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Hydrogen Stable Supported Ionic Liquid Membranes with Silver Carriers: Propylene and Propane Permeability and Solubility

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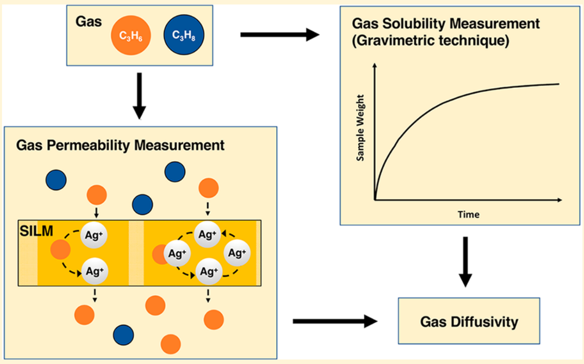
Supporting Information

ABSTRACT: Pure gas permeabilities of propylene and propane through ionic liquids supported on porous alumina membranes were determined as a function of silver salt concentration from 0 to 1 M and feed pressure from 0.15 to 2.0 bar at 35 °C. Two ionic liquids were tested: 1-hexyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([hmmim][Tf$_2$N]) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf$_2$N]). Propylene permeability increased with increasing silver content due to facilitated transport, but it decreased with increasing feed pressure. Permeability selectivity exhibited a nonlinear upward trend with silver concentration, indicating the formation of higher order silver-propylene complexes at higher silver concentrations. Solubility measurements were performed gravimetrically, which allowed for simultaneous determination of diffusion coefficients. Permeabilities were hindered by low diffusion coefficients due to increasing viscosity with increasing silver content. The most surprising result was the stability of the membrane after exposure to hydrogen gas, suggesting that the ionic liquids significantly slowed silver ion reduction.



1. INTRODUCTION

The separation of olefins from paraffins is one of the most important separations in the petrochemical industry. Currently, this separation is achieved via cryogenic distillation, but this process is very costly in terms of capital and operating costs and accounts for about 75% of the cost to produce olefins.[1,2] The separation of these mixtures using energy-saving and cost-effective techniques has been the target for many years, but no commercial solution exists.[3] Among various techniques, we focus on the use of membrane technology in this work because of its low cost and simple operation.

The separation of olefin/paraffin mixtures using conventional polymeric membranes is challenging due to similar physicochemical properties of the olefins and the paraffins (e.g., molecular sizes and gas solubilities).[4−6] Therefore, attention has shifted to facilitated transport membranes because olefins have been known for over a century to reversibly react with transition metal ions (e.g., silver) via a π-bond complexation mechanism where the transition metal cation acts as an electron acceptor and the olefin acts as an electron donor.[7−10] Facilitated transport is ubiquitous in nature, with O_2 transport via hemoglobin in blood being one example.[11,12] In facilitated transport membranes, specific chemical functionality is added to membranes that can markedly increase solubility of one component in a gas mixture (e.g., olefins in an olefin/paraffin mixture) via selective, reversible chemical interactions between, for example, the silver ions and olefins.[13,14] In this way, facilitated transport provides an additional pathway for penetrant transport across a membrane, above and beyond the typical transport mechanism associated with ordinary physical dissolution and diffusion of gas molecules across a polymer membrane.[15,16] Moreover, addition of chemical carriers to a polymer matrix can decrease the affinity of the matrix for the component not able to participate in specific interactions with the carrier species.[17] Both of these effects act to increase the selectivity of, for example, olefins over paraffins.

Among various types of facilitated transport membranes, supported ionic liquid membranes (SILMs) containing silver salt have been widely studied in the past decade for olefin/paraffin separation.[1,18−22] A SILM is an ionic liquid immobilized in the pores of a porous support by capillary forces. Since the gases diffuse through the liquid, permeabilities of gases through SILMs are often higher than through solids.[23] However, the pressure drop across the SILM must be less than that needed to expel the ionic liquid from the pores of the membrane. SILMs are more favorable than conventional supported liquid membranes since ionic liquids are nonvolatile, can have high thermal stability, and can solubilize many gases.[24]

Several studies have been published on facilitated transport of olefins for olefin/paraffin separation using ionic liquid

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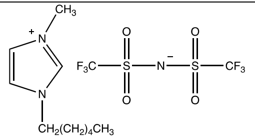
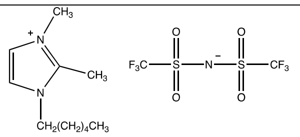
Table 1. Chemical Structures and Nomenclature of ILs Used in This Study

Abbreviation	Chemical Structure	Nomenclature
[hmim][Tf2N]		1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[hmmim][Tf2N]		1-hexyl-2,3- dimethylimidazolium bis(trifluoromethylsulfonyl)imide

supported membranes.[7,18,25−27] For example, Ortiz et al.[18] determined mixed gas permeabilities and selectivities of propylene and propane for SILMs containing 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid ([bmim]-[BF_4]) and silver tetrafluoroborate ($AgBF_4$), but they observed a decrease in performance in long-term studies. Marrucho et al.[25] studied polymeric ionic liquid membranes and utilized silver bis(trifluoromethylsulfonyl)imide ($AgTf_2N$) for the separation of ethylene and ethane and compared their results to polymer membranes on the upper bound. Zhang et al.[26] studied pure and mixed gas ethylene and ethane permeabilities through SILMs containing cuprous chloride and 1-butyl-3-methylimidazolium chloride ([bmim][Cl]).

Although promising, facilitated transport membranes have failed to achieve commercial success due, in part, to the instability of the transition metal ions.[3] Ag^+ is irreversibly reduced to elemental silver (Ag^0) upon exposure to hydrogen, and this form of silver is inactive for facilitated transport.[17] Since hydrogen is present in any olefin/paraffin mixture of industrial interest (in at least low ppm quantities), it is necessary to slow/prevent the reduction of silver ions by hydrogen gas for facilitated transport membranes to be commercially viable.

In this study, pure gas permeabilities of propane and propylene were determined for 1-hexyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([hmmim][Tf_2N]) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide ([hmim][Tf_2N]) SILMs containing $AgTf_2N$ as a function of feed pressure and silver concentration. These ionic liquids were chosen due to their similar structure but varying viscosity. $AgTf_2N$ was chosen because it has the same anion as the ionic liquids, and others have shown that this leads to a higher olefin sorption capacity.[25,28] In addition, propane and propylene solubilities and diffusivities were determined in the ILs to further understand gas transport in these membranes. Membrane permeation performance was also studied in the presence of hydrogen gas to determine the stability of these silver containing SILMs.

2. EXPERIMENTAL SECTION

2.1. Materials. Propylene (99.5%), propane (99.99%), and hydrogen (99.999%) were purchased from Airgas and used without further purification. Both ionic liquids (ILs) used in this work were synthesized in our laboratory and are depicted in Table 1. Details of the synthesis of these ILs are reported elsewhere.[29] The purity of each IL was evaluated using ^1H NMR (Bruker AVANCE III HD 400 MHz spectrometer) spectroscopy after dissolving the sample in DMSO-d6 (99.9 atom % D, Sigma-Aldrich). The spectra are shown in the Supporting Information. Any residual halide in the IL after the synthesis was not detectable by adding an $AgNO_3$ aqueous solution, which ensures that the halide content is below 2000 ppm. The ILs were dried at 60 °C under vacuum for at least 24 h prior to use. The water content of each IL was less than 0.05% by weight (or 500 ppm), as determined by a Brinkman 831 Karl Fischer coulometer with ± 3 μg H_2O resolution. The silver salt was silver bis(trifluoromethylsulfonyl)imide purchased from Alfa Aesar and used as received. Care was taken to prevent exposure of the silver salt to light, since light can promote the reduction of Ag^+ to Ag^0. The porous supports used in this work were Anopore membrane discs purchased from Whatman (P/N 6809-5502) with a nominal pore size of 20 nm and a thickness of 60 μm.

2.2. Density Measurements. The densities of the pure ionic liquids and IL/silver salt mixtures were measured using a DMA 4500 Anton Paar oscillating U-tube densitometer from 25 to 50 °C. All measurements were performed at ambient pressure. The instrument uncertainty is ± 0.00005 g/cm^3. However, taking the sample impurity into account, we estimate the experimental uncertainty to be 0.2% of the measured value.

2.3. Viscosity Measurements. Viscosities of the pure ILs and IL/silver salt mixtures were measured from 10 to 70 °C using an ATS Rheosystems Viscoanalyzer with an ETC-3 Joule-Thomson effect temperature cell, equipped with a 20 mm cone and plate spindle. The measurements were conducted under a nitrogen atmosphere to minimize water uptake. The viscosities measured have an uncertainty of 5% of the measured value.

2.4. Propylene and Propane Solubility Measurements. Gas solubilities were determined gravimetrically using an intelligent gravimetric analyzer (IGA-001) produced by Hiden Analytical. Details on the equipment, as well as accounting for buoyancy effects, are fully described elsewhere.[30−33] Briefly, the experimental method was as follows. A small sample of IL or IL/silver salt mixture (about 100 mg) was added to the sample bucket, and the chamber was evacuated to 10^{-6} bar to remove any water or other impurities from the sample. The temperature was set to 35 °C, and the chamber was pressurized to the desired pressure. Equilibrium was confirmed by a constant mass reading for at least 60 min. This procedure was repeated for various pressures until a full isotherm was obtained. The sample was regenerated under vacuum, and the procedure was repeated for the next gas. The effect of buoyancy was accounted for in the solubility

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calculation using the measured values of the density. The experimental uncertainty is estimated to be ±0.001 in mole fraction, mostly due to the temperature fluctuation of the control unit, and the purity of the ionic liquid which affects the solubility measurements through the buoyancy correction. The uncertainties in the temperature and pressure readings are 0.1 °C and 0.001 bar.

2.5. SILMs Preparation. The ionic liquid (IL) solutions containing silver carriers were prepared as follows. Under dark conditions, a desired amount of silver salt was weighed and added to a vial containing a magnetic stirrer. A corresponding amount of ionic liquid was then added to achieve the target concentration. The solutions were left to stir overnight prior to use.

A concentric hole was bored through a brass disc, and an Anopore membrane disc (60 μm in thickness) was attached to the underside of the brass support ring with epoxy. After allowing the epoxy to cure overnight, the area of exposed membrane was determined by scanning the support with a LiDE 210 scanner from Canon and analyzing the scanned image using ImageJ software, and the effective areas of the SILMs studied were generally around 1.23 cm^2. After this, drops of the IL or IL/silver salt solution were spread over the surface of the membrane until complete wetting was achieved. Residual ionic liquid was wiped from the surface of the membrane using a Kimwipe. Wetting was confirmed by observing the membrane turn from translucent to transparent. In addition, the membranes were weighed before and after IL impregnation to obtain the percentage of IL loading, and this percentage was consistent for multiple different membranes, indicating that the pores were completely filled with the IL. A layer of hydrophobic polytetrafluoroethylene (0.45 μm pore size, Millipore Sigma FHLP04700) was placed on the underside of the Anopore disc for extra mechanical support. The membrane was then immediately installed in the permeation apparatus.

2.6. Pure Gas Permeation Measurements. The pure gas permeabilities of propylene and propane through the SILMs were measured using the constant volume-variable pressure method. The permeation system used was designed in-house and is described elsewhere.[34] All permeation values are reported at 35 °C, and the upstream pressure ranged from 0.15 to 2 bar. Samples were evacuated *in situ* at 1.3×10^{-5} bar for at least 24 h to remove any dissolved gases, water, or other impurities before permeation measurements were performed. Then either propane or propylene was introduced to the upstream side and allowed to permeate through the membrane into a known volume that was initially under vacuum (1.3×10^{-5} bar). After steady state was achieved, the permeability was calculated as follows[34]

$$P_{\text{apparent}} = \frac{V_d l}{p_2 ART}\left[\left(\frac{dp_1}{dt}\right)_{\text{SS}} - \left(\frac{dp_1}{dt}\right)_{\text{leak}}\right] \quad (1)$$

where P_{apparent} is the apparent permeability, V_d is the downstream volume, l is film thickness, p_2 is upstream pressure, A is membrane area, $\left(\frac{dp_1}{dt}\right)_{\text{SS}}$ is the steady state rate of pressure rise in the downstream chamber, and $\left(\frac{dp_1}{dt}\right)_{\text{leak}}$ is the leak rate of the downstream volume. All permeabilities reported in this study are apparent permeabilities at 35 °C. $\left(\frac{dp_1}{dt}\right)_{\text{leak}}$ was the increase in pressure as a function of time when the system was sealed under vacuum, and the value was less than 1% of the value of $\left(\frac{dp_1}{dt}\right)_{\text{SS}}$, normally in the range between 1.3×10^{-8} and 1.3×10^{-9} bar/s. Uncertainty in the measurements is represented as one standard deviation based on propagation of error techniques.[35]

Gas transport through SILMs occurs by a solution-diffusion mechanism where permeability can be written as the product of gas solubility and gas diffusivity[36]

$$P_{\text{apparent}} = (S_{\text{IL}} \times D_{\text{IL}})(\phi/\tau) \quad (2)$$

where S_{IL} is the gas solubility in pure ionic liquid or IL/silver salt mixture, D_{IL} is the gas diffusivity in pure ionic liquid or IL/silver salt mixture, ϕ is the membrane porosity, and τ is the membrane tortuosity. The porosity to tortuosity ratio was determined for the Anopore disc by determining the apparent permeability of CO_2 in a [hmim][Tf_2N]/Anopore SILM at 25 and 40 °C. Literature values for the solubility[37] and diffusivity[38] of CO_2 in [hmim][Tf_2N] at 25 and 40 °C were used to back out the porosity to tortuosity ratio by taking the average of the values obtained at both temperatures:

$$(\phi/\tau) = \frac{P_{\text{apparent}}}{S_{\text{IL}} \times D_{\text{IL}}} \quad (3)$$

These calculations are shown in the Supporting Information. With knowledge of P_{apparent}, ϕ/τ, and solubility of propane and propylene in the ILs and IL/silver salt mixtures (S_{IL}), the diffusivities of these gases in the IL and IL/silver salt mixtures were calculated as follows:

$$D_{\text{IL}} = \frac{P_{\text{apparent}}(\tau/\phi)}{S_{\text{IL}}} \quad (4)$$

3. RESULTS AND DISCUSSION

3.1. Gas Permeability. Pure gas permeability measurements were performed to determine the effect of silver salt concentration and gas pressure on propane and propylene permeability, as well as the pure gas propylene/propane selectivity. The effect of transmembrane pressure was studied over a pressure range from 0.15 to 2 bar, and the effect of silver ion concentration was studied from 0 to 1 M. The $AgTf_2N$ was completely soluble in [hmim][Tf_2N] and [hmmim][Tf_2N] over this concentration range.

3.1.1. [hmim][Tf_2N] Permeability and Selectivity. As shown in Figure 1, increasing $AgTf_2N$ concentration in [hmim]-[Tf_2N] from 0 to 1.0 M increased the propylene permeability due to facilitated transport effects and decreased propane permeability, likely due to the solution viscosity increasing with increasing silver content resulting in hindered gas diffusion. The viscosities as a function of $AgTf_2N$ concentration are shown in the Supporting Information. Transmembrane pressure clearly has an effect on propylene permeability when silver ions are present. However, the propane permeability is not affected by changes in transmembrane pressure. That is, with increasing pressure, the propane and silver-free propylene permeabilities remain constant. When silver salt is present, propylene permeability decreases with increasing pressure, likely due to the silver ion carriers becoming saturated with increasing pressure. This behavior

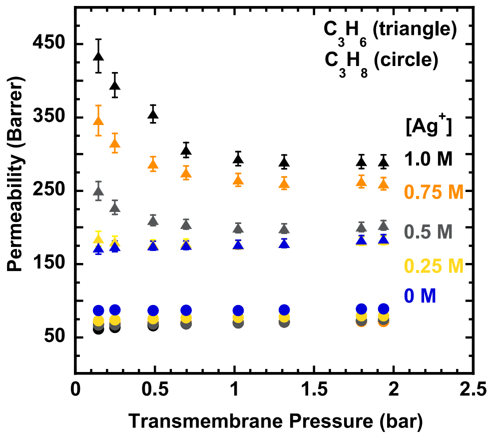

Figure 1. Propane and propylene permeability as a function of transmembrane pressure and Ag^+ concentration in [hmim][Tf_2N] at 35 °C.

has been observed by others.[39,40] The permeability data is recorded in tabular form in the Supporting Information.

As shown in Figure 2, propylene/propane selectivity as a function of transmembrane pressure followed a similar trend as that of propylene permeability. For the silver salt containing membranes, selectivity is highest at lower pressures. As pressure increases, selectivity decreases until reaching a steady value. As the complexation sites become saturated, the olefin flux becomes essentially constant, and any increases in flux with increasing pressure are due to small increases in the physical solubility of gas in the IL, which occurs for both propane and propylene.[39,41] Thus, at low feed pressure, chemical complexation effects dominate the propylene/propane selectivity, while at higher feed pressures, physical solubility effects become increasingly important.

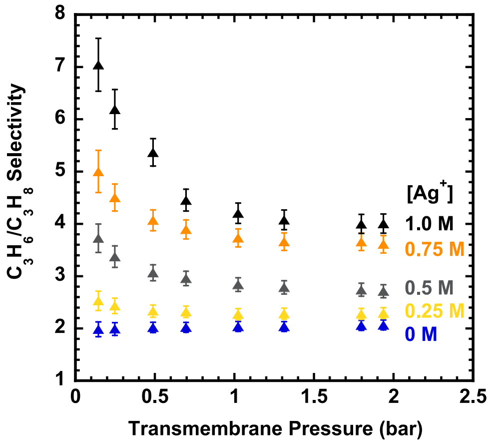

Figure 2. Propylene/propane permeability selectivity as a function of transmembrane pressure and Ag^+ concentration in [hmim][Tf_2N] at 35 °C.

3.1.2. [hmmim][Tf_2N] Permeability and Selectivity. The effect of changing ionic liquid structure was investigated by studying [hmmim][Tf_2N] which incorporates a methyl group at the C2 position instead of a hydrogen. As shown in Figures 3 and 4, similar trends in permeability and selectivity with transmembrane pressure and silver salt concentration were observed with this ionic liquid as were observed for [hmim][Tf_2N], although the permeabilities are over 50% lower for [hmmim][Tf_2N]. This result is expected since [hmmim][Tf_2N] is more viscous than [hmim][Tf_2N]; see viscosity data in the Supporting Information. Interestingly, the relative decrease in propane permeability with increasing silver salt content was larger in [hmmim][Tf_2N] than in [hmim][Tf_2N]. The more pronounced decrease in propane permeability in [hmmim][Tf_2N] is thought to be due to a greater increase in viscosity compared to that of [hmim][Tf_2N] when silver salt was added. The propylene/propane selectivity was higher in [hmmim][Tf_2N] than in [hmim][Tf_2N], illustrating the well-known trade-off between permeability and selectivity.[42−44]

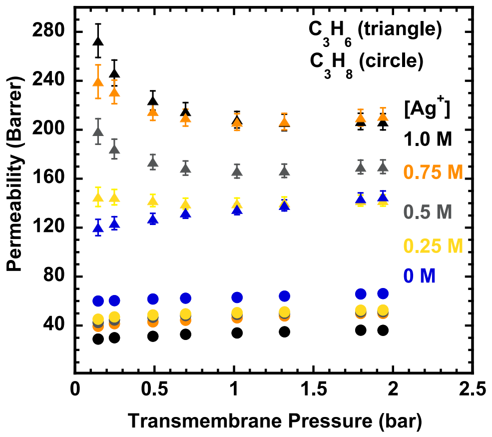

Figure 3. Propane and propylene permeability as a function of transmembrane pressure and Ag^+ concentration in [hmmim][Tf_2N] at 35 °C.

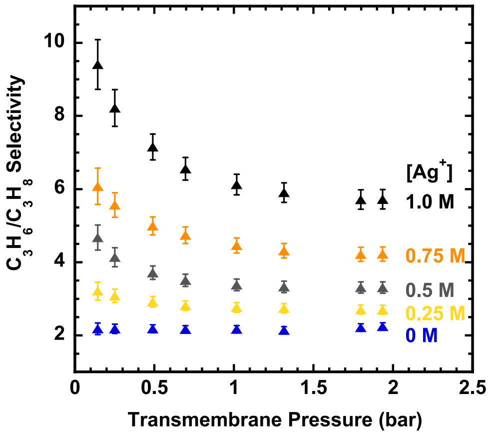

Figure 4. Propylene/propane permeability selectivity as a function of transmembrane pressure and Ag^+ concentration in [hmmim][Tf_2N] at 35 °C.

Figure 5 compares the propylene/propane selectivity in [hmim][Tf_2N] and [hmmim][Tf_2N] as a function of silver salt content at 0.25 bar. In both cases, selectivity increases with increasing silver salt content and exhibits a nonlinear upward trend. This nonlinear increase in selectivity may indicate that at higher silver ion loadings, there may be a larger fraction of $(Ag(propylene)_2)^+$ present, as has been reported by other groups in highly concentrated silver salt solutions,[9,45] whereas in dilute solutions only the $(Ag(propylene))^+$ complex has been observed.

3.2. Solubility. Pure gas sorption isotherms for propane and propylene were measured at 35 °C as a function of silver

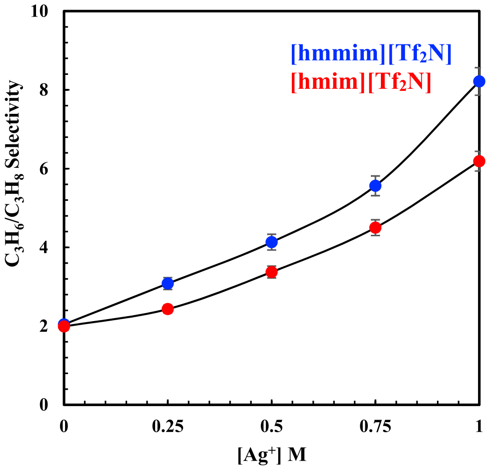

Figure 5. Influence of silver ion content on propylene/propane permeability selectivity in [hmmim][Tf_2N] and [hmim][Tf_2N] at 0.25 bar.

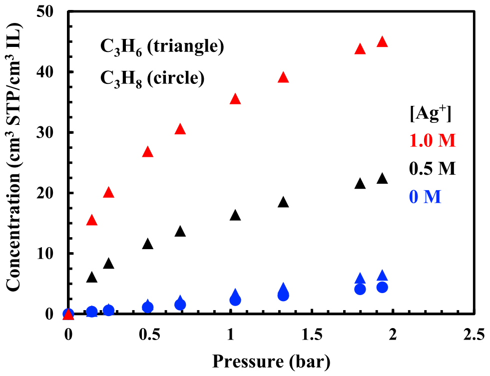

Figure 6. Propane and propylene sorption isotherms in [hmim][Tf_2N] and [hmim][Tf_2N]/$AgTf_2N$ mixtures at 35 °C.

ion concentration from 0 to 1 M, as well as a function of pressure from 0.15 to 2 bar, to determine the influence of these parameters on the amount of gas sorbed. Figure 6 presents propane and propylene sorption isotherms in [hmim][Tf_2N]. As shown in Figure 6, both propane and propylene exhibit Henry's law behavior (i.e., a linear increase in gas concentration with pressure) in silver-free ionic liquid. The solubility of propylene is higher than propane, which has been attributed to the higher polarizability of unsaturated hydrocarbons, resulting in stronger solvation in ionic liquids compared to saturated hydrocarbons.[45] Henry's law constants are recorded in Table 2. With increasing silver salt content, propylene sorption increases, as shown in Figure 6, and this increase is due to chemical solubility effects since propylene interacts with Ag^+. Thus, the observed solubility is a contribution of both chemical and physical solubility effects. The solubility data, both in units of cm^3 STP/cm^3 IL or IL mixture and mole fraction, is shown in tabular form in the Supporting Information. Also shown in the Supporting Information are the densities of the IL and IL/silver salt mixtures, which were needed for the buoyancy correction of the raw gravimetric data.

Table 2. Henry's Law Constants (bar) for Propane and Propylene at 35 °C in Silver-Free Ionic Liquid

	[hmmim][Tf_2N]	[hmim][Tf_2N]
propane	40.6 ± 1.4	32.3 ± 0.8
propylene	25.4 ± 1.2	22.7 ± 0.5

In this study, propane sorption at different silver salt concentrations is assumed to be that of silver-free ionic liquid. Due to propylene impurities in the propane (even the 99.99% purity sample), the propane concentration as a function of silver salt content could not be accurately measured since the presence of these impurities skewed the solubility values to higher values with increasing silver salt content.

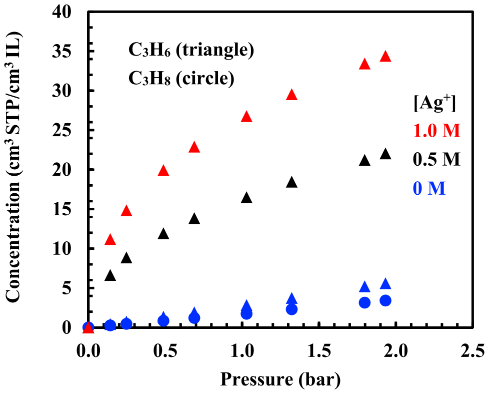

Figure 7. Propane and propylene sorption isotherms in [hmmim][Tf_2N] and [hmmim][Tf_2N]/$AgTf_2N$ mixtures at 35 °C.

The measurements were repeated in [hmmim][Tf_2N] to allow for comparisons of solubility and, later, diffusivity. Figure 7 presents propane and propylene sorption isotherms at different concentrations of Ag^+. These data are also shown in tabular form in the Supporting Information. Similar to [hmim][Tf_2N], propane and propylene exhibit Henry's law behavior in silver-free ionic liquid, so only physical solubility is observed. Both propane and propylene showed slightly higher gas solubilities in [hmim][Tf_2N] than in [hmmim][Tf_2N] (cf. Table 2). However, the percent increase in solubility was higher for propane than for propylene, so the propylene/propane solubility selectivity was highest in [hmmim][Tf_2N] for silver-free ionic liquid.

Figure 8 shows the propylene sorption in [hmim][Tf_2N] and [hmmim][Tf_2N] as a function of silver ion content. At a silver salt concentration of 0.5 M, the solubility is very similar in the two ILs. However, at a silver salt concentration of 1.0 M, the propylene solubility is higher in [hmim][Tf_2N], indicating that there may be more $(Ag(propylene)_2)^+$ complexes present in [hmim][Tf_2N] than in [hmmim][Tf_2N]. This phenomenon is even easier to see in Figures 9 and 10, where the sorption data are plotted as moles of propylene per mole of Ag^+. In Figure 10, we have subtracted the physical solubility of propylene in [hmim][Tf_2N] and [hmmim][Tf_2N]. The physical solubility was determined from the solubility values of propylene in silver-free ionic liquids where only physical dissolution occurred. These results suggest that the improved permeability selectivity for [hmmim][Tf_2N]/silver salt mixtures may be related to its higher carrying capacity. Clearly, the choice of IL can be used to tune the amount of the higher loading $(Ag(propylene)_2)^+$ complexes present.

3.3. Diffusivity. Permeability and solubility results were used to calculate diffusivities according to eq 4. The results for [hmmim][Tf_2N] are shown in Figure 11; the corresponding

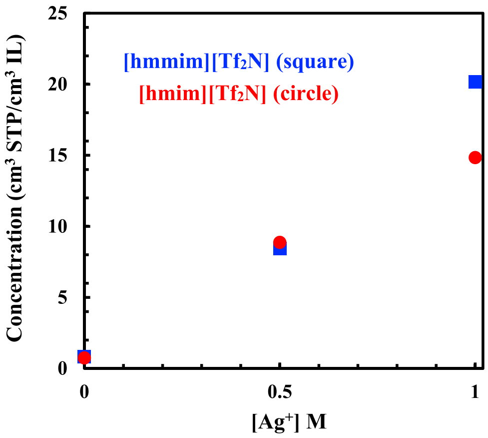

Figure 8. Influence of silver ion content on propylene sorption isotherms in [hmmim][Tf$_2$N] and [hmim][Tf$_2$N] at 0.25 bar and 35 °C.

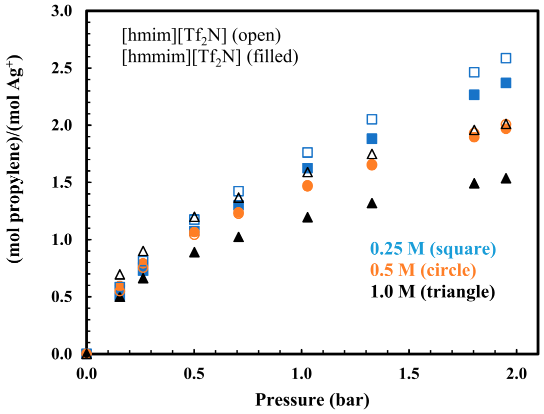

Figure 9. Total uptake of propylene in [hmim][Tf$_2$N]/AgTf$_2$N and [hmmim][Tf$_2$N]/AgTf$_2$N mixtures as a function of pressure at 35 °C.

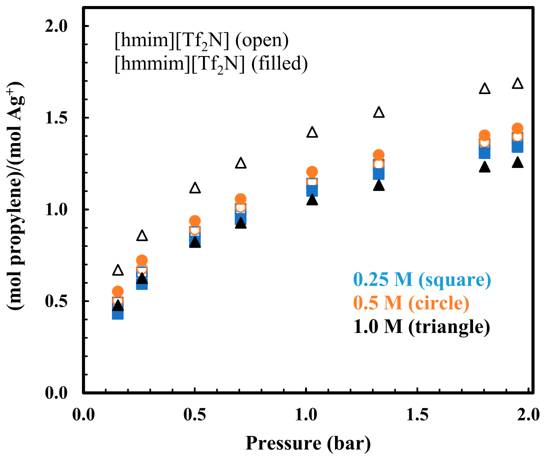

Figure 10. Sorption *due to chemical complexation* of propylene in [hmim][Tf$_2$N]/AgTf$_2$N and [hmmim][Tf$_2$N]/AgTf$_2$N mixtures as a function of pressure at 35 °C. The sorption due to physical dissolution was subtracted from the total sorption levels shown in Figure 9 to arrive at these values.

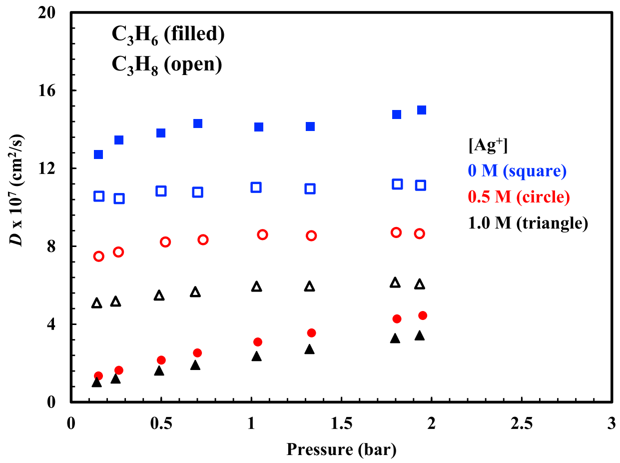

Figure 11. Propane and propylene diffusivities in [hmmim][Tf$_2$N] and [hmmim][Tf$_2$N]/AgTf$_2$N mixtures at 35 °C, as estimated from permeability and solubility data.

graph for [hmim][Tf$_2$N] can be found in the Supporting Information. In silver-free ionic liquid, the propylene diffusivity is greater than that of propane due to the smaller Lennard-Jones diameter of propylene.[15,46] With increasing silver salt content, the diffusivity of both propane and propylene decreased. However, the propylene diffusion coefficient decreased much more than that of propane. For propane, the decrease in diffusion coefficients is attributed to the increase in viscosity with increasing silver salt concentration. For propylene, the more pronounced decrease in diffusion coefficient is thought to result from a combination of increased viscosity and a much larger effective diameter of the diffusing species. To maintain electroneutrality, the silver-propylene complex must carry a Tf$_2$N$^-$ anion along with it. Given the large size of a Tf$_2$N$^-$ anion, the increase in kinetic diameter of the complex compared to a free propylene molecule is large, leading to decreased diffusion coefficients.

If a simple inverse relationship exists between viscosity and diffusion coefficient, then the ratio of gas diffusion coefficient (D) multiplied by solution viscosity (μ) for silver containing ionic liquid to silver-free ionic liquid should be near 1. An approximation for this ratio, $(D\mu)_{\text{silver}}/(D\mu)_{\text{silver-free}}$, is presented in Figure 12. It is an approximation because the viscosity values used are those shown in Tables S2 and S3 of the Supporting Information, which are for the IL and IL/silver salt mixtures without any dissolved gas. The diffusivities are the ones from eq 4 at 35 °C and 0.25 bar and shown in Figure 11. As can be seen in Figure 12, with increasing silver ion content,

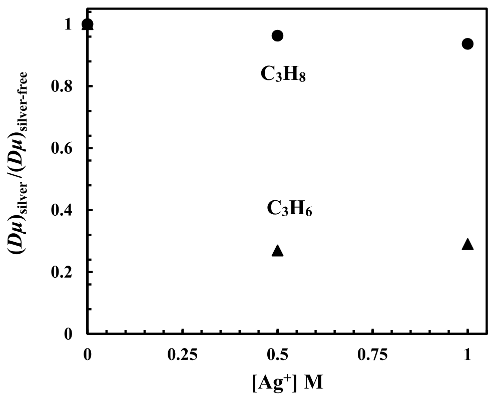

Figure 12. Normalized propane and propylene diffusivities in [hmmim][Tf$_2$N] at 35 °C and 0.25 bar as a function of Ag$^+$ concentration.

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the ratio of diffusivities is near 1 for propane. Thus, the decrease in propane diffusivity is largely due to an increase in viscosity with increasing silver salt content. However, for propylene, changes in viscosity alone do not explain the decrease in diffusivity with increasing silver salt content. We attribute the much lower $D \times \mu$ values for propylene, when silver is present, to the much larger size of the complex (propylene + silver salt) that is diffusing.

Figure 13 presents a comparison of the diffusion coefficients of propane and propylene as a function of silver ion content for both ionic liquids studied. In all cases, the [hmim][Tf$_2$N] containing ionic liquid/silver salt mixtures displayed higher diffusivities than those of [hmmim][Tf$_2$N]. This result is expected, since the viscosity of [hmmim][Tf$_2$N] is higher than that of [hmim][Tf$_2$N] (see Tables S2 and S3 of the Supporting Information).

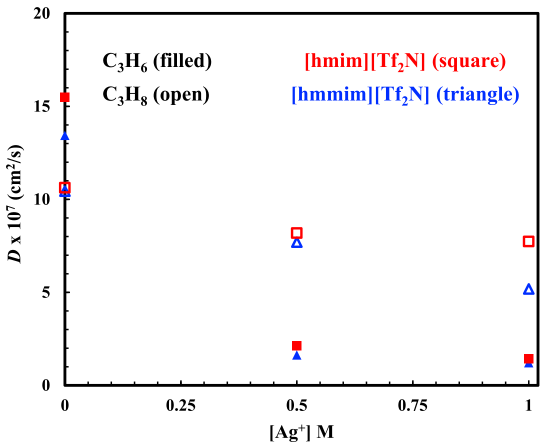

Figure 13. Propane and propylene diffusivities in [hmmim][Tf$_2$N] and [hmim][Tf$_2$N] and their mixtures with AgTf$_2$N, at 0.25 bar and 35 °C as a function of Ag$^+$ concentration.

To further understand the effect that diffusivity and solubility have on permeability selectivity, it is useful to analyze diffusivity and solubility selectivity separately. Table 3 displays solubility and diffusivity selectivities for both ionic liquids at 0.25 bar and 35 °C. Solubility selectivities increased with increasing silver salt content and reach values in excess of 30 for 1.0 M AgTf$_2$N. However, the high solubility selectivities are countered by low diffusivity selectivities. Nonetheless, the increases in solubility selectivity with added AgTf$_2$N are greater than the decreases in diffusivity selectivity at low gas partial pressures.

Table 3. Propylene/Propane Solubility Selectivity and Diffusivity Selectivity through SILMs Containing [hmmim][Tf$_2$N] and [hmim][Tf$_2$N] and their Mixtures with AgTf$_2$N, at 0.25 bar and 35 °C

	[hmim][Tf$_2$N]		[hmmim][Tf$_2$N]	
[Ag$^+$] M	solubility selectivity	diffusivity selectivity	solubility selectivity	diffusivity selectivity
0	1.4	1.5	1.6	1.3
0.5	14	0.26	19	0.21
1.0	33	0.19	32	0.23

3.4. Hydrogen Stability. The stability of the membranes in the presence of hydrogen was studied via hydrogen permeation experiments. Hydrogen reacts with silver ions to form elemental silver, which is not usable for facilitated transport:[14]

$$2Ag^+ + H_2 \rightarrow 2Ag^0 + 2H^+ \qquad (5)$$

First, the membrane performance (i.e., permeability of propylene and propane) was monitored for 3 days prior to starting hydrogen experiments to ensure that the selectivity was not changing with time. The permeabilities were determined at 0.25 bar and 35 °C for a [hmmim][Tf$_2$N] SILM containing 0.9 M AgTf$_2$N. These permeabilities and resulting selectivities are shown in Figure 14 as day -2, day -1, and day 0, and the values are consistent with those shown in Figures 3 and 4. Then, hydrogen was introduced into the system at a pressure of 2.0 bar and 35 °C for 1 h, followed by remeasurement of the propylene and propane permeabilities. The propylene and propane permeabilities dropped slightly, resulting in a statistically insignificant increase in the selectivity, as shown in Figure 14. Then the membrane was exposed to H$_2$ permeation at 2 bar for an additional 4 days, with propylene and propane permeabilities being determined after 1 day and after the full 4 days of exposure to hydrogen. The results of these experiments are shown in Figure 14, and the raw data can be found in Table S10, Supporting Information. The observed reduction in propylene/propane permeability selectivity was approximately 11% after 4 days of hydrogen exposure. In a similar experiment carried out by Merkel et al.[17] on membranes composed of a Pebax 2533/AgBF$_4$ selective layer, more than 65% reduction in ethylene/ethane permeability selectivity was observed after 4 days of hydrogen permeation at 2.0 bar. We noticed that the ionic liquid appears to enhance silver salt stability in these membranes in the presence of hydrogen gas compared to silver salt stability in polymer membranes. One might postulate that the enhanced stability is due to the low solubility of hydrogen in ionic liquids. However, hydrogen solubility in the ionic liquid is actually higher than its solubility in water. Specifically, at 20 °C and 1 bar, the solubility of hydrogen is 8.08 × 10^{-4} mol/L in water[47] and 1.60 × 10^{-3} mol/L in [hmim][Tf$_2$N].[48] Therefore, the low solubility of hydrogen in ionic liquids does not explain the enhanced stability of the membrane. Unfortunately, the

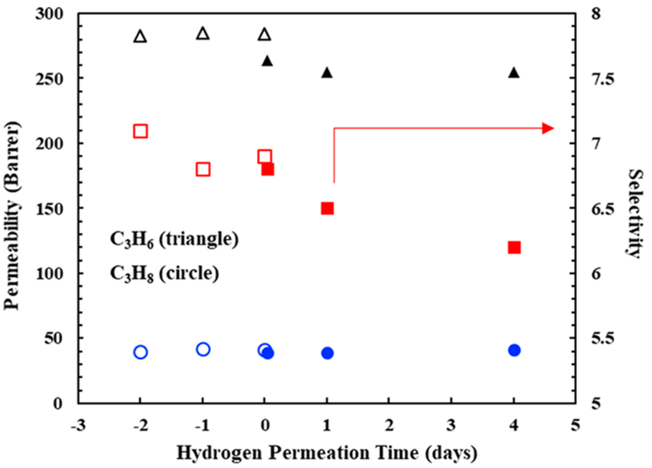

Figure 14. Propane/propylene permeabilities and selectivities at 0.25 bar and 35 °C before (open symbol) and after (filled symbol) hydrogen exposure at 2 bar in a 0.9 M [Ag$^+$] [hmmim][Tf$_2$N] membrane.

reason behind this enhanced stability is not presently understood.

We note that the ionic liquids did not provide enhanced stability of the silver salt upon exposure to light. Therefore, we used amber glass vials to store and prepare samples containing silver salts. Additionally, we covered the amber vials with aluminum foil to protect them further from the daylight. The IL/silver salt mixtures appear to be stable even after ten months, with no sign of silver reduction. A photograph of the IL/silver salt mixture after ten months is shown in the Supporting Information.

4. CONCLUSIONS

A range of [hmim][Tf_2N] and [hmmim][Tf_2N] supported ionic liquid membranes containing up to 1 M $AgTf_2N$ was successfully prepared for propane/propylene separation. At 35 °C and transmembrane pressures from 0.15 to 2 bar, the pure gas permeabilities ranged from 172 to 434 barrer for propylene and 62 to 89 barrer for propane, yielding permeability selectivities as high as 7 for [hmim][Tf_2N]. The equivalent results for [hmmim][Tf_2N] were pure gas permeabilities ranging from 120 to 273 barrer for propylene and 29 to 66 barrer for propane, yielding permeability selectivities up to 9.4. Experimental results showed extremely favorable propylene/propane solubility selectivities, including values greater than 30 at low gas pressures and high $AgTf_2N$ loadings. However, slow propylene diffusion hindered the overall permeability selectivity with increasing silver salt concentration. The propane diffusion coefficient decreased with increasing silver salt concentration due to increased viscosity of the IL/silver salt mixture compared to the pure IL. The propylene diffusivity was further decreased with increasing $AgTf_2N$ due to the increased size of the diffusing species, which is the propylene-silver cation complex along with a large Tf_2N^- anion needed to maintain electroneutrality. The most surprising and important result from this study is that the silver ions in these SILMs are significantly more resistant to reduction by hydrogen gas than silver salts in IL-free polymer membranes under similar conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b04886.

> ^{1}H, ^{13}C (only for [hmim][Tf_2N]), and ^{19}F NMR spectra for two synthesized ILs, calculation of porosity to tortuosity ratio for Anopore discs, tables of all experimental data (density, viscosity, permeability, solubility, diffusivity), and graph of propane and propylene diffusivities in [hmim][Tf_2N] (PDF)

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Notes

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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