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Physically Gelled Ionic Liquids: Solid Membrane Materials with Liquidlike CO_2 Gas Transport

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CO_2 separation is needed in many industrial applications (e.g., natural gas sweetening, respiratory gas enrichment in life-support systems, and CO_2 scrubbing of power plant combustion exhaust).[1] Currently, there are three primary methods of gas separation: cryogenic condensation, pressure-swing adsorption, and aqueous amines.[2] Each method has significant energy costs for refrigeration or regeneration of the separation medium. Membranes represent a fourth mechanism for gas separations that may offer significant operating cost savings over the three prior methods because it requires only a pressure differential.[3]

In dense solid polymer membranes, separation is afforded by differences in the solubility (S) of each gas in the polymer and/or differences in their diffusivity (D) through the membrane material.[4] In this solution-diffusion ($S-D$) mechanism, the permeability ($P = SD$) is the pressure gradient-normalized flux of gas through the media, and gauges how easily gas moves through a dense material to separate it from other gases in the same mixture. Unfortunately, there is typically a trade-off between gas flux and separation selectivity for dense polymer membranes which is linked to the limitation in the $S-D$ mechanism of gas transport.[5] In many cases, if a liquid is used as the active separation medium, diffusion, and in turn permeability, will be greater than in a dense, solid membrane. Despite greater transport properties, the liquid-phase separation material must be supported in a solid porous matrix to prevent flow under applied pressure. As a consequence, supported liquid membranes (SLMs) must operate at low differential pressures (0.1−1 MPa), to avoid forcing the liquid material out of the pores of the support.[6] Another disadvantage of SLMs is loss of liquid to the gas phase through evaporation.

RTILs (i.e., organic salts that are liquid at 1 atm and 25 °C)[7] are promising materials for SLMs for light gas separations. RTILs have negligible vapor pressure, and as a result, there is no solvent loss to the gas phase. Gas solubility and selectivity in RTILs can be easily tuned by modifying the structure of the RTIL cation and anion to select for certain gases.[8] Previous studies with supported ionic liquid membranes (SILMs) have shown enhanced selectivity and good P values compared to conventional polymer membranes.[9] Although SILMs do not suffer from the evaporation problem that SLMs based on conventional liquids have, they still suffer from being displaced at low differential pressure. The ideal SLM material should be nonvolative and have the transport properties of an RTIL but with the mechanical stability of a solid polymer membrane. Progress in combining liquidlike and solidlike properties in a single RTIL gas separation material has recently been achieved by blending RTILs with polymerized RTILs.[10]

Herein, we present a new type of RTIL material for CO_2 separation applications based on physical gelation of a common RTIL, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_6mim][Tf_2N]$, with a small weight percent (1.5 wt %) of the low-molecular-weight gelator (LMOG), 12-hydroxystearic acid (Figure 1). The resulting RTIL gel has good mechanical stability (i.e., it is a firm, gelatinous, cuttable solid), while maintaining liquidlike gas transport properties similar to that of the neat RTIL. Because it is >98 wt % liquid, the RTIL gel exhibits CO_2 gas permeability on par with traditional SLMs. Initial tests also show that CO_2 permeability in this gel in a supported membrane format is 2 orders of magnitude higher than similar RTIL-based solid polymers. The gel's CO_2/N_2 selectivity is similar to the neat $[C_6mim][Tf_2N]$, lower than other neat RTILs and near the upper limit for flux-selectivity for known dense, CO_2/N_2 separation materials. The RTIL gel also has increased mechanical stability with little loss in CO_2 gas selectivity. This unique combination of performance properties suggests that RTIL gels are promising new membrane materials for gas separations that bridge functional liquids and solid polymers.

By way of background, LMOGs are small molecules that can solidify organic liquids at very low loading levels via physically bonding with each other through H-bonding, van der Waals forces, and/or and $\pi-\pi$ bond stacking.[11]

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[1] Klara, S. M.; Srivastava, R. D. *Environ. Prog.* **2002**, *2*, 247.

[2] Kidnay, A. J.; Parrish, W. R. Fundamentals of Gas Processing; CRC Press: Boca Raton, FL, 2006.

[3] Ulbricht, M. *Polymer* **2006**, *47*, 2217.

[4] Wijmans, J. G.; Baker, R. W. *J. Membr. Sci.* **1995**, *107*, 1.

[5] (a) Freeman, B. D. *Macromolecules* **1999**, *32*, 375. (b) Dal-Cin, M. M. *J. Membr. Sci.* **2008**, *323*, 299.

[6] Krull, F. F.; Fritzmann, C.; Melin, T. *J. Membr. Sci.* **2008**, *325*, 509.

[7] Koel, M.; Anderson, J. E. Ionic Liquids in Chemical Analysis; CRC Press: Boca Raton, FL, 2008.

[8] Bara, J. E.; Carlisle, T. K.; Gabriel, C. J.; Camper, D.; Finotello, A.; Gin, D. L.; Noble, R. D. *Ind. Eng. Chem. Res.* **2009**, *48*, 2739.

[9] Scovazzo, P.; Kieft, J.; Finan, D. A.; Koval, C.; DuBois, D.; Noble, R. *J. Membr. Sci.* **2004**, *238*, 57.

[10] Bara, J. E.; Hatakeyama, E. S.; Gin, D. L.; Noble, R. D. *Polym. Adv. Technol.* **2008**, *19*, 1415.

[11] Sangeetha, N. M.; Maitra, U. *Chem. Soc. Rev.* **2005**, *34*, 821.

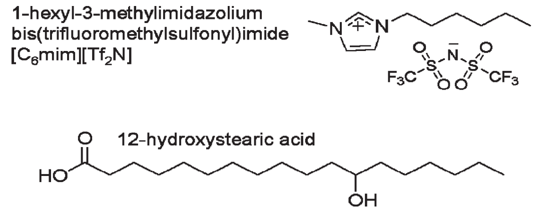

Figure 1. Structures of the RTIL [C_6mim][Tf_2N] and LMOG (12-hydroxystearic acid) components of the RTIL gel.

This affords a noncovalent network that immobilizes the surrounding liquid, affording a stable gel that will not flow, with a thermally reversable sol–gel phase transition. Although a large number of LMOGs are known that gel water[12] and conventional polar organic solvents,[13] only four examples of LMOGs that can gel an RTIL have been reported.[14–17] However, none of these RTIL gel systems have been examined for their gas separation properties.

[C_6mim][Tf_2N] was selected for this proof-of-concept gas separation study because it is a commonly available and easily synthesized RTIL with inherent solubility selectivity for CO_2 over N_2. Although other RTILs would have better selectivity, they did not form a gel with 12-hydroxystearic acid. Imidazolium-based RTILs in general have excellent solubility and solubility-selectivity for CO_2 over N_2.[8]

Figure 2 shows the phase diagram for the [C_6mim]-[Tf_2N]/12-hydroxystearic acid system. The maximum loading of 12-hydroxystearic acid in [C_6mim]-[Tf_2N] was found to be approximately 1.5 wt %, above which two phases formed: a RTIL-rich phase and an LMOG-rich phase. The minimum LMOG concentration needed to form a gel was found to be 0.5 wt %, indicating a maximum gelation efficiency of 400 [C_6mim]-[Tf_2N] ion pairs for every 12-hydroxystearic acid present. The resulting RTIL gels are soft solids that are able to support their own weight and do not phase-separate or lose any mass over many months at room temperature.

The most mechanically and thermally stable gel was found to exist at a maximum LMOG loading level of 1.5 wt % with a temperature of gelation of 67 °C. As such, this gel composition was selected for the subsequent gas solubility and permeability performance studies. The solubility of gas in the gel and neat [C_6mim][Tf_2N] was determined for CO_2 and N_2 using a gas adsorption unit. As seen in Table 1, the RTIL gel has a CO_2 solubility of 2.2 cm^3 gas at 1 atm/cm^3 RTIL and a N_2 solubility of 0.070 cm^3 at 1 atm/cm^3. These values are slightly lower than those of neat [C_6mim][Tf_2N]. However, the CO_2/N_2 solubility selectivity is approximately the same for both the gel and neat RTIL. These similarities in gas solubility performance are not unexpected because the two materials are compositionally very similar (i.e., the gel is 98.5 wt % [C_6mim][Tf_2N]). Compared to some typical organic solvents (Table 1),[18] the observed CO_2 solubility of the gel and pure RTIL are lower. However, their CO_2/N_2 selectivity values are in the middle of the range. Despite their lower CO_2 solubility, RTIL-based materials have an important advantage in membrane operation compared to regular solvents: they have no evaporative loss because of the negligible vapor pressure of RTILs.

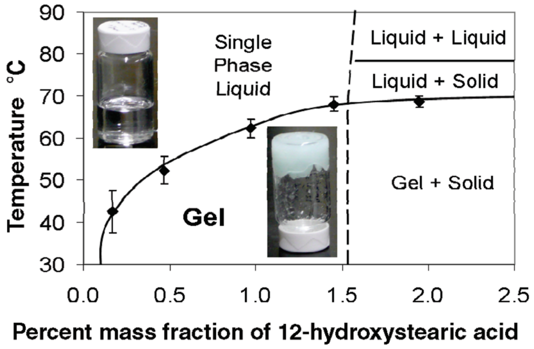

Figure 2. Phase diagram of [C_6mim][Tf_2N] and 12-hydroxystearic acid.

Table 1. Solubility of CO_2 and N_2 in the RTIL Gel, Neat RTIL, and Other Organic Solvents[a]

	gas solubility (cm^3 atm/mL)		
material	CO_2	N_2	solubility selectivity (CO_2/N_2)
[C_6mim][Tf_2N] neat	2.68 ± 0.02	0.082 ± 0.002	33
[C_6mim][Tf_2N] gel	2.2 ± 0.1	0.070 ± 0.005	31
n-hexane	2.1[b]	0.24[b]	8.8
acetone	6.6[b]	0.17[b]	40
acetonitrile	7.1[b]	0.11[b]	64

[a] The ideal solubility selectivity is the ratio of the solubilities of the gases obtained from single-gas experiments. [b] Data obtained from ref [18].

Table 2 shows the results of CO_2 and N_2 gas transport studies on the supported gel and pure RTIL test membranes. The permeability of CO_2 was determined to be 650 barrers for the gelled [C_6mim][Tf_2N] membrane and 700 barrers for the neat [C_6mim][Tf_2N] membrane. The permeability of N_2 was also similar, 29 barrers for the gel and 31 barrers for the neat RTIL membrane. The supported gel and neat RTIL membranes exhibited similar permeability selectivity for CO_2/N_2 of 22 and 23, respectively. These observed permeability and selectivity values are exceeded by only three polymer membranes in the literature (polymers containing intrinsic micropores (PIM-1, PIM-7)[19] and amino-modified poly(dimethylsiloxane)).[20] Also listed is an example of a recent PEO composite membrane.[21]

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(12) Estroff, L. A.; Hamilton, A. D. *Chem. Rev.* **2004**, *104*, 1201.
(13) Amaike, M.; Kobayashi, H.; Shinkai, S. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2553.
(14) Ikeda, A.; Sonoda, K.; Ayabe, M.; Tamaru, S.; Nakashima, T.; Kimizuka, N.; Shinkai, S. *Chem. Lett.* **2001**, 1154.
(15) Hanabusa, K.; Fukui, H.; Suzuki, M.; Shirai, H. *Langmuir* **2005**, *21*, 10383.
(16) Mohmeyer, N.; Kuang, D.; Wang, P.; Schmidt, H. W.; Zakeeruddin, S. M.; Gratzel, M. *J. Mater. Chem.* **2006**, *16*, 2978.
(17) Kubo, W.; Kambe, S.; Nakade, S.; Kitamura, T.; Hanabusa, K.; Wada, Y.; Yanagida, S. *J. Phys. Chem. B* **2003**, *107*, 4374.
(18) Lin, H.; Freeman, B. D. *J. Mol. Struct.* **2005**, *739*, 57.
(19) Budd, P. M.; Msayib, K. J.; Tattershall, C. E.; Ghanem, B. S.; Reynolds, K. J.; McKeown, N. B.; Fritsch, D. *J. Membr. Sci.* **2005**, *251*, 263.
(20) Senthilkumar, U.; Reddy, B. S. R. *J. Membr. Sci.* **2007**, *292*, 72.
(21) Powell, C. E.; Qiao, G. G. *J. Membr. Sci.* **2006**, *279*, 1.

Table 2. Permeability and Selectivity of CO$_2$ and N$_2$ in the RTIL Gel, Neat RTIL, the Three Known Polymers with Better Gas Transport Properties, and Recent PEO Composite[a]

	gas permeability (barrers)		
material	CO$_2$	N$_2$	permeability selectivity (CO$_2$/N$_2$)
[C$_6$mim][Tf$_2$N] neat	700 ± 10	31 ± 1	23
[C$_6$mim][Tf$_2$N] gel	650 ± 10	29 ± 1	22
PIM-1	2300[b]	92[b]	25
PIM-7	1100[b]	42[b]	26
modified PDMS	2000[c]	59[c]	34
PEO composite	238[d]	4.9[d]	49

[a] The ideal permeability selectivity is the ratio of the permeability values of CO$_2$ and N$_2$ from single-gas experiments. [b] Data obtained from ref [19]. [c] Data obtained from ref [20]. [d] Data obtained from ref [21].

The gas transport properties of this new supported RTIL gel membrane can be compared to other types of membranes using a "Robeson plot" (Figure 3), which tracks permeability vs the selectivity on a log−log scale.[22] The resulting plot has an empirical upper-bound for dense polymer membranes (•) illustrating a well-established flux-selectivity trade-off.[5] Any material at or above this line (i.e., in the upper right quadrant) is considered to have good transport properties (i.e., high permeability and high selectivity).

Supported neat [C$_6$mim][Tf$_2$N] and the [C$_6$mim][Tf$_2$N] gel membranes are located to the upper-right of most dense polymer membranes. They have good transport properties even without optimization. Other SILMs have similar permeability values but much higher selectivity values due to lower N$_2$ solubilities.[9] Recent examples of solid-state, poly(RTIL) membranes[23] retain the high CO$_2$ solubility of conventional liquid RTIL materials, but suffer from lower D and P values because of their dense solid natures. These materials are also below the empirical upper-bound line. Recently, liquid RTILs have been combined with poly(RTIL)s to generate composites with higher gas permeabilities without sacrificing selectivity. These RTIL-based solid−liquid (i.e., 20% liquid) hybrid materials show a pronounced shift to the right on the Robeson plot compared to the parent solid poly(RTIL)s.[10] However, as demonstrated in Figure 3, the [C$_6$mim][Tf$_2$N] gel exhibits a CO$_2$ permeability that is ca. 100 times higher than that of chemically similar imidazolium-based polymers and only a slightly lower CO$_2$/N$_2$ selectivity. Moreover, the [C$_6$mim][Tf$_2$N] gel also shows a ca. 12 times higher permeability than a similar poly(RTIL)+RTIL solid−liquid composite. The observed selectivity and permeability for the solid RTIL gel are both virtually identical to those of pure liquid [C$_6$mim][Tf$_2$N] in an SLM configuration.

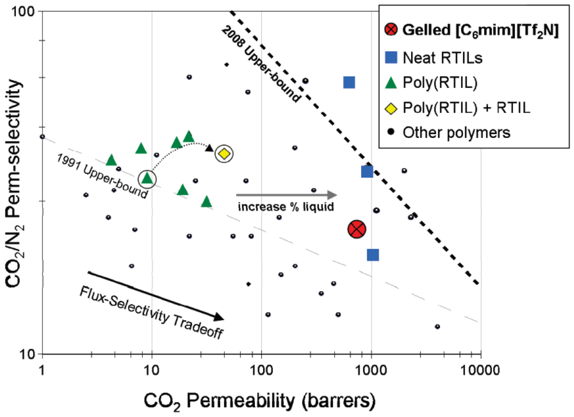

Figure 3. Robeson Plot comparing CO$_2$ and N$_2$ transport properties of various dense membrane materials.

The Robeson plot is good for comparing transport properties; however, it does not take into account other physical properties that are essential for a membrane material to be considered industrially viable. For instance, the supported RTIL gel membrane has better mechanical stability compared to conventional SILMs. In conventional SILMs, if enough pressure is applied, the active liquid component will be expelled out the permeate side (i.e., burst pressure). It was found that the burst pressure for a neat [C$_6$mim][Tf$_2$N] SLM on Supor support was 2.2 ± 0.1 MPa. In contrast, the burst pressure for the supported [C$_6$mim][Tf$_2$N] gel membrane was found to be 2.7 ± 0.2 MPa (23% higher). Although the absolute value is lower than other SLMs, this can be attributed to the relatively large pore size.[6] This combination of better solidlike mechanical stability and liquidlike gas permeability makes these RTIL gels valuable new platforms for RTIL-based CO$_2$ separation systems.

This initial proof-of-concept study successfully demonstrates that commercial LMOGs can be used to form stable RTIL gels that simultaneously exhibit liquidlike gas transport properties and the solid mechanical properties desired for membrane applications. The gas selectivity of these RTIL gels may be improved by using functionalized RTILs with better targeted selectivity for certain gases. For industrial applications, a membrane that is stable up to 150 °C is desirable in order to withstand the temperature of hot flue gases. Increased thermal and mechanical stability in these RTIL gels may be accomplished by synthesizing new LMOGs with stronger noncovalent gelling interactions. Our research group is currently pursuing both these directions.

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Supporting Information Available: Detailed procedures for preparing the RTIL gels and supported membranes; procedures for gas solubility and permeability testing (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Robeson, L. M. *J. Membr. Sci.* **2008**, *320*, 390.
(23) Bara, J. E.; Lessmann, S.; Gabriel, C. J.; Hatakeyama, E. S.; Noble, R. D.; Gin, D. L. *Ind. Eng. Chem. Res.* **2007**, *46*, 5397.