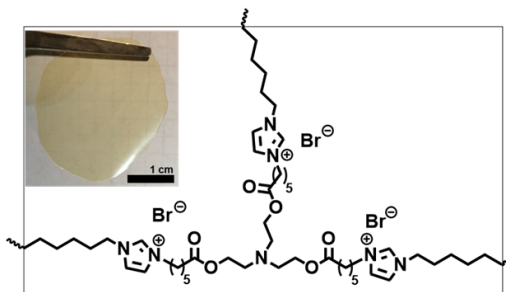*Understanding Organic Liquid Separations in Polymerized Ionic Liquid Networks and Blends*
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Membranes are a promising route to energy efficient separations of species which require much less energy input than techniques such as distillation. Ionic liquids (ILs), composed entirely of molecular cations and anions, have recently shown promise as membranes for gas (CO_2) and liquid (hydrocarbon) separations. Typically, they are supported in a porous framework which can lead to leaching of the IL under pressure or due to solubility with a neighboring phase. Our project is focused on the molecular design and development of polymerized ionic liquid (PIL) membranes where one of the ions is tethered to a polymer network, preventing ions from diffusing out of the separator and can lead to a more robust yet flexible membrane. Additionally, we are designing the cations (aromatic and nonaromatic), anions (hydrophilic vs hydrophobic, varying size and electrostatics), and network chemistry (silicone, hydrocarbon, ethylene oxide) to control interactions with penetrant liquid molecules. The first system of interest is toluene-heptane, which both have seven carbons and similar boiling points, to understand how to use ion-pi and aromatic interactions in designing membrane separations.

Imidazolium bromide polymerized ionic liquid membranes were synthesized via the step growth polymerization of a tribromo monomer and a bisimidazole monomer at 80°C in DMSO between two glass slides separated by a spacer (**Figure 1**).[1] The cation of the PILM is fixed as imidazolium to promote toluene solubility, while both tetrafluoroborate (BF_4) and bis(trifluoromethane sulfonamide) (TFSI) anions were examined to determine how they impact solute interactions. Using a combination of di- and trifunctional monomers, the crosslink density was also systematically varied while retaining precision between ionic sites. The membranes were first studied by time-dependent swelling experiments to determine single component diffusion coefficients (in the initial Fickian regime) as well as equilibrium solubilities to evaluate how ion selection

Figure 1: Chemical repeat unit of PILM membranes studied in ref 1.

and mesh size impact ideal separation performance. Non-monotonic trends were found which can inform the design of high-performance membranes for aromatic-aliphatic separations (**Table 1**). Varying the anion from BF_4 to TFSI led to an increase in toluene diffusion and equilibrium swelling, while the equilibrium heptane swelling decreased. One possible explanation is that the reduced electrostatic interaction between TFSI and imidazolium could allow for greater aromatic interactions between imidazolium and toluene. A tighter binding BF_4 anion may inhibit such interactions, thus limiting the solubility of toluene in the system. Likewise, the increase in heptane solubility for the $ImC_{11}BF_4$ sample is likely because of a lower dielectric constant[2] and being able to accommodate more heptane than TFSI systems.

Toluene diffusion coefficients, D_t (**Table 1**), are larger in TFSI membranes due to the fact that T_s is ~ 25 °C lower than that for $ImC_{11}BF_4$ and increased segmental mobility allows toluene to diffuse faster into the PILM. Upon decreasing the crosslink density from 100% to 50% in the TFSI membranes, toluene diffusion increased but remained relatively constant upon further decreasing to 33%. Our interpretation is that the mesh size, which increases with decreasing crosslink density, initially is small enough to provide some barrier to diffusion. Decreasing the crosslink density from 100% to 50% lead to a slightly larger heptane diffusion coefficient, however decreasing the crosslink density further to 33% resulted in tripling the diffusion coefficient. Similar to the toluene diffusivity, it is believed that the mesh size of the 100% and 50% network polymerized ionic liquids is too small, providing high resistance to the diffusion of heptane into the network polymerized ionic liquids. However, decreasing the crosslink density further to 33% makes the mesh size sufficiently large to allow unhindered transport of heptane into the network, resulting in an increase in the heptane diffusion coefficient. The greater swelling of toluene may explain why there is little difference in diffusion coefficients for 50% and 33% crosslinked samples, if the mesh is already large enough to allow transport unhindered by the network.

Table 1: Pure component ideal solubility, diffusive, and permselectivies of the developed PILMs, indicating a maximum in the 50% ImC$_{11}$TFSI system.

	100% ImC$_{11}$BF$_4$	100% ImC$_{11}$TFSI	50% ImC$_{11}$TFSI	33% ImC$_{11}$TFSI
S$_T$ / S$_H$	9.12 ± 0.35	16.03 ± 1.01	17.01 ± 0.66	18.42 ± 0.48
D$_T$ / D$_H$	3.26 ± 0.29	36.2 ± 5.2	65.8 ± 3.5	22.6 ± 6.0
P$_T$ / P$_H$	29.7 ± 2.9	580 ± 91	1120 ± 73	416 ± 111

Binary permeation experiments have also been carried out in a diaphragm cell where toluene and heptane were added at 100 mM concentration in dodecane. This solution was allowed to diffuse through the membrane into a pure dodecane phase with aliquots taken and analyzed via GCMS (**Table 2**). As expected, the permselectivities decreased from the pure component swelling experiments, but appear to show the same general trend. A maximum permselectivity of 12.02 was obtained for the 50% ImC$_{11}$TFSI system, comparable to the maximum selectivity of 11 obtained by Matsumoto et al.[3] separating toluene and heptane with a PVDF SILM swollen with [Bmim][PF$_6$], indicating the promise of PILMs for membrane separations.

Table 2: Binary permeability coefficients and permselectivities of the developed PILMs

	100% ImC$_{11}$BF$_4$	100% ImC$_{11}$TFSI	50% ImC$_{11}$TFSI	33% ImC$_{11}$TFSI
P$_T$ (cm/s)	1.28E-7 ± 6.45E-8	6.31E-7 ± 1.68E-7	9.96E-7 ± 1.24E-7	2.01E-6 ± 7.23E-7
P$_H$ (cm/s)	1.75E-8 ± 7.21E-9	7.03E-8 ± 2.24E-8	8.54E-8 ± 2.43E-8	2.55E-7 ± 4.26E-9
α	7.15 ± 0.76	9.16 ± 1.61	12.02 ± 1.91	7.92 ± 2.97

In summary, precise network polymerized ionic liquid membranes with tethered imidazolium cations, variable anion, and controlled crosslink density were developed to understand how molecular structure impacts solubility and diffusion in the context of toluene-heptane separations. Decreasing the crosslink density of the ImC$_{11}$TFSI system from 100% to 33% resulted in a maximum ideal permselectivity at 50% crosslink density due to the interplay of toluene and heptane diffusion with changing network mesh size. The toluene equilibrium swelling increased with decreasing crosslink density, while the heptane equilibrium swelling increased from 100% to 50% crosslink density but remained relatively constant from 50% to 33% crosslink density.

This work has contributed to the PI establishing platform for membrane separations which will be of interest to the broader community. Having obtained promising results, this will be useful for pursuing future funding on organic liquid separations. The graduate student working on this project has learned a number of valuable skills related to transport and diffusion which will be useful in his next project looking at molecular diffusion in strained membranes.

References
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[3] M. Matsumoto, Y. Inomoto, K. Kondo, "Selective separation of aromatic hydrocarbons through supported liquid membranes based on ionic liquids, *J. Membr. Sci*. **2005**, *246*, 77-81.