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Carbon Dioxide Separation with Supported Ionic Liquid Membranes

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Abstract

Supported liquid membranes are a class of materials that allow the researcher to utilize the wealth of knowledge available on liquid properties as a direct guide in the development of a capture technology. These membranes also have the advantage of liquid phase diffusivities higher than those observed in polymeric membranes which grant proportionally greater permeabilities. The primary shortcoming of the supported liquid membranes demonstrated in past research has been the lack of stability caused by volatilization of the transport liquid. Ionic liquids, which possess high carbon dioxide solubility relative to light gases such as hydrogen, are an excellent candidate for this type of membrane since they have negligible vapor pressure and are not susceptible to evaporation.

A study has been conducted evaluating the use of several ionic liquids, including 1-hexyl-3-methyl-imidazolium bis(trifuoromethylsulfonyl)imide, 1-butyl-3-methyl-imidazolium nitrate, and 1-ethyl-3-methyl-imidazolium sulfate in supported ionic liquid membranes for the capture of carbon dioxide from streams containing hydrogen. In a joint project, researchers at the University of Notre Dame lent expertise in ionic liquid synthesis and characterization, and researchers at the National Energy Technology Laboratory incorporated candidate ionic liquids into supports and evaluated the resulting materials for membrane performance. Initial results have been very promising with carbon dioxide permeabilities as high as 950 barrers and significant improvements in carbon dioxide/hydrogen selectivity over conventional polymers at 37C and at elevated temperatures. Results include a comparison of the performance of several ionic liquids and a number of supports as well as a discussion of innovative fabrication techniques currently under development.

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Introduction

One means of addressing the problems of continued energy production in a carbon constrained world is capture and sequestration of carbon dioxide produced including fossil fuel-based power generation. The United States Department of Energy's carbon sequestration programmatic goals demand technologies capable of capturing 90% of carbon dioxide from new power plants by 2012 with no more than a 10% increase in the cost of electricity. Carbon dioxide capture and sequestration from coal gasification processes, which may make up a significant fraction of future power generation, is an important area of exploration in energy research. Capture in these gasification systems will most likely take place after water-gas shift produces a fuel gas mixture containing hydrogen, carbon dioxide, water and contaminants. Carbon dioxide capture technologies for shifted fuel gas should work at elevated temperature (250^oC or above) to maximize the efficiency of the power generation process and should be able to handle other components present in the fuel gas. Carbon dioxide selective membranes are a promising capture technology for use under these conditions.

Supported liquid membranes (SLMs) consist of a liquid transport medium through which gas may pass at a high rate and a porous solid support. Stability is a concern because evaporation of the liquid may lead to unfilled pores, gas phase diffusion, and membrane failure [1]. Despite this shortcoming, performance results for SLMs have been encouraging [2, 3].

Ionic liquids are salts that are liquid at or slightly above room temperature [4, 5]. Among a number of other interesting properties, they are known to have negligible vapor pressure. With the variety of cations and anions available, a nearly unlimited number of ionic liquids can be synthesized, and this variety allows tailoring for high carbon dioxide solubility. With the negligible vapor pressure and high solubility for carbon dioxide, ionic liquids could make ideal candidates for SLMs.

In the present work, supported ionic liquid membranes (SILMs) have been prepared from three different ionic liquids: 1-hexyl-3-methyl-imidazolium bis(trifuoromethylsulfonyl)imide ([hmim][Tf_2N]), 1-butyl-3-methyl-imidazolium nitrate ([bmim][NO_3], and 1-ethyl-3-methyl-imidazolium ethylsulfate ([emim][ESO_4]) and a polysulfone support. These membranes have been tested at 37 and 100 ^oC to determine performance in the selective separation of CO_2/H_2. In addition to the initial study of various ionic liquids for SILMs, the ionic liquid

[hmim][Tf_2N] was used in an investigation evaluating polymeric supports up to temperatures of 300^oC.

Experimental

Materials

The ionic liquid [hmim][Tf_2N] was synthesized at the University of Notre Dame using standard procedures [6, 7]. The ionic liquids [bmim][NO_3] and [emim][SO_4] were obtained from Sigma-Aldrich and Solvent Innovation, respectively. HT Tuffryn® (polysulfone) and Biodyne® A (crosslinkable nylon) polymeric porous substrates from Pall Corporation were used as supports for ionic liquid membranes. The support discs were 25 mm in diameter with an active membrane area of 2.2 cm^2.

Membrane Performance Testing

Testing was performed in a flow system where the permeate and retentate gas compositions were measured using a HP 5890 or a Perkin Elmer Clarus 500 gas chromatograph with twin TCD detectors and Alltech hayesep D 100/120 packed columns. Flows were measured with a digital, bubble flow meter. Temperature was measured by a Type K thermocouple in contact with the surface of the testing cell. The membrane was placed on the permeate side of a Millipore® filter holder and an unmodified substrate identical to the one used to prepare the membrane was place against the membrane on the feed side to reduce the stress on the membrane. The feed gas flowed at approximately 30 ml/min and consisted of 20.01% carbon dioxide, 19.97 % hydrogen and the balance argon. A sweep on the permeate side of 1.0 to 2.0 ml/min argon was used. The pressure was approximately 108 kPa for the feed and the permeate pressure was less then 102 kPa.

Results and Discussion

Ionic Liquid Scan

Table 1 shows performance results for the various ionic liquids used in this study. All three sets of SILMs had significantly higher carbon dioxide permeability at 37^oC than most polymeric membranes with a maximum carbon dioxide permeability of 740 barrer for the [hmim][Tf_2N] based SILMs. The CO_2/H_2 selectivity at 37^oC ranged from a maximum of 6.0 for the [hmim][Tf_2N] based SILMs to as low as 4.7 for [emim][ESO_4] based SILMs. The [hmim][Tf_2N] based SILM compares favorably with other membranes including SLMs [8], other SILMs [9-11] and plasticized polymers [12]. When the temperature was increased from 37 to 100^oC, the permeability increased for both carbon dioxide and hydrogen for all three SILM sets. However, whereas the carbon dioxide permeability for the [hmim][Tf_2N] based SILMs increased significantly with increased temperature, [bmim][NO_3] increased moderately and [emim][ESO_4] had a very slight increase.

The hydrogen permeability increased at a faster rate than carbon dioxide permeability for all three SILMs. This trend resulted in a decrease in the selectivity for all membranes at 100^{o}C, with [emim][ESO_4] and [bmim][NO_3] based SILMs showing the largest decreases.

Solution diffusion is the dominant transport mechanism in SILMs. A gas molecule dissolves into the membrane, diffuses across the membrane, and evolves on the other side of the membrane. When the temperature increases for a membrane, the solubility coefficients of the membrane decrease and the diffusivity coefficient increases which typically results in a net increase in the permeability. The carbon dioxide permeability is largely dependent on its solubility coefficient within the membrane, while inversely, hydrogen is largely dependent on the diffusivity coefficient of the membrane. With increasing temperature, a loss in CO_2/H_2 selectivity can be expected with a solution diffusion mechanism, and the data in Table 1 reflects this conclusion.

High Temperature

Table 1. The permeability and selectivity for three SILMs supported on HT Tuffryn®

	37^{o}C		**100^{o}C**	
Ionic Liquid	P_{CO_2} **(Barrer)**	α_{CO_2/H_2}	P_{CO_2} **(Barrer)**	α_{CO_2/H_2}
[hmim][TF_2N]	740	6.00	1120	3.00
[emim][ESO_4]	330	4.71	370	1.37
[bmim][NO_3]	440	5.20	610	2.10

The ionic liquid [hmim][Tf_2N] was used in the high temperature study because of the encouraging results from the initial SILMs scan. Initially the HT Tuffyrn® support was used in this study. Helium was used as a surrogate for hydrogen in this portion of the experiment. In the temperature range from 37 to 125^{o}C, the permeability of carbon dioxide increased from 744 to 1200 barrer. Helium permeability increases from 86 to 270 barrer over the temperature range of 37 to 100^{o}C. Over these temperature ranges, both permeability increases with Arrhenius dependencies. At 135^{o}C, the permeability for both carbon dioxide and helium dropped significantly to 155 and 50 barrer, respectively. The CO_2/He selectivity decreased from 8.7 at 37^{o}C to 3.1 at 135^{o}C with the entire temperature range showing Arrhenius dependence. Above 135^{o}C, membrane failure occurred.

The second portion of the elevated temperature experiments was conducted to identify a possible support that is stable at elevated temperature. For this section, Biodyne® A supports were used because these materials may be crosslinked for greater thermal stability. The ionic liquid [hmim][Tf_2N] was used as the liquid medium for these experiments. Over the temperature range of 37 to 300^{o}C, the permeability increased from 500 to 1170 barrer and 55

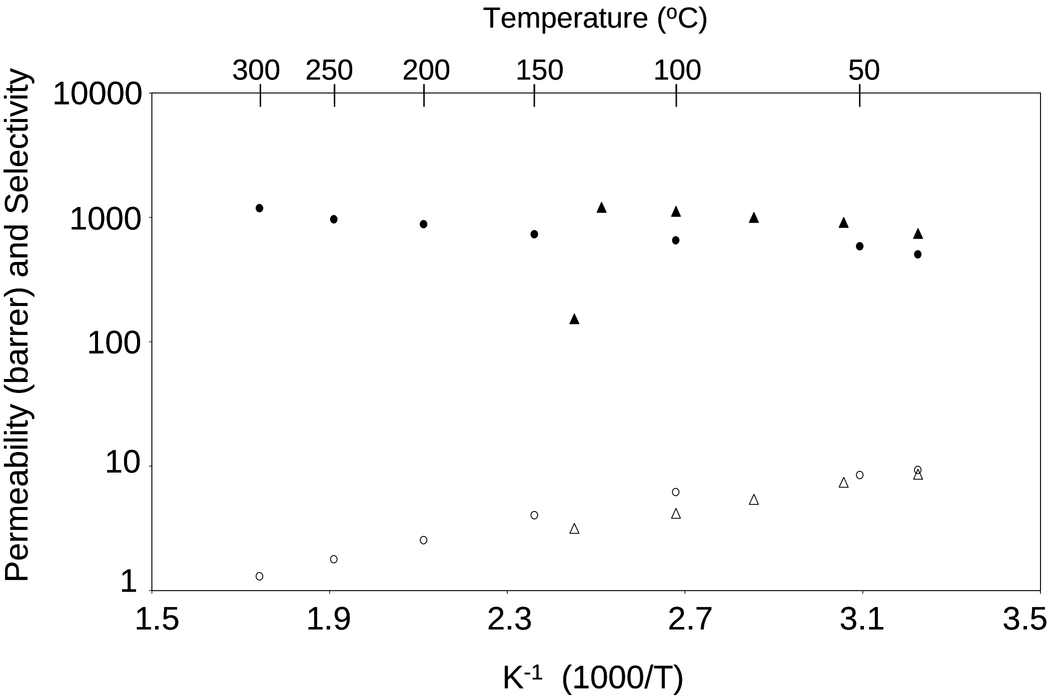

Figure 1. The carbon dioxide permeability for [hmim][Tf_2N] based SILM for HT Tuffryn ® (▲) and Biodyene® A (●). Also shown is the selectivity of CO_2/He (Δ) and CO_2/H_2 (○) for the HT Tuffryn® and Biodyene® A membrane respectively. All data are shown as a function of 1000/K over the temperature range of 37 – 300°C.

to 920 barrer, for carbon dioxide and hydrogen, respectively. The CO_2/H_2 selectivity decreased from 9.0 to 1.3 over the same temperature range. The permeabilities and selectivity showed Arrhenius dependence over the entire temperature range. Figure 1 shows elevated temperature results for both the HT Tuffyrn® and Biodyne® A.

Several reasons may be hypothesized explaining the differences in permeability and CO_2/H_2 selectivity between HT Tuffyrn® and Biodyne® A in the lower temperature range of operation. The porosity of the Biodyne® A substrate is not known. Differences in porosity could significantly affect the comparison of permeability between the two supports. There could also be different interactions between the ionic liquid and the two supports which could alter both the permeability and selectivity of the two ionic liquid membranes.

The results of the high temperature experiments showed several key finding. The decrease in permeability of the HT Tuffryn® SILM at 135°C was attributed to the collapse of the pores reducing the porosity of the membrane [13]. This reduction in porosity reduced the available pathway for gas transport. Since the selectivity retained an Arrhenius dependence, it suggests that the mechanism for transport across the membrane is through the ionic liquid. Another important observation is that the CO_2/H_2 selectivity at 300°C was 1.3. The results were very encouraging because the selectivity is expected to decrease with increasing temperature in a solution diffusion transport mechanism and thus indicated that the mechanical integrity of the membrane and substrate were not compromised and that throughout the temperature range, the permeability showed Arrhenius dependence. The next step is to find an ionic liquid that is capable of high selectivity for CO_2/H_2 at elevated temperatures.

Conclusions

The use of several different ionic liquids to produce SILMs shows that the choice of the ionic liquid is important. While the results of the three ionic liquids tested were quite different, all sets of the SILMs showed higher carbon dioxide permeability and improved CO_2/H_2 selectivity when compared to traditional polymeric membranes. Although the [hmim][Tf_2N]-based SILMs compared favorably to the many current membranes, much more work is required.

Results from the high temperature experiments revealed several important concepts. The significant drop in permeability of the HT Tuffyrn® SILM at $135^{o}C$ can be attributed to a decrease in the porosity and not a degradation of the ionic liquid, and the Biodyne® A support are mechanically stable at temperatures to at least $300^{o}C$. An ionic liquid that has good selectivity at elevated temperature will be the next requirement in the development of a CO2 selective membrane for precombustion capture of carbon dioxide.

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References

1. **Bao LH, Trachtenberg MC: Facilitated transport of CO2 across a liquid membrane: Comparing enzyme, amine, and alkaline. *Journal of Membrane Science* 2006, 280:330-334.**
2. **Teramoto M, Takeuchi N, Maki T, Matsuyama H: Gas separation by liquid membrane accompanied by permeation of membrane liquid through membrane physical transport. *Separation and Purification Technology* 2001, 24:101-112.**
3. **Ito A, Duan SH, Ikenori Y, Ohkawa A: Permeation of wet CO2/CH4 mixed gas through a liquid membrane supported on surface of a hydrophobic microporous membrane. *Separation and Purification Technology* 2001, 24:235-242.**
4. **Welton T: Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chemical Reviews* 1999, 99:2071-2083.**
5. **Wasserscheid P, Keim W: Ionic liquids - New "solutions" for transition metal catalysis. *Angewandte Chemie-International Edition* 2000, 39:3773-3789.**
6. **Crosthwaite JM, Aki S, Maginn EJ, Brennecke JF: Liquid phase behavior of imidazolium-based ionic liquids with alcohols: effect of hydrogen bonding and non-polar interactions. *Fluid Phase Equilibria* 2005, 228:303-309.**
7. **Crosthwaite JM, Aki S, Maginn EJ, Brennecke JF: Liquid phase behavior of imidazolium-based ionic liquids with alcohols. *Journal of Physical Chemistry B* 2004, 108:5113-5119.**
8. **Teramoto M, Nakai K, Ohnishi N, Huang QF, Watari T, Matsuyama H: Facilitated transport of carbon dioxide through supported liquid membranes of aqueous amine solutions. *Industrial & Engineering Chemistry Research* 1996, 35:538-545.**
9. **Scovazzo P, Kieft J, Finan DA, Koval C, DuBois D, Noble R: Gas separations using non-hexafluorophosphate [PF6](-) anion supported ionic liquid membranes. *Journal of Membrane Science* 2004, 238:57-63.**
10. **Scovazzo P, Visser AE, Davis JH, Rogers RD, Koval CA, DuBois DL, Noble RD: Supported ionic liquid membranes and facilitated ionic liquid membranes. In *Ionic Liquids. Volume* 818. Washington: Amer Chemical Soc; 2002: 69-87: *Acs Symposium Series*].**
11. **Baltus RE, Counce RM, Culbertson BH, Luo HM, DePaoli DW, Dai S, Duckworth DC: Examination of the potential of ionic liquids for gas separations. *Separation Science and Technology* 2005, 40:525-541.**
12. **Lin HQ, Van Wagner E, Freeman BD, Toy LG, Gupta RP: Plasticization-enhanced hydrogen purification using polymeric membranes. *Science* 2006, 311:639-642.**
13. **Rezac ME, Moore NS, Back A: Effect of temperature on the transport properties and morphology of polymeric asymmetric membranes. *Separation Science and Technology* 1997, 32:505-525.**