Example outline

Supported ionic liquid membranes with silver carriers for propylene/propane separation

1. Introduction

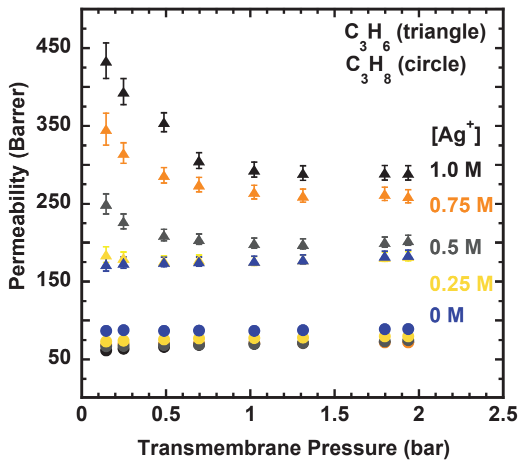
Importance of olefin/paraffin separation, and current separation method
What is a SILM and benefits over dense membranes
Facilitated Transport
Reduction of silver by hydrogen gas and other poisoning species
What groups have looked at IL + membranes for this separation

2. Experimental Section

2.1 Materials
2.2 Density measurements
2.3 SILMs preparation
2.4 Gas Permeation Measurements
$P_{IL} = S_{IL} \times D_{IL} = (\text{tortuosity/porosity}) * P_{apparent}$
(tortuosity/porosity) determined experimentally for Anopore disc
D from P and S
2.5 Gas Solubility Measurements

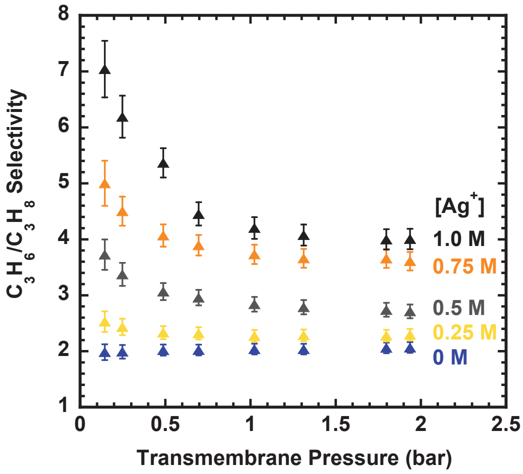
3. Results and Discussion

3.1 Gas Permeability and Selectivity Results



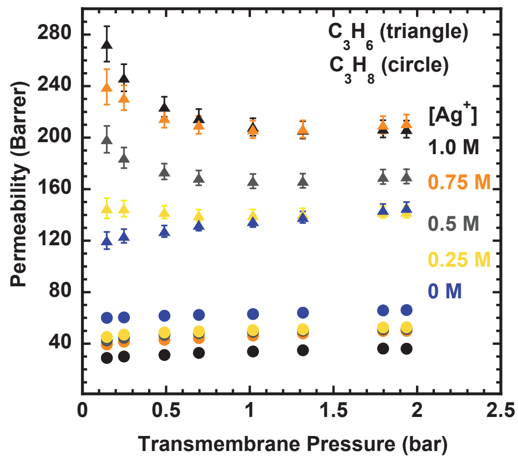
[hmim][Tf_2N]

Main Point: With increasing silver content the permeability increases for propylene due to facilitated transport. With increasing silver content the permeability of propane decreases. Propylene permeability decreases with increasing pressure due to carriers becoming saturated



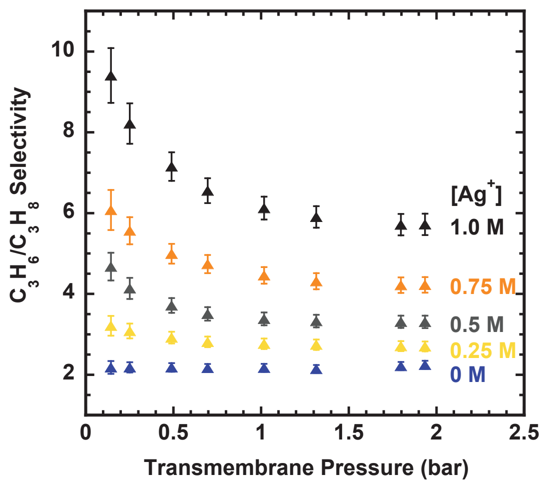
[hmim][Tf_2N]

Main Point: Selectivity highest for highest concentration of silver. Selectivity is highest at lowest pressure because chemical effects dominate.



[hmmim][Tf_2N]

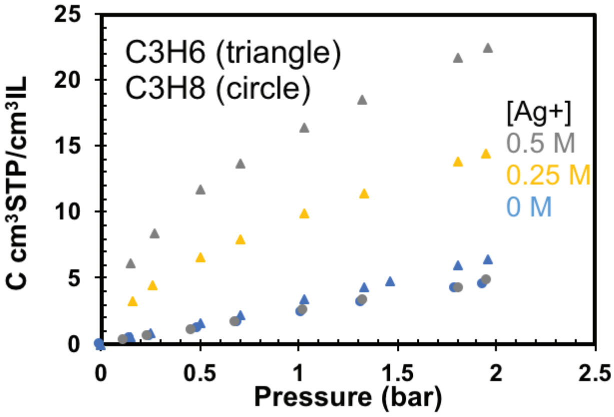
Main Point: Changing the ionic liquid to something similar in structure resulted in an overall decrease in permeabilities but similar trends as those observed in [hmim][Tf_2N] are seen. The decrease in propane permeability with increasing silver content was more pronounced in [hmmim][Tf_2N] than in [hmim][Tf_2N]



[hmmim][Tf_2N]

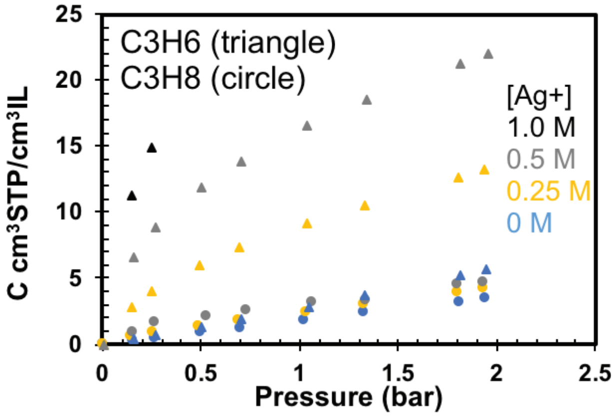
Main Point: Similar trends as in [hmim][Tf_2N]. Higher selectivities observed in [hmmim][Tf_2N] than in [hmim][Tf_2N] for same silver content.

3.2 Gas Solubility Measurements- (still in progress, I will make matching figures when complete)



[hmim][Tf_2N]

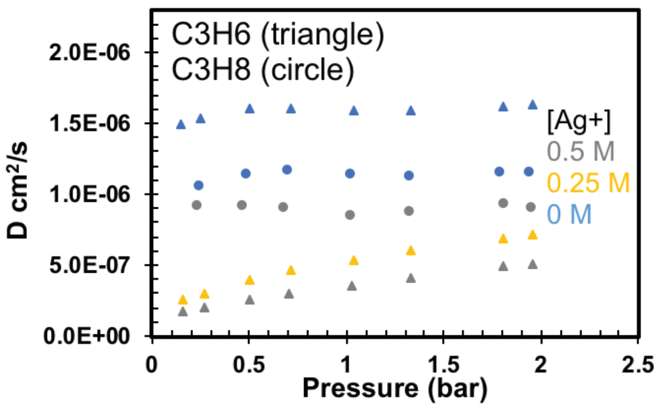
Main point: With no silver loading both gases display Henry's law sorption behavior. With increase in silver content the solubility of propylene increases due to chemical effects from interactions with silver. With increase in silver content the solubility of propane is unchanged, and this is expected because propane does not interact with silver.



[hmmim][Tf_2N]

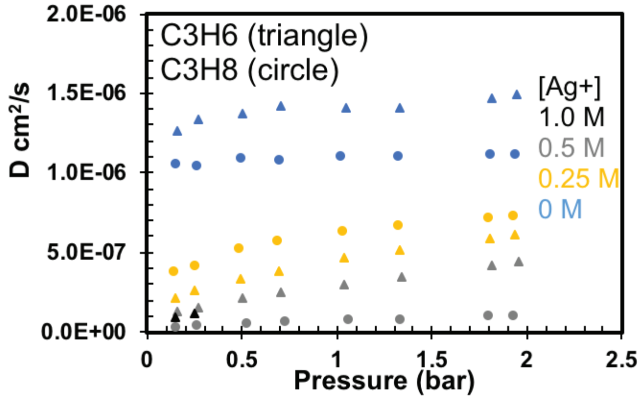
Main Point: propylene uptake is about the same for both [hmmim][Tf_2N] and [hmim][Tf_2N] at the same silver concentration. However, propane solubility increases with increasing silver content in [hmmim][Tf_2N] but not in [hmim][Tf_2N] suggesting some chemical interaction is occurring. The propane purity used for testing was 99.99 % in both cases.

3.3 Diffusion from Permeability and Solubility



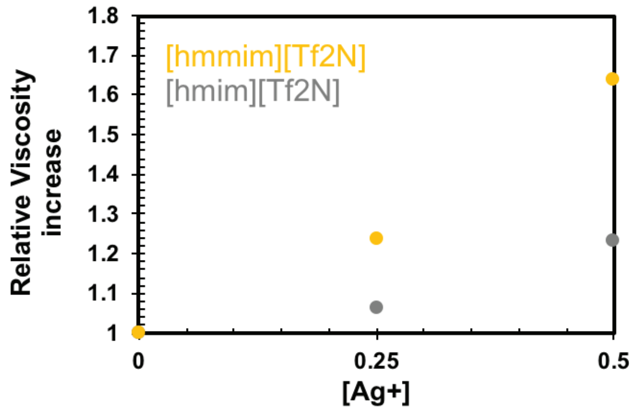
[hmim][Tf_2N]

Main Point: diffusion coefficient in the silver free case is higher for propylene than propane because of its smaller size. With increasing silver content the diffusion for both decrease and it decreases much more for propylene. The decrease for propane is attributed to an increase in solution viscosity. The decrease for propylene is attributed to an increase in viscosity and also due to the larger size of the propylene-silver complex which, to maintain electroneutrality, must travel along with a large Tf_2N^- anion.



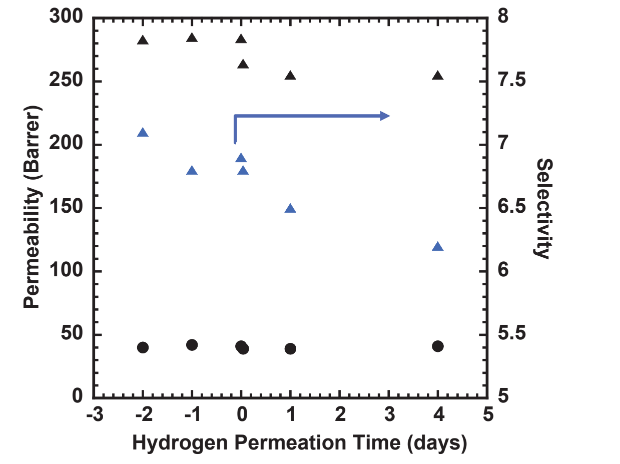
[hmmim][Tf_2N]

Main point: similar behavior observed in the 0 M case for propane and propylene in both [hmmim][Tf_2N] and [hmim][Tf_2N]. Also, approximately the same drop in diffusion coefficient is observed for propylene with increasing silver content in [hmmim][Tf_2N] and [hmim][Tf_2N]. However, with increasing silver content the drop in diffusion coefficient is more pronounced for propane in [hmmim][Tf_2N] than in [hmim][Tf_2N].



Main Point: Comparing the propane diffusion coefficient at 1 bar for [hmim][Tf_2N] at 0.5 M and 0 M the decrease is approximately 22 % which is approximately the same as the observed increase in solution viscosity of 23 %. However, for [hmmim][Tf_2N] this is not observed; the decrease in propane diffusion coefficient at 1 bar from 0 M to 0.5 M is about 94 % but the increase in solution viscosity was only about 64 %. The more polar nature of [hmmim][Tf_2N] compared to [hmim][Tf_2N] may explain the observed viscosity behavior.

3.4 Hydrogen stability



H_2 Permeation Time (Days)	C_3H_6 Permeability (Barrer)	C_3H_8 Permeability (Barrer)	Selectivity
-2	283	40	7.1
-1	285	42	6.8
0	284	41	6.9
0.042 (1 hour)	264	39	6.8
1	255	39	6.5
4	255	41	6.2

Main point: propylene/propane selectivity constant for 3 days before hydrogen exposure. After 4 days of pure hydrogen exposure the selectivity only drops approximately 10 %. Compare this to polymer case where selectivity dropped about 65 % after 4 days of hydrogen exposure at same conditions.

4. Conclusions

- Permeability measured in [hmim][Tf_2N] and [hmmim][Tf_2N] supported ionic liquid membranes with silver
- Solubility independently measured and used to back out diffusion coefficient
- Increasing silver content increases solution viscosity which decreases diffusivity. The size of propylene-silver complex decreases the observed diffusivity for propylene
- promising hydrogen stability

5. Acknowledgement

NSF

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