

This article was downloaded by:

On: 25 January 2011

Access details: Access Details: Free Access

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Examination of the Potential of Ionic Liquids for Gas Separations

Ruth E. Baltus^a; Robert M. Counce^b; Benjamin H. Culbertson^b; Huimin Luo^c; David W. DePaoli^c; Sheng Dai^d; Douglas C. Duckworth^d

^a Department of Chemical Engineering, Clarkson University, Potsdam, NY, USA ^b Department of Chemical Engineering, The University of Tennessee, Knoxville, TN, USA ^c Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA ^d Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

To cite this Article Baltus, Ruth E. , Counce, Robert M. , Culbertson, Benjamin H. , Luo, Huimin , DePaoli, David W. , Dai, Sheng and Duckworth, Douglas C.(2005) 'Examination of the Potential of Ionic Liquids for Gas Separations', Separation Science and Technology, 40: 1, 525 — 541

To link to this Article: DOI: 10.1081/SS-200042513

URL: <http://dx.doi.org/10.1081/SS-200042513>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Examination of the Potential of Ionic Liquids for Gas Separations

Ruth E. Baltus

Department of Chemical Engineering, Clarkson University, Potsdam,
NY, USA

Robert M. Counce and Benjamin H. Culbertson

Department of Chemical Engineering, University of Tennessee,
Knoxville, TN, USA

Huimin Luo and David W. DePaoli

Nuclear Science and Technology Division, Oak Ridge National
Laboratory, Oak Ridge, TN, USA

Sheng Dai and Douglas C. Duckworth

Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge,
TN, USA

Abstract: Ionic liquids have received increasing interest in recent years for “green” synthesis and separations because they have essentially no vapor pressure. We have begun an investigation of the potential of ionic liquids for gas separations, including the removal of carbon dioxide from stack gas generated in coal-fired power plants. In this paper, we report results from measurements of the permeance of nitrogen and carbon dioxide in supported ionic liquid membranes. Preliminary results for a porous alumina membrane saturated with 1-butyl-3-methyl imidazolium

This article is not subject to U.S. copyright law.

Research sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

Address correspondence to Ruth E. Baltus, Department of Chemical Engineering, Clarkson University, Potsdam, NY 13699-5705, USA. E-mail: baltus@clarkson.edu

bis[trifluoromethylsulfonyl] amide yielded a CO₂:N₂ selectivity of 127. Using previously reported measurements of CO₂ solubility in ionic liquids (1) and the measured membrane transport characteristics, a preliminary economic analysis of a separation process based on supported ionic liquid membranes has been performed. A comparison of cost estimates for this membrane-based separation to cost estimates reported for carbon dioxide removal using a conventional amine scrubbing operation shows that, with continued technology development, an ionic liquid membrane process may potentially be economically competitive with amine scrubbing. A preliminary cost estimate for an ionic liquid scrubber indicates that an ionic liquid absorption process shows less favorable economics than a supported ionic liquid membrane or an amine scrubber. However, results indicate that a more comprehensive technical and economic assessment is warranted.

INTRODUCTION

Carbon Dioxide Removal from Flue Gas Streams

Fossil fuel power plants are a major source of carbon dioxide emissions in North America. Because carbon dioxide is generally recognized as the main greenhouse gas leading to global warming, there has been increasing interest in the development of economically viable technologies for the removal of carbon dioxide from flue gas streams.

Amine scrubbing is the most widely accepted process for CO₂ removal from flue gas streams. This technology has been used for many years for acid gas scrubbing but is relatively new for flue gas treatment (2). Simbeck (3) performed an economic comparison of options for capture of carbon dioxide from existing coal-fired power plants. An economic assessment of retrofitting an existing power plant with amine scrubbing resulted in an estimated cost of \$33 per metric ton of CO₂ emissions avoided.

Ionic Liquids

We are interested in examining alternative processes for carbon dioxide separation that employ room-temperature ionic liquids. Ionic liquids are a relatively new class of compounds that have received increased attention in recent years as “green” designer solvents that may potentially replace many conventional volatile organic solvents in reaction and separation processes (4–13). These unique compounds are organic salts that are liquid over a wide range of temperatures near and at room temperature. Ionic liquids have no measurable vapor pressure; hence there has been considerable interest in using them in place of volatile organic solvents that can emit problematic vapors.

The most commonly investigated room-temperature ionic liquids have an alkyl-substituted methyl imidazolium salt as the cation. The

imidazolium-based salts are relatively easy to synthesize and have physical properties that make them attractive for many chemical processes. The generally accepted acronym for the alkyl-substituted methyl imidazolium cations is $C_n\text{mim}^+$ where n is the number of carbon atoms on the alkyl side chain. Common anions used in ionic liquids include bis[trifluoromethylsulfonyl] amide (Tf_2N^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-) and ethyl sulfate (EtSO_4^-), although ionic liquids with a variety of other anions have also been synthesized (14, 15).

We have begun an investigation of the potential of ionic liquids for separating carbon dioxide from flue gas streams (1, 16). This investigation has involved solubility measurements, gas transport measurements through supported ionic liquid membranes and a preliminary economic analysis that provides target characteristics for ionic liquids used in a supported ionic liquid membrane process that can be economically competitive with amine scrubbing.

The solubility of carbon dioxide in various ionic liquids was measured using a quartz crystal microbalance (1). Measurements yielded the Henry's constant for carbon dioxide in each liquid at 25°C. The H values determined from these measurements have been previously reported and values of interest to this study are summarized in Table 1. These H values range from 35 to 50 bar for commonly studied imidazolium-based ionic liquids; those results are in general agreement with results from other laboratories obtained using different measurement techniques. Significant enhancement of the solubility of carbon dioxide was observed with an ionic liquid containing a fluorinated imidazolium cation, with $H = 6$ bar. However, attempts by another laboratory to confirm our value for the ionic liquid with the fluorinated cation have not been successful (17). We are undertaking new experiments to identify the source of discrepancy between the solubility value measured in our laboratory for this ionic liquid and the value determined by others using microbalance absorption.

Table 1. Summary of Henry's constants for CO_2 in ionic liquids (1) (uncertainties are the 95% confidence limits)

| Ionic liquid | H_{CO_2} (bar) |
|---|-------------------------|
| C_3mimPF_6 | 52 ± 5 |
| $\text{C}_4\text{mimTf}_2\text{N}$ | 37 ± 3 |
| $\text{C}_8\text{mimTf}_2\text{N}$ | 30 ± 1 |
| $\text{C}_8\text{F}_{13}\text{mimTf}_2\text{N}$ | 6 ± 1^a |
| 58 mol% $\text{C}_8\text{mimTf}_2\text{N}$ /42 mol% $\text{C}_8\text{F}_{13}\text{mimTf}_2\text{N}$ | 15 ± 1 |

^aValue revised from (1) by further analysis.

Membrane Separations

There are a number of different process options for utilizing ionic liquids to separate CO₂ from a flue gas stream. Our efforts have primarily focused on examining CO₂ separations in a supported ionic liquid membrane where the pores of a porous membrane are saturated with an ionic liquid. Ionic liquids are particularly attractive in a membrane separation device because their extremely low volatility will minimize solvent losses from the membrane.

There have been few studies that have examined the transport of some target species through supported ionic liquid membranes. Scovazzo et al. (11) measured the permeability to CO₂ and air of polyethersulfone membranes that were saturated with C₄mim PF₆. Results yielded CO₂ selectivity relative to air of 29. Branco et al. (8) measured the relative flux rates for primary, secondary and tertiary amines (hexylamine, diisopropylamine, and triethylamine) in a supported ionic liquid membrane comprising of C₄mim PF₆ immobilized in a porous polyvinylidene fluoride membrane. Results showed the membrane to be selective for the diisopropylamine relative to the other amines. The membrane exhibited good stability over a 14-day operation.

The objective of this study was to measure the permeance of supported ionic liquid membranes to CO₂ and N₂ and to use the results from these measurements to estimate the cost of retrofitting an existing coal-fired power plant with a membrane-based separator for CO₂ removal.

EXPERIMENTAL

Ionic Liquids

All of the ionic liquids were synthesized as described in the literature (14, 18–22). For the ionic liquid with the fluorinated cation (C₈F₁₃mimTf₂N), our synthesis followed the method reported by Merrigan et al. (22) for C₈F₁₃mimI. This iodide salt was converted into the bis[trifluoromethyl sulfonyl] amide salt using a method that we have previously reported (1).

It is recognized that ionic liquids with the PF₆[−] anion are particularly sensitive to water (12). However, our previous results showed that CO₂ solubility was not strongly influenced by the presence of water for C₈mimTf₂N in contact with gas with relative humidity less than 40% (1). Our membrane permeation experiments were limited to measurements with C₄mimTf₂N and C₈F₁₃mimTf₂N. Because these ionic liquids with the Tf₂N[−] anion are not expected to be sensitive to water, and because in practical application the ionic liquid would be exposed to flue gases with significant water content, efforts were not made to remove water from the ionic liquids prior to incorporation into the membranes.

Membranes

Porous anodic alumina membranes (Whatman) with 47-mm diameter, 0.02- μm pore size and 60- μm thickness were used for the supported ionic liquid membranes. The ionic liquid was applied to the membrane surface using a cotton swab. Excess liquid was removed from the surface using a lint-free wipe. The membrane was then spun at 3000 rpm in a spin-coater for 5 min, producing a visually uniform surface.

Membrane Permeance Measurements

The experimental system used to measure CO_2 and N_2 permeance in the supported ionic liquid membranes is shown in Fig. 1. The membrane was positioned in a custom built holder which included a metal support screen on the downstream face of the membrane. These measurements involved single gases only, which enabled us to determine membrane permeance by monitoring the pressure increase with time that occurs as the target gas permeates across the membrane from a constant high pressure on one side of the membrane to a

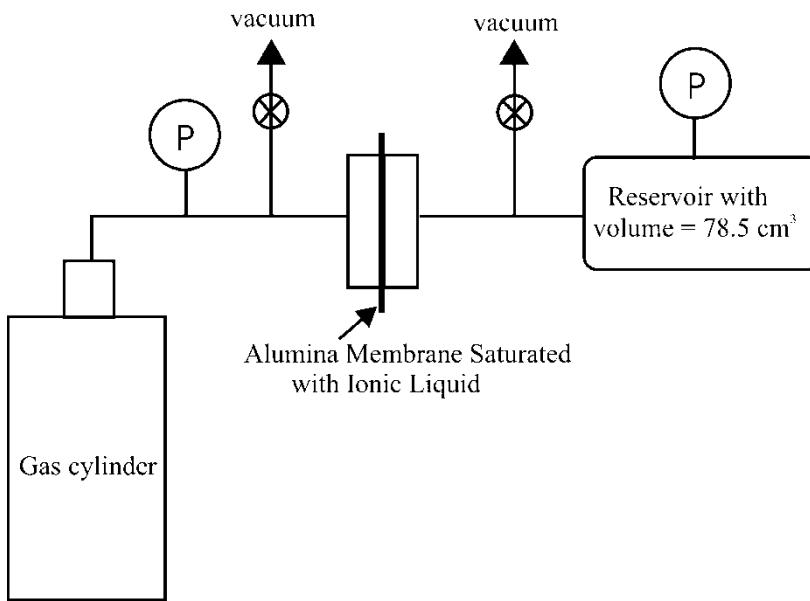


Figure 1. Schematic diagram of experimental system used to measure membrane permeance to CO_2 and N_2 .

fixed volume (78.5 cm^3) on the downstream side. The pressure on each side of the membrane was monitored using Sensotec SC pressure sensors.

To begin an experiment, both the upstream and downstream chambers were evacuated and then purged several times with the test gas. A pressure difference of less than 5 psi was then established across the membrane at time = 0 with the upstream pressure at 14 to 17 psia. The upstream pressure was maintained at a constant value, while the downstream pressure was recorded as a function of time.

The permeance of species i across the membrane is defined as the proportionality factor between the flux of i and the partial pressure driving force across the membrane and is related to gas solubility and diffusivity as well as membrane characteristics:

$$J_i = \text{Permeance}_i \times \Delta P_i = \frac{\text{Solubility}_i \times \text{Diffusivity}_i}{\text{Membrane Thickness}} \times \Delta P_i \quad (1)$$

If it is assumed that the gas on both sides of the membrane is pure i , an analysis of gas transport across the membrane yields the following expression for the time dependence of the pressure in the downstream chamber:

$$\frac{P_{\text{upstream}} - (P_{\text{downstream}} - P_0)}{P_{\text{upstream}}} = \exp \left[\frac{ART}{V_{\text{downstream}}} \text{Permeance}_i \times t \right] \quad (2)$$

where P_{upstream} is the constant pressure on the upstream side of the membrane, P_0 is the initial pressure in the downstream chamber and $P_{\text{downstream}}$ is the pressure on the downstream chamber at time t , A is the membrane area available for transport, and $V_{\text{downstream}}$ is the volume of the downstream chamber. By measuring the downstream pressure as a function of time, the permeance can be determined from the slope of an appropriate semi-log plot because all other parameters in Eq. (2) are known. Experiments were performed to measure the permeance to CO_2 and N_2 of supported ionic liquid membranes containing $\text{C}_4\text{mimTf}_2\text{N}$ and $\text{C}_8\text{F}_{13}\text{mimTf}_2\text{N}$. The ideal selectivity of each membrane to CO_2 relative to N_2 was estimated from the ratio of the permeance to each gas:

$$\text{Selectivity} = \frac{\text{Permeance}_{\text{CO}_2}}{\text{Permeance}_{\text{N}_2}} \quad (3)$$

RESULTS AND DISCUSSION

A semilog plot of $(P_{\text{upstream}} - (P_{\text{downstream}} - P_0))/P_{\text{upstream}}$ as a function of time for the transport of CO_2 through a supported ionic liquid membrane containing $\text{C}_4\text{mimTf}_2\text{N}$ is shown in Fig. 2. Results show the linear relationship predicted by Eq. (2). The CO_2 permeance was calculated from the

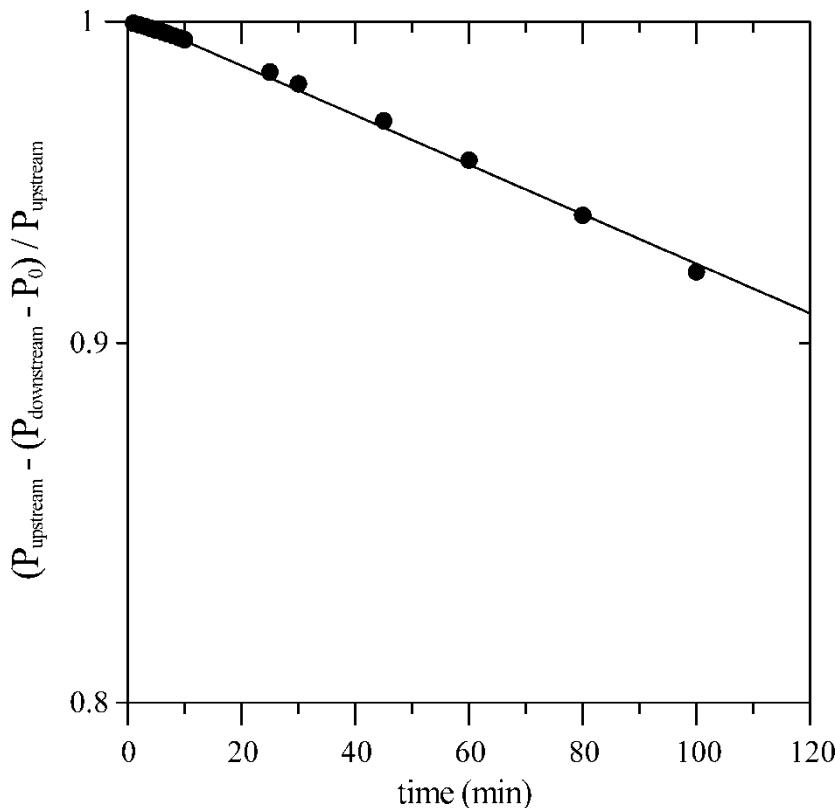


Figure 2. Experimental results for CO₂ permeability in C₄mimTf₂N, plotted according to Eq. (2). Permeance value was determined from the slope of the best fit line.

slope of the resulting line. Results for the measured permeance values and the resulting selectivity are summarized in Table 2.

The solubility measurements (Table 1) show considerably higher CO₂ solubility in C₈F₁₃mimTf₂N when compared to C₄mimTf₂N. However, the opposite trend was observed with the permeance values, with C₄mimTf₂N

Table 2. Measured CO₂ and N₂ permeance in supported ionic liquid membranes

| Supported ionic liquid | Gas | Permeance mol bar ⁻¹ cm ⁻² sec ⁻¹ | Ideal selectivity |
|---|-----------------|---|-------------------|
| C ₄ mimTf ₂ N | CO ₂ | 4.0×10^{-9} | 127 |
| | N ₂ | 3.2×10^{-11} | |
| C ₈ F ₁₃ mimTf ₂ N | CO ₂ | 1.5×10^{-9} | 72 |
| | N ₂ | 2.1×10^{-11} | |

being over twice as permeable to CO₂ as C₈F₁₃mimTf₂N. These observations can be explained by recognizing that the permeance of a supported liquid membrane to a particular species reflects both the solubility as well as the diffusion coefficient of the gas in the liquid. The fluorinated ionic liquid was noticeably more viscous than the nonfluorinated C₄mimTf₂N. This higher viscosity will yield a smaller diffusivity for CO₂; the slower diffusion apparently counters the favorable thermodynamics for this ionic liquid. This explanation is supported by examination of the N₂ permeance values that also show a larger permeance in the C₄mimTf₂N ionic liquid membrane. As noted earlier, it is also possible that the CO₂ solubility in C₈F₁₃mimTf₂N may not be as favorable as indicated by our measurements.

In an earlier report from CO₂ permeability measurements through ionic liquid membranes with C₄mim PF₆ in polyethersulfone membranes, Scovazzo et al. (9) report a CO₂ permeance value of similar magnitude (4.6×10^{-9} mol bar⁻¹ cm⁻² sec⁻¹) and a CO₂/air selectivity of 29. Our solubility measurements indicate CO₂ is slightly less soluble in C₃mimPF₆ than in C₄mimTf₂N and we do not expect significant solubility differences for CO₂ in C₄mimPF₆ when compared to C₃mimPF₆. The C₃mimPF₆ used in our solubility measurements was somewhat more viscous than the C₄mimTf₂N. Given this difference in viscosity and the observed difference in CO₂ solubility, one would expect CO₂ permeance in C₄mimPF₆ to be less than that observed with C₄mimTf₂N. The opposite trend was observed when comparing the permeance value measured with C₄mimTf₂N to the value reported by Scovazzo et al. with C₄mimPF₆. However, a direct comparison of the permeability of the membrane used by Scovazzo et al. and the membranes used in our measurements is difficult because different support membranes were used. The fact that the trend observed from permeability measurements is different than expected based on ionic liquid characteristics can be explained by recognizing that there are likely differences in the porosity and/or thickness of the two different support membranes. It is also possible that CO₂ and N₂ are soluble in the polyethersulfone membranes used by Scovazzo et al. Additional quantitative information about the physical properties of these ionic liquids as well as the support membranes is needed before a firmer explanation for the permeance differences can be proposed.

ECONOMIC COMPARISON

The characteristics of the ionic liquids that have been reported in this paper provide the basis needed to make a preliminary economic assessment of processes based on ionic liquids for removing carbon dioxide from power plant flue gases. This analysis follows the approach of earlier work by Simbeck (3) in which the cost of retrofitting an existing coal-fired power plant with an amine scrubber was estimated. The basis of that work was an

existing pulverized coal process utilizing 152.6 mt/hr of coal and generating 290 MW of electricity and 283 mt/hr (0.971 mt/MW hr) of CO₂. Retrofitting this process with an amine scrubber requires an additional boiler to provide the steam needed for stripping as well as the additional power needed for CO₂ drying and compression to 2000 psig for effective transport and utilization of the recovered CO₂. This additional power generation capacity was added to the process for comparison purposes so that the retrofitted process maintained the same net power output as the original power plant. The amine scrubbing process also requires a low-pressure steam generator to provide steam for stripping the amine solution of CO₂. An economic analysis of the retrofitted operation showed that the carbon dioxide removal retrofit would cost \$33/mt CO₂ emissions avoided, with the cost in 1999 U.S. dollars. Because this is assumed to be a retrofit of an existing plant that will presumably still have original capital that has yet to be amortized, the remaining "old" capital (assumed to be 10% of the original \$284 MM capital cost) was refinanced along with the new capital required for the CO₂ removal. This cost analysis also assumes that there is a CO₂ credit of \$10/mt because the recovered CO₂ can be used for enhanced oil recovery, a reasonable assumption for certain regions in North America.

Our objective was to compare the feasibility of retrofitting this same power plant with an ionic liquid-based membrane separation process to the amine scrubbing retrofit discussed above. A proposed design for the addition of a supported ionic liquid separator to an existing process is shown in Fig. 3. Our analysis began by using the thermodynamic and

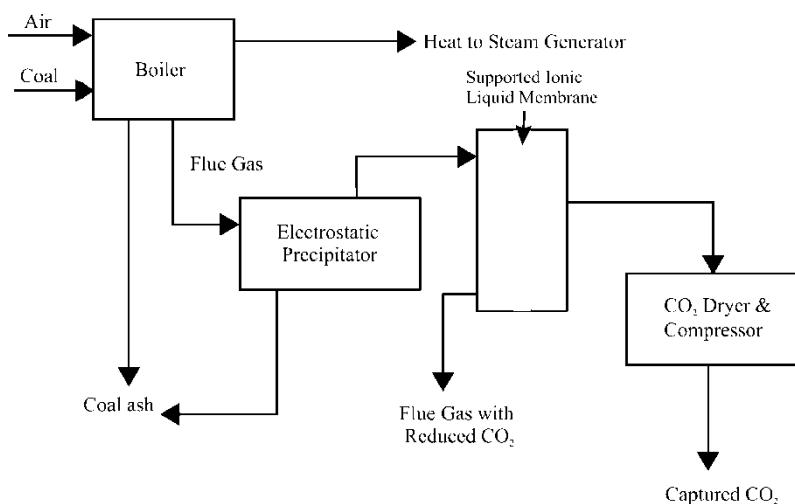


Figure 3. Process diagram for retrofit of existing coal-fired power plant with supported ionic liquid membrane separator for CO₂ capture.

transport properties of C_4mimTf_2N that are listed in Tables 1 and 2. It was assumed that supported membranes could be fabricated with an ionic liquid film that was five times thinner than the 60- μm thickness of the membranes used for our measurements, yielding permeance values five times larger than the values reported in Table 2. The supported liquid membrane would be in a tubular or hollow fiber geometry rather than the film geometry used for our permeance measurements. While a membrane with 12- μm thickness will probably not have the integrity needed for the gas separation process considered here, a membrane with a 12- μm ionic liquid separation layer on a structural support membrane does seem to be a reasonable possibility.

By comparing membrane mass before and after applying ionic liquid, it was found that $\sim 0.056\text{ g}$ of ionic liquid was applied to the 15.6- cm^2 anodic membrane films used for our measurements. If we assume that the porosity of the process scale membranes will be the same as the porosity of these anodic films, the mass of ionic liquid required per membrane area can be estimated. The cost of ionic liquid was estimated to be \$1000/kg, based on prices cited by various ionic liquid suppliers for small quantities of ionic liquid (5-kg maximum sample size). This is likely a conservative estimate, since it is anticipated that there will be significant economy of scale if these liquids are ultimately prepared for processes such as the separations considered in this report.

Cost estimation for porous membranes was based on a value of \$55 MM for a membrane area of $30 \times 10^6\text{ m}^2$ (23). The cost of membranes with area different than this was assumed to scale directly with membrane area.

With the membrane separator, a steam generator is not needed but power (above that provided by the original power plant) is still required for the CO_2 compressor. Following Simbeck (3), the additional power for this process is assumed to be supplied by a natural gas combined cycle plant (NGCC). Capital as well as operating costs were assumed to be directly proportional to the amount of power required.

With the assumptions noted here, it was estimated that the addition of the ionic liquid-based separation process to the existing power plant would cost a total of \$68 per metric ton of CO_2 emissions avoided, which is \$35 more per metric ton of CO_2 emission in comparison to the corresponding amine scrubber system. This analysis indicates that a membrane process utilizing C_4mimTf_2N is not competitive with amine scrubbing.

The economic analysis was then reconsidered by examining the cost for CO_2 removal using a supported ionic liquid membrane containing an ionic liquid having more attractive permeance characteristics. A comparison of the cost for CO_2 removal as a function of membrane permeance relative to the value of $4.0 \times 10^{-9}\text{ mol bar}^{-1}\text{ cm}^{-2}\text{ sec}^{-1}$ that was measured for CO_2 with C_4mimTf_2N is shown in Fig. 4. As the membrane permeance increases, processing costs for removing CO_2 decrease significantly, with the supported ionic liquid membrane process matching the \$33/mt CO_2

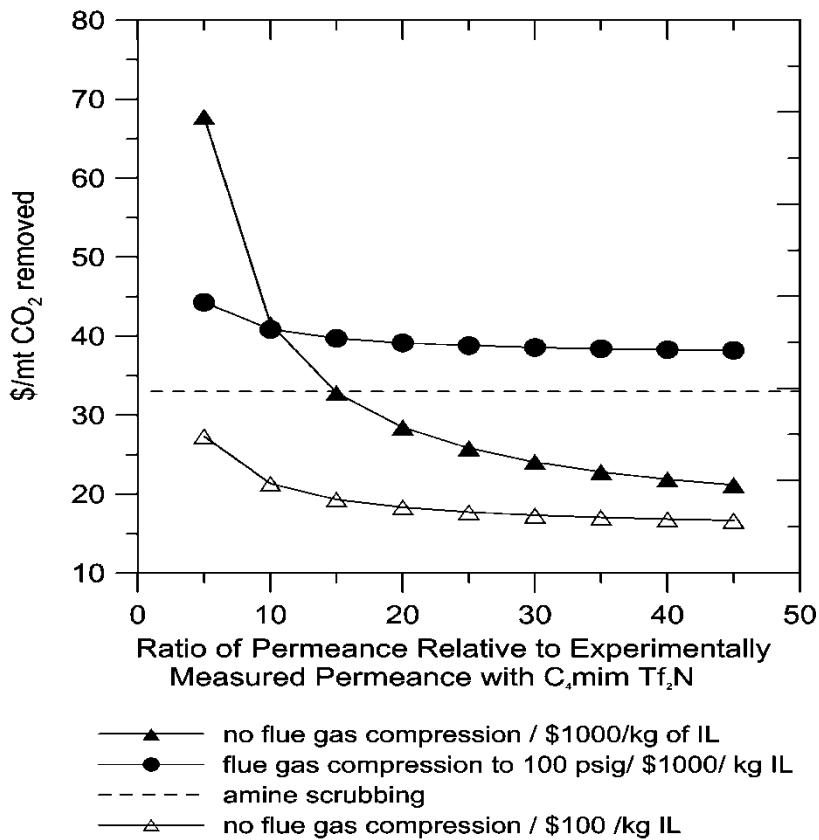


Figure 4. Comparison of costs for CO₂ removal for different membrane separation processes with amine scrubbing. Estimate for amine scrubbing is from Simbeck (3).

estimated for amine scrubbing for a membrane with permeance 15 times greater than the experimental measurement with C₄mimTf₂N.

It is important to note that there are a number of different ways that membrane permeance can be increased. This economic analysis began with one approach—to use an ionic liquid film with considerably shorter path length for transport than the 60-μm thickness of the membranes used for our measurements. To prepare a membrane containing a liquid film with thickness ~12 μm, one would need to use a different immobilization approach, probably with an asymmetric film having a separation layer of thickness comparable to the thickness of desired liquid film. The membrane permeance can also be changed by altering the characteristics of the ionic liquids used in the membranes. We have already identified several ionic liquids with advantageous thermodynamic properties but will need to synthesize ionic liquids with both advantageous thermodynamics as well as

transport characteristics. The results from our economic analysis presented in Figure 4 show that a membrane film with thickness of $\sim 12 \mu\text{m}$, a Henry's constant of 12 bar and CO_2 diffusivity comparable to that for $\text{C}_4\text{mimTf}_2\text{N}$, can be economically competitive with amine scrubbing. While we are not there yet, we feel that an ionic liquid membrane with these characteristics is achievable as we continue to explore new chemistry options as well as different avenues to prepare thin ionic liquid films.

The cost estimates discussed here were based on an ionic liquid cost of \$1000/kg, a value obtained from averaging current prices for small quantities of ionic liquid. The cost of a membrane-based separation process has also been estimated by assuming a considerably lower ionic liquid cost of \$100/kg, and results from this analysis are also included in Figure 4. This analysis shows that an ionic liquid-based separation in a membrane separator with a 12- μm ionic liquid film with the same thermodynamic and transport characteristics as $\text{C}_4\text{mimTf}_2\text{N}$ is \$27/metric ton of CO_2 removed, a cost 18% lower than Simbeck's estimate for amine scrubbing (3). As improved thermodynamic and/or transport characteristics of the ionic liquid are considered, the economics improves to $\sim \$18/\text{metric ton of CO}_2$ for an ionic liquid membrane with permeance ~ 20 times of the value measured in our experiments. This corresponds to a 12- μm ionic liquid film with $H = 9$ bar when CO_2 diffusivity is the same as $\text{C}_4\text{mimTf}_2\text{N}$.

Another approach that was considered for a supported ionic liquid membrane separator was to include a flue-gas compressor to increase the driving force for CO_2 transport through the membrane. The capital cost of this compressor was estimated using the same approach as used to cost the CO_2 compressor (\$1000/kW). To provide the power for this compressor, the size of the NGCC as well as the amount of natural gas used to fuel this unit was increased in proportion to the additional power requirements. The results are included in Fig. 4, where we have compared estimated economics with compression to 100 psig, and no compression. The analysis shows that addition of a flue-gas compressor improves the economics relative to the membrane process without compressing the flue gas when the membrane permeability is less than 5–10 times greater than our experimental values with $\text{C}_4\text{mimTf}_2\text{N}$. However, the economics are primarily dictated by the compressor costs and are much less sensitive to the membrane characteristics. An additional technical factor in the feasibility of gas compression will be the development of thin supported liquid membranes that retain membrane integrity at significant pressure difference across the membrane.

A comparison of CO_2 removal costs for a membrane with permeance five times greater than our experimental value for $\text{C}_4\text{mimTf}_2\text{N}$ as a function of the flue gas pressure entering the membrane separator is shown in Fig. 5. As pressure increases, the cost for CO_2 removal initially decreases as the membrane and ionic liquid cost decrease because of the increased driving

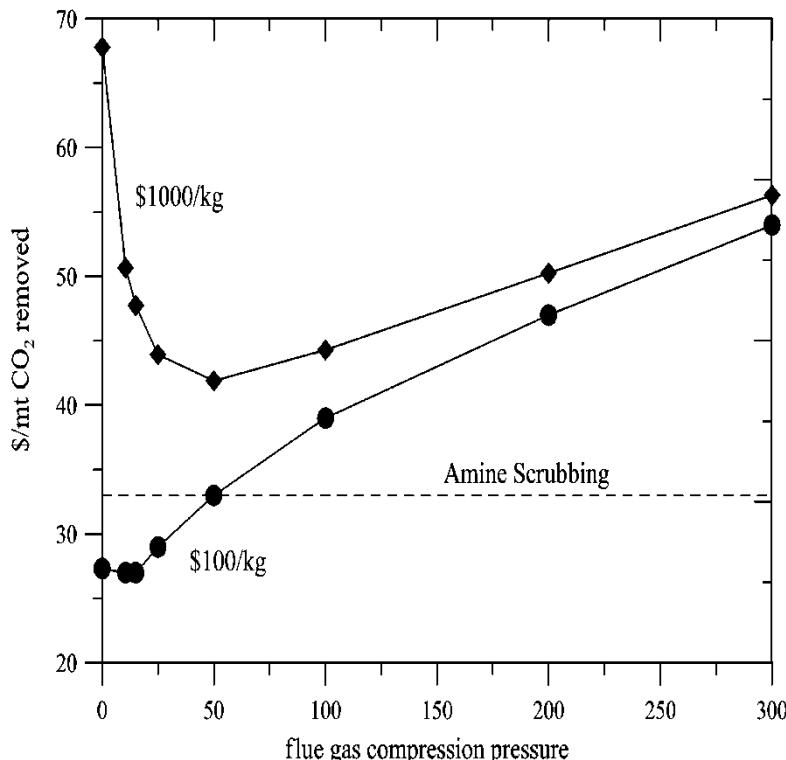


Figure 5. Effect of flue gas compression on CO₂ removal costs for supported ionic liquid membrane. Calculations assumed that the membrane permeance was five times greater than experimentally measured values with C₄mimTf₂N (i.e., ionic liquid film $\sim 12\text{-}\mu\text{m}$ thick).

force for CO₂ transport when ionic liquid costs are set at \$1000/kg. However, a cost minimum is experienced as the cost for increased compression counters the reduced membrane costs at a flue gas pressure of about 50 psig, and this minimum is at $\sim \$42/\text{mt CO}_2$ removed, about \$9/mt more than amine scrubbing. It appears that adding a flue gas compressor to the process will not provide an economically competitive process when compared to an amine scrubber with steam stripping when ionic liquid costs \$1000/kg. The cost estimates for the membrane process with flue gas compression when ionic liquid is available at \$100/kg show that, for flue gas compression to less than $\sim 20\text{ psig}$, the cost of CO₂ removal is generally insensitive to the flue gas pressure, with costs of \$27/metric ton of CO₂. As the flue gas pressure is increased, the cost of the compression becomes important and any gains that are made because of reduced membrane area are overcome by the increased cost resulting from compression.

Another option for utilizing ionic liquids for CO₂ removal from flue gas streams is to use the ionic liquids in an absorption tower. While the ionic liquids are considerably more expensive than typical amine solutions and the CO₂-ionic liquid solubilities are not as favorable as the stoichiometry of CO₂ removal via reaction with an amine, the process can be operated without the steam stripper because the absorbed CO₂ can be removed from the ionic liquid phase by a small drop in pressure or with an air stripper. Our objective was to perform a preliminary economic analysis in order to evaluate these competing phenomena.

To estimate costs for an ionic liquid based absorber that are consistent with Simbeck's analysis for an amine scrubber, it was necessary to estimate the amount of ionic liquid in the tower because the liquid cost may be significant. We began by assuming typical dimensions for the amine scrubber, a height of 50 ft and a diameter of 4 ft, giving a total column volume of 17.8 m³. If we assume 10% of this volume is occupied by liquid and there is an additional 1.5-ft length of column holding liquid at the bottom, the volume of liquid in the tower is 2.3 m³. If we assume the stripper is the same size and that there is 50% additional liquid in piping, the total amount of liquid is ~ 7 m³.

We have assumed that an ionic liquid scrubber will cost the same as an amine scrubber of the same size. However, it is anticipated that the cost of a stripper in an ionic liquid-based process will be considerably less than the \$130,000/mt CO₂/hr used to estimate the steam stripper cost in Simbeck's analysis. Therefore, for this analysis, a base cost of \$25,000/mt CO₂/hr was used for the stripper.

The thermodynamics of CO₂ removal will be different in an ionic liquid absorber when compared to an amine scrubber. It is noted in Chapel et al. (2) that the Fluor Daniel Econamine process removes approximately 0.25 mole of CO₂ per mole of solvent. If it is assumed this represents the equilibrium mole ratio of CO₂ to amine in an amine solution in contact with a feed gas with 20 mole% CO₂, the equivalent Henry's constant for CO₂ in amine can be estimated to be ~ 1 bar, a value smaller than the most favorable ionic liquid that we have investigated (Table 1). Therefore, an ionic liquid scrubber will require additional column length or additional units to achieve the same CO₂ removal level as an amine scrubber. In our analysis, we have considered the cost with additional absorber and stripper units. We have neglected any operating costs that will accompany the stripper which could be a slight vacuum or air for stripping.

A summary of the results from this analysis is presented in Fig. 6 where the cost per metric ton of CO₂ removed is plotted as a function of the number of equivalent absorbers and strippers for different ionic liquid costs. This analysis shows that the cost of an ionic liquid scrubber and stripper retrofit is generally insensitive to the cost of the ionic liquid but is strongly dependent upon the number of units (or height) that is required. Because of

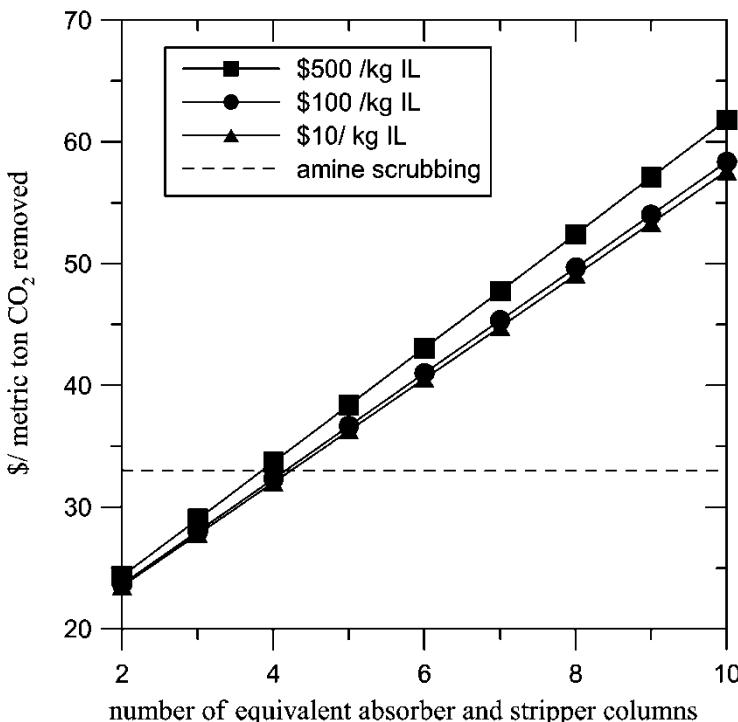


Figure 6. Cost estimates for CO₂ removal with an ionic liquid scrubber. The number of equivalent absorber and stripper columns is relative to a typical size of an amine stripper.

the different thermodynamic constraints for the ionic liquid process when compared to amine scrubbing, it is anticipated that at least five to six equivalent columns will be needed for an ionic liquid process. While these preliminary cost estimates indicate that the cost for such an ionic liquid process are greater than the \$33/mt CO₂ estimated by Simbeck for an amine scrubbing process, the difference between the estimated costs for the two types of processes is not significant, indicating that the ionic liquid process warrants a more thorough technical as well as economic evaluation.

CONCLUSIONS

An experimental investigation of CO₂ solubility and transport in a number of different ionic liquids has been performed. The membrane permeance values measured in this work are comparable to values reported by others using

similar supported ionic liquid membranes. The CO₂/N₂ selectivity measured in this work is improved over reports from other laboratories. The results illustrate that both transport as well as thermodynamic characteristics must be considered in developing ionic liquids for separation processes.

A preliminary economic assessment of a CO₂ separation process utilizing supported ionic liquid membranes indicates that such a separation may potentially be competitive with amine scrubbing. While the results from a similar economic analysis of an ionic liquid absorber are not as favorable, the results indicate that a more thorough analysis is warranted.

Among the developments that are needed before a realistic separation process can be demonstrated and a definitive evaluation of process feasibility can be made are the following: the durability and retention of the solvent in real process conditions must be demonstrated; ionic liquids must be immobilized in robust, high-flux supports; ionic liquids with more favorable combinations of solubility and transport properties must be developed; and potential environmental impacts must be considered (24).

REFERENCES

1. Baltus, R.E., Culbertson, B.H., Dai, S., Luo, H., and DePaoli, D.W. (2003) The Low-Pressure Solubility of Carbon Dioxide in Room-Temperature Ionic Liquids Measured with a Quartz Crystal Microbalance. *J. Phys. Chem.*, 108: 721.
2. Chapel, D., Ernest, J., and Mariz, C. Recovery of CO₂ from Flue Gases: Commercial Trends, Canadian Society of Chemical Engineers Annual Meeting, Saskatoon, Saskatchewan, October 4–6, 1999.
3. Simbeck, D.R. CO₂ Mitigation Economics for Existing Coal-Fired Power Plants, U.S. Department of Energy National Energy Technology Laboratory First National Conference on Carbon Sequestration, Washington, D.C., May 14–17, 2001.
4. Brennecke, J.F. and Maginn, E.J. (2001) Ionic Liquids: Innovative Fluids for Chemical Processing. *AIChE J.*, 47: 2384.
5. Brennecke, J.F.; Maginn, E.J. Purification of Gas with Liquid Ionic Compounds. US Patent 6,579,343, June 17, 2003.
6. Davis, J.H. and Fox, P.A. (2003) From Curiosities to Commodities: Ionic Liquids Begin the Transition. *Chem. Comm.* 1209.
7. Marsh, K., Deev, A., Wu, A.C.-T., Tran, E., and Klamt, A. (2002) Room Temperature Ionic Liquids as Replacements for Conventional Solvents—A Review. *Korean J. Chem. Eng.*, 19: 357.
8. Branco, L.C., Crespo, J.G., and Afonso, C.A.M. (2002) Highly Selective Transport of Organic Compounds by Using Supported Liquid Membranes Based on Ionic Liquids. *Angew. Chem. Int. Ed.*, 41: 2771.
9. Scovazzo, P., Visser, A.E., Davis, J.H., Rogers, R.D., Koval, C.A., Dubois, D.L., and Noble, R.D. (2002) Supported Ionic Liquid Membranes (SILMs) and Facilitated Ionic Liquid Membranes (FILMs). *ACS Symp. Series*, 818: 69.
10. Bates, E.D., Mayton, R.D., Ntai, I., and Davis, J.H. (2002) CO₂ Capture by a Task-Specific Ionic Liquid. *J. Amer. Chem. Soc.*, 124: 926.

11. Scovazzo, P., Poshuta, J., DuBois, D., Koval, C., and Noble, R. (2003) Electrochemical Separation and Concentration of <1% Carbon Dioxide from Nitrogen. *J. Electrochem. Soc.* D91.
12. Seddon, K.R., Stark, A., and Torres, M.-J. (2000) Influence of Chloride, Water and Organic Solvents on the Physical Properties of Ionic Liquids. *Pure Appl. Chem.* 2275.
13. Anthony, J.L., Maginn, E.J., and Brennecke, J.F. (2002) Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Phys. Chem. B*, 106: 7315.
14. Bonhôte, P., Dias, A.P., Papageorgiou, N., Kalyanasundaram, K., and Gratzel, M. (1996) Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.*, 35: 1168.
15. Wilkes, J.S. (2002) A Short History of Ionic Liquids—From Molten Salts to Neoteric Solvents. *Green Chem.*, 4: 73.
16. Culbertson, B.H. CO₂ Separation and Fuel Desulfurization Involving Room-Temperature Ionic Liquids. M.S. Thesis University of Tennessee: Knoxville 2003.
17. Brennecke, J.F. University of Notre Dame, personal communication.
18. Papageorgiou, N., Atnanassov, Y., Armand, M., Bonhôte, P., Pettersson, H., Azam, A., and Gratzel, M. (1996) The Performance and Stability of Ambient Temperature Molten Salts For Solar Cell Applications. *J. Electrochem. Soc.*, 143: 3099.
19. Dai, S., Ju, Y.H., and Barnes, C.E. (1999) Solvent Extraction of Strontium Nitrate by a Crown Ether using Room-Temperature Ionic Liquids. *J. Chem. Soc., Dalton Trans.* 1201.
20. Dai, S., Shin, Y., Toth, L.M., and Barnes, C.E. (1997) Comparative UV-Vis Studies of Uranyl Chloride Complex in Two Basic Ambient-Temperature Melt Systems: The Observation of Spectral and Thermodynamic Variations Induced via Hydrogen Bonding. *Inorg. Chem.*, 36: 4900.
21. Liang, C., Yuan, C.-Y., Warmack, R.T., Barnes, C.E., and Dai, S. (2002) Ionic Liquids: A New Class of Sensing Materials for Detection of Organic Vapors Based on the Use of a Quartz Crystal Microbalance. *Anal. Chem.*, 74: 2172.
22. Merrigan, T.L., Bates, E.D., Dorman, S.C., and Davis, J.H., Jr. (2000) New Fluorous Ionic Liquids Function as Surfactants in Conventional Room-Temperature Ionic Liquids. *Chem. Commun.* 2051.
23. Pope, B. Air Products Corporation, personal communication.
24. Jastorff, B., Stormann, R., Ranke, J., Molter, K., Stock, F., Oberheitmann, B., Hoffmann, W., Hoffmann, J., Nuchter, M., Ondruschka, B., and Filser, J. (2003) How Hazardous are Ionic Liquids? Structure-activity Relationships and Biological Testing as Important Elements for Sustainability Evaluation. *Green Chem.*, 5: 136.