19] J.E. Bara, C.J. Gabriel, E.S. Hatakeyama, T.K. Carlisle, S. Lessmann, R.D. Noble, D.L. Gin, Improving CO₂ selectivity in polymerized room-temperature ionic liquid gas separation membranes through incorporation of polar substituents, *J. Membr. Sci.* 321 (2008) 3.
- [20] J.L. Anthony, E.J. Maginn, J.F. Brennecke, Solubilities and thermodynamic properties of gases in the ionic liquid 1-*N*-butyl-3-methylimidazolium hexafluorophosphate, *J. Phys. Chem. B* 106 (2002) 7315.
- [21] S. Hanioka, T. Maruyama, T. Sotani, M. Teramoto, H. Matsuyama, K. Nakashima, M. Hanaki, F. Kubota, M. Goto, CO₂ separation facilitated by task-specific ionic liquids using a supported liquid membrane, *J. Membr. Sci.* 314 (2008) 1.
- [22] J.E. Bara, C.J. Gabriel, T.K. Carlisle, D.E. Camper, A. Finotello, D.L. Gin, R.D. Noble, Gas separations in fluoroalkyl-functionalized room-temperature ionic liquids using supported liquid membranes, *Chem. Eng. J.* 147 (2009) 43.
- [23] H. Jin, B. O'Hare, J. Dong, S. Arzhantsev, G.A. Baker, J.F. Wishart, A.J. Benesi, M. Maroncelli, Physical properties of ionic liquids consisting of the 1-butyl-3-methylimidazolium cation with various anions and the bis(trifluoromethylsulfonyl)imide anion with various cations, *J. Phys. Chem. B* 112 (2008) 81.
- [24] O.O. Okoturo, T.J. VanderNoot, Temperature dependence of viscosity for room temperature ionic liquids, *J. Electroanal. Chem.* 568 (2004) 167.
- [25] L. Galan Sanchez, J. Ribe Espel, F. Onink, G.W. Meindersma, A.B. de Haan, Density, viscosity, and surface tension of synthesis grade imidazolium, pyridinium, and pyrrolidinium based room temperature ionic liquids, *J. Chem. Eng. Data* 54 (2009) 2803.
- [26] L. Ferguson, P. Scovazzo, Solubility, diffusivity, and permeability of gases in phosphonium-based room temperature ionic liquids: data and correlations, *Ind. Eng. Chem. Res.* 46 (2007) 1369.
- [27] J. Tong, L. Su, K. Haraya, H. Suda, Thin and defect-free pd-based composite membrane without any interlayer and substrate penetration by a combined organic and inorganic process, *Chem. Commun.* (2006) 1142.
- [28] J. Ilconich, C. Myers, H. Pennline, D. Luebke, Experimental investigation of the permeability and selectivity of supported ionic liquid membranes for CO₂/He separation at temperatures up to 125 °C, *J. Membr. Sci.* 298 (2007) 41.
- [29] P. Scovazzo, D. Havard, M. McShea, S. Mixon, D. Morgan, Long-term continuous mixed-gas dry fed CO₂/CH₄ and CO₂/N₂ separation performance and selectivities for room temperature ionic liquid membranes, *J. Membr. Sci.* 327 (2009) 41.
- [30] Y. Park, B. Kim, Y. Byun, S. Lee, E. Lee, J. Lee, Preparation of supported ionic liquid membranes (SILMs) for the removal of acidic gases from crude natural gas, *Desalination* 236 (2009) 342.