

DEVELOPMENT OF PRACTICAL SUPPORTED IONIC LIQUID MEMBRANES: A SYSTEMATIC APPROACH

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Introduction

Current technology has taken several approaches to address greenhouse gas emissions, but a critical component of any strategy remains the capture and sequestration of carbon dioxide (CO₂). There are several ways to reduce CO₂ emissions which include: increasing process efficiency; the use of lower-carbon content fuels such as natural gas and biofuels including ethanol from corn and cellulose; and decreasing fuel consumption. These methods are essential, but not sufficient, to meet the goal of ending the rise in atmospheric CO₂ concentration. It is also necessary to address the capture and sequestration of CO₂. The reason is that fossil fuels, while an important energy source, are also the principal green house gas source. A significant portion of our future energy production will rely on the ability to produce zero emission power from fossil fuels, where the majority of expense in overall emissions reduction will be associated with CO₂. The optimum place to start is the capture of CO₂ from point sources such as power plants.

Investigative studies and research have closely examined and are beginning to address the problems associated with CO₂ capture for various types of plants: i.e. a gasifier cannot be retrofit to any existing system. Holding the most promise for the future is the Integrated Gasification Combined Cycle (IGCC), a clean coal technology and a significant component of future power generation which allows efficiency enhancement, offers the potential to benefit the environment and could provide low carbon fuel by producing hydrogen, electricity, and liquid hydrocarbons. The possibility for hydrogen (H₂) and/or CO₂ separation prior to combustion in the IGCC makes it even more promising. The greatest CO₂ capture efficiency in IGCC systems is achieved by separating concurrently with the equilibrium limited water gas shift reaction. By removing CO₂, a product, the reaction is forced to completion allowing a smaller reactor and the use of less steam.

Several technologies have been investigated for co-production of high purity hydrogen with recovery of CO₂ ready for sequestration. Focus has turned towards membrane technology for its simplicity, modular design, and ease of scaling. Membranes have already demonstrated the capability to separate H₂ and CO₂ in various applications and types of systems but must overcome elevated temperatures and pressures as well as degradation by contaminant gases and particulates [1].

Supported liquid membranes (SLMs) are a class of materials that allow researchers to utilize the wealth of knowledge available on liquid properties to optimize membrane performance. These membranes also have the advantage of liquid phase diffusivities, which are higher than those observed in polymers and 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 may possess high CO₂ solubility relative to light gases such as H₂, are excellent candidates for this type of membrane. They are stable at elevated temperatures and have negligible vapor pressure.

A study has been conducted evaluating the use of a variety of ionic liquids in supported ionic liquid membranes for the capture of CO₂ from streams containing H₂. In a joint project, researchers at the University of Notre Dame synthesized and characterized ionic liquids, while the researchers at the National Energy Technology Laboratory incorporated candidate ionic liquids into supports then evaluated the membrane performance for the resulting materials.

Experimental

The ionic liquids [hmim][Tf₂N], [NH₂C₃mim]Tf₂N], and [NH₂C₃mpy][Tf₂N] were synthesized at the University of Notre Dame using standard procedures [2,3]. Polyethersulfone, 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 cm².

The SILMs were made by placing the polymeric support in a container and slowly depositing the ionic liquid drop wise on top of the membrane with a pipette. Enough ionic liquid was added to completely cover the surface of the substrate and the membrane was allowed to absorb the ionic liquid for at least eight hours. The SILMs were then removed from the container and the excess ionic liquid was removed by blotting the SILM.

The membrane was placed on the permeate side of a Millipore® stainless steel filter holder and an unmodified substrate identical to the one used to prepare the membrane was then placed against the membrane on the feed side to reduce the mechanical stress. The feed gas flowed at approximately 30 ml/min and consisted of ~20% carbon dioxide, ~20% hydrogen and the balance argon with one mixture containing ~1% hydrogen sulfide. A sweep gas, argon, was used on the permeate side with a flow between 1.0 to 2.0 ml/min. The flows and pressures were controlled by a Cole Parmer® flowmeter and Honeywell® pressure transducers and digital readout, respectively. The pressure was approximately 108 kPa for the feed and the permeate pressure was less than 102 kPa. Between experiments, the system was purged overnight with either UHP helium or UHP argon and then allowed to stabilize with the desired gas before testing began.

Testing was performed in a flow system in which the permeate and retentate gas compositions were determined using either a HP 5890 or a Perkin Elmer Clarus 500 gas chromatograph with twin TCD detectors and Alltech Hayesep D 100/120 packed columns. The gas analysis was collected and stored using Total Chrom Navigator® software. Flows were measured with the OPTIFLOW 520 Digital Flowmeter, Humonics®. Temperature was measured by a Type K thermocouple in contact with the surface of the testing cell. The temperature was controlled by a Thermo Electron Corporation furnace controller. Thermal control was carried out by ramping to the desired temperature at 1°C/minute (small temperature gaps i.e. 15°C) or 2°C/minute (larger temperature gaps i.e. >20°C) and holding for several hours or longer during the testing.

Results and Discussion

Several steps have been taken in the development of practical ionic liquid membranes. Proof-of-concept was established by showing that ionic liquids could be used as the transport media in SLMs. A base ionic liquid [HMIM][Tf₂N] was chosen to be placed on polysulfone (PSF) and polyethersulfone (PES) supports which were then tested over the temperature range 37-135°C. Both sets of membranes showed similar performance at room temperature, but increasing the temperature to 50°C caused the PES supported membranes to fail. The PSF had a lower glass temperature when not in contact with the ionic liquid; however with the

IL its glass transition temperature was only slightly depressed as opposed to that of PES which was greatly affected. The results for PSF are shown in Figure 1.

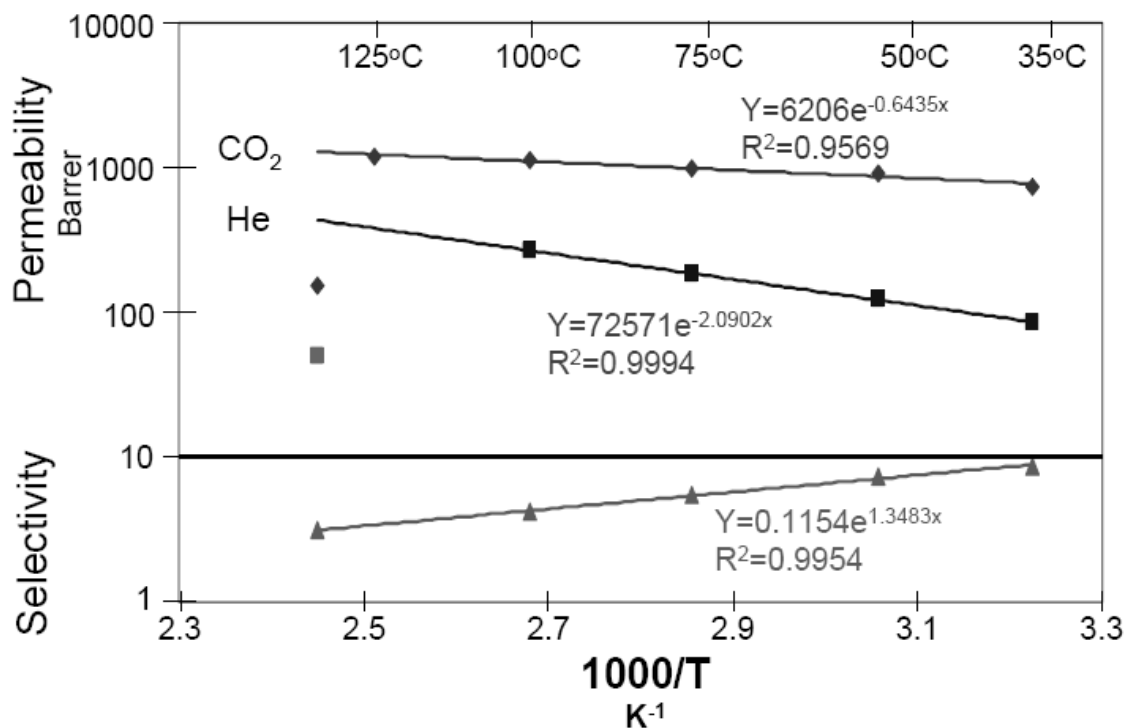


Figure 1. CO₂ (♦) and helium (▪) permeability and the selectivity (▲) as a function of temperature.

CO₂ permeability is higher than that of helium, used as a surrogate for H₂ in the initial study. Selectivity and permeability for both He and CO₂ show the Arrhenius dependence expected for solution diffusion up to 125°C. Above 125°C, the Arrhenius dependence of the permeabilities fail, but that of selectivity remains intact. This behavior is an indication that pore collapse occurs within the support restricting effective membrane area without changing the transport mechanism [4].

The results of the proof of concept study made it clear that support improvements would be necessary in order to operate at the temperatures of interest for CO₂/H₂ separations. Several supports were examined using the base ionic liquid [HMIM][Tf2N] over the temperature range 37-300°C. The supports that showed the most promise and stability were Budyne® A (crosslinkable nylon) polymeric porous substrate supports from Pall Corporation. The difference between the two supports, Budyne®1 and Budyne®2, was pore size; Budyne®1 had larger pores. Table 1 and Figure 2 show how the different pore sizes affected the permeability of CO₂ and H₂ and the selectivity over the temperature range 37-300°C but more importantly that both are stable to 300°C.

Table 1. CO₂ and H₂ permeability and selectivity from 37-300°C. [HMIM][Tf₂N]- Biodyne®

| | Temp. °C | | | | | | |
|---|----------------|------|------|------|------|------|------|
| | 37 | 50 | 100 | 150 | 200 | 250 | 300 |
| CO ₂ (Barrer) | <i>average</i> | | | | | | |
| BIODYNE®1 | 417 | 446 | 508 | 606 | 699 | 767 | 825 |
| BIODYNE®2 | 502 | 571 | 772 | 861 | 1009 | 942 | 1165 |
| H ₂ (Barrer) | <i>average</i> | | | | | | |
| BIODYNE®1 | 43 | 50 | 72 | 122 | 199 | 323 | 567 |
| BIODYNE®2 | 54 | 67 | 123 | 205 | 367 | 535 | 918 |
| CO ₂ /H ₂ Selectivity | | | | | | | |
| BIODYNE®1 | 9.72 | 9.03 | 6.84 | 4.72 | 3.13 | 2.13 | 1.44 |
| BIODYNE®2 | 9.30 | 8.47 | 6.24 | 4.18 | 2.74 | 1.76 | 1.27 |

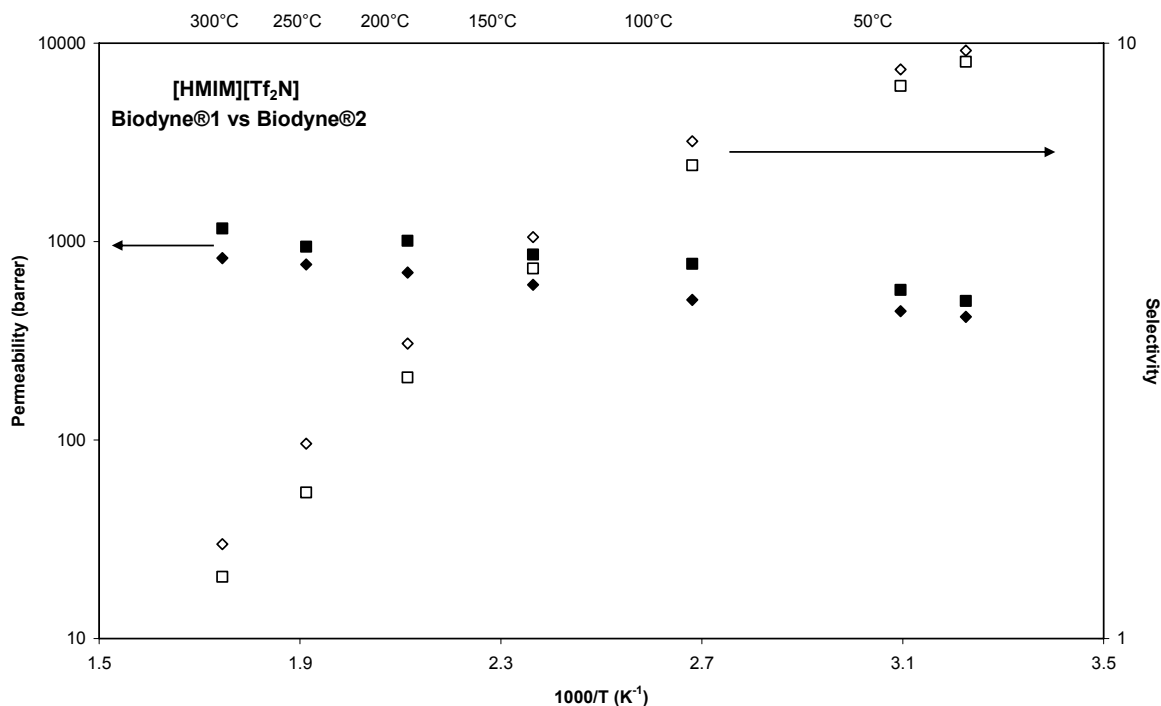


Figure 2. CO₂ permeability (solid figures) and selectivity (open figures) of BIODYNE®1(◆) and BIODYNE®2 (▪) as a function of temperature.

Preliminary testing showed that PALL supports had stability over the greater temperature range, but selectivity was still low at elevated temperature. Now that the supports

could operate at high temperatures while maintaining their properties, it was necessary to investigate other ionic liquids in order to increase selectivity. It was hypothesized that the use of other ionic liquids including those that form chemical complexes with CO₂ based on amine interactions could improve performance at elevated temperatures by allowing a facilitated transport mechanism to become dominant.

Two complexing ionic liquids were placed on the Biotyne®2 support, which was chosen since its overall performance was higher and tested in the temperature range 37-300°C. Test results for the complexing ionic liquid membranes were compared to the base ionic liquid [HMIM][Tf₂N] on the BIODYNE®2 support. The first amine-based IL tested on the BIODYNE®2 support was [NH₂PMIM][Tf₂N] as shown in Figure 3.

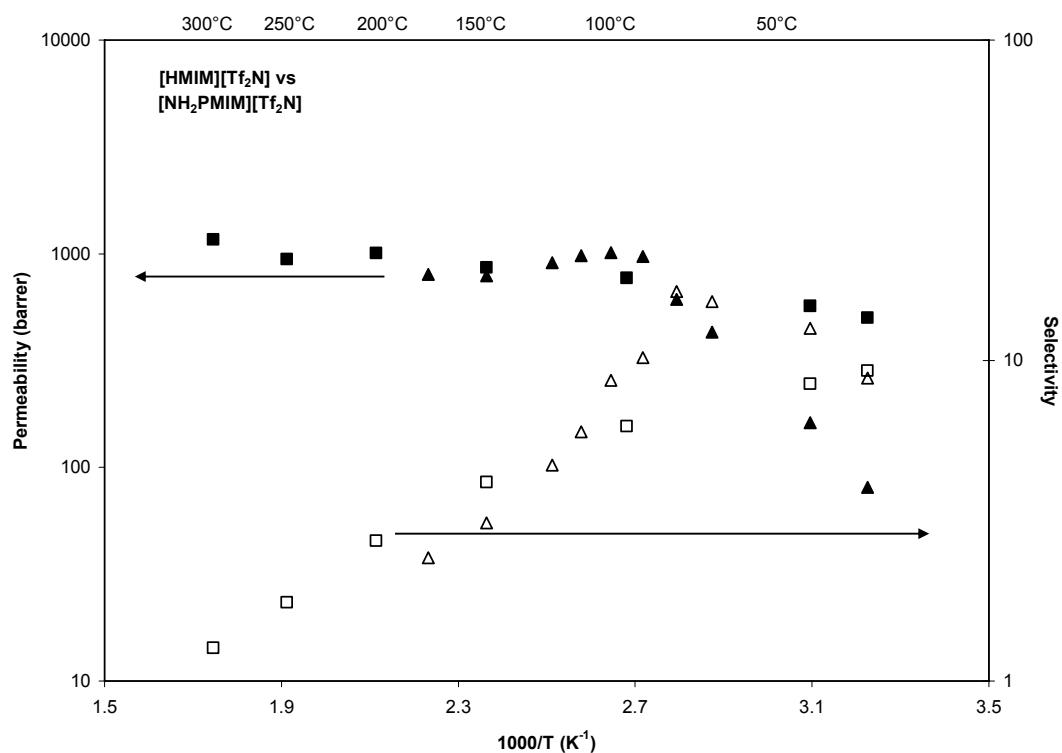


Figure 3. CO₂ permeability (solid figures) and selectivity (open figures) of [HMIM][Tf₂N] (◻) and [NH₂PMIM][Tf₂N] (◻) as a function of temperature.

At the lower temperature, the CO₂ permeability of the complexing ionic liquid membrane increases rapidly compared to the base ionic liquid, but as the temperature increases, the complexing IL peaks then begins to taper off similarly to the base ionic liquid. The peak observed in selectivity is not observed in solution diffusion, but rather is the effect of facilitated transport, in which chemically complexed CO₂ results in stronger interactions at higher temperatures and a change in rate limiting step from decomplexing of CO₂ to diffusion. The next complexing ionic liquid, [NH₂PMPY][Tf₂N], showed similar behavior but with slightly diminished performance as shown in Figure 4.

The CO₂ permeability and selectivity of [NH₂PMPY][Tf₂N] is slightly lower than [NH₂PMIM][Tf₂N], and [NH₂PMIM][Tf₂N] reached its maximum selectivity at 75°C while the peak for [NH₂PMPY][Tf₂N] appeared at 50°C. Since it is probable that stronger complexes lead to peak selectivity at a higher temperature and increased selectivity, it is possible to

suggest that [NH₂PMIM][Tf₂N] forms a more stable complex with CO₂. Table 2 below shows a summary of the base ionic liquid [HMIM][Tf₂N] and the two complexing ionic liquids.

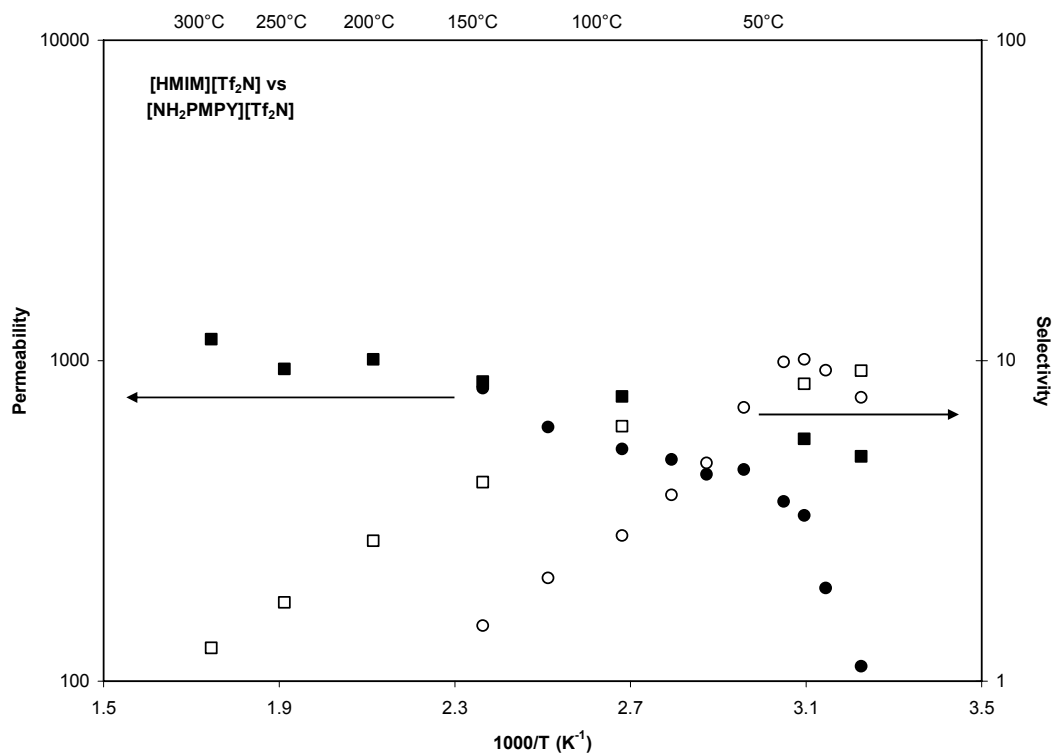


Figure 4. Results of CO₂ permeability (solid figures) and selectivity of [HMIM][Tf₂N] (•) and [NH₂PMPY][Tf₂N] (°) as a function of temperature.

Table 2. Summary of base and complexing ionic liquids with Biodyne®2 support.

| | | |
|---|------|-------|
| [HMIM][Tf ₂ N] | 37°C | 300°C |
| CO ₂ (barrer) | 502 | 1165 |
| H ₂ (barrer) | 54.0 | 918 |
| Selectivity CO ₂ /H ₂ | 9.30 | 1.27 |
| [NH ₂ PMIM][Tf ₂ N] | 37°C | 75°C |
| CO ₂ (barrer) | 80.5 | 429 |
| H ₂ (barrer) | 10.8 | 28 |
| Selectivity CO ₂ /H ₂ | 9.58 | 15.3 |
| [NH ₂ PMPY][Tf ₂ N] | 37°C | 50°C |
| CO ₂ (barrer) | 102 | 329 |
| H ₂ (barrer) | 14.4 | 32.5 |
| Selectivity CO ₂ /H ₂ | 7.69 | 10.11 |

Table 3 shows the base ionic liquid on Biodyne®2 in a commercial application of CO₂ selective membranes, natural gas sweetening. Interesting results for CO₂/H₂ separation led us to question the usefulness of these membranes in other applications.

Table 3. Natural Gas Sweetening

| [HMIM][Tf ₂ N]- | 37°C | 60°C |
|--|------|------|
| CO ₂ (barrer) | 378 | 416 |
| CH ₄ (barrer) | 41.0 | 59.0 |
| α (CO ₂ /CH ₄) | 9.30 | 7.09 |

The data in Table 3 are comparable to the commercial gas sweetening membranes, but the results were not as high as expected. It is believed that methane solubility, presumably much greater than H₂ solubility, leads to unexpectedly low selectivity.

Conclusions

We have demonstrated that CO₂ selective membranes can be fabricated from ionic liquids. These membranes are capable of operating at high temperatures. Further development will include ionic liquid improvements to increase complex strength and performance, identification of the effect of contaminants, work to increase transmembrane pressure tolerance, and scale up to modules.

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Disclaimer

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

References

1. Ritter, James A., Ebner, Armin D., (2007), "State-of-the-Art Adsorption and Membrane Separation Processes for Hydrogen Production in the Chemical and Petrochemical Industries," *Separation Science and Technology*, 42, pp. 1123-1193.
2. J.M. Crosthwaite, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke, (2004) "Liquid phase behavior of imidazolium-based ionic liquids with alcohol," *Journal of Physical Chemistry B*, 108, p. 5113.
3. J.M. Crosthwaite, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke, (2005) "Liquid phase behavior of imidazolium-based ionic liquids with alcohols: effect of hydrogen bonding and non-polar interactions," *Fluid Phase Equilib.*, 228, p 303.

4. Ilconich, Jeffery, Myers, Christina, Pennline, Henry, Luebke, David (2007), "Experimental investigation of supported ionic liquid membranes for CO₂/He separation at temperatures up to 125°C," *Journal of Membrane Science*, 298, pp. 41-47.