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Determination of the upper limits, benchmarks, and critical properties for gas separations using stabilized room temperature ionic liquid membranes (SILMs) for the purpose of guiding future research

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ABSTRACT

The literature reports that supported ionic liquid membranes (SILMs) outperform standard polymers for the separations of CO_2/N_2 and CO_2/CH_4, even under continuous flow mixed gas conditions. Before the expenditure of more resources to develop new room temperature ionic liquids (RTILs) and SILMs, it is time to consider what benchmarks for SILM performance exist and if upper limits could be projected based on the physical chemistry of RTILs. At this juncture, we should ask if the current research efforts are properly focused based on the successes and failures in the literature. We summarize literature data, along with adding new data, on the SILM permeabilities and selectivities for the following gas pairs: CO_2/N_2, CO_2/CH_4, O_2/N_2, ethylene/ethane, propylene/propane, 1-butene/butane, and 1,3-butadiene/butane. The analysis predicts a maximum CO_2-permeability for SILMs and an upper bound for permeability selectivity vs. CO_2-permeability with respect to the CO_2/N_2 and CO_2/CH_4 separations. Also summarized are the representative successes and failures for improving the separation performance of SILMs via functionalization and facilitated transport in the context of the CO_2/N_2, CO_2/CH_4, and olefin/paraffin separations. In the context of the CO_2-separations, the analysis recommends a number of future research foci including research into SILMs cast from RTILs with smaller molar volumes. In the context of olefin/paraffin separations, the preliminary data is encouraging when considering the use of facilitated transport via silver carriers. Since RTIL-solvent/solvent interactions dominate in terminating the overall SILM performance, past attempts at enhancing solute/solvent interactions via the addition of functional groups to the RTILs have not produced SILMs with better separation performance compared to the unfunctionalized RTILs. Future research into functionalized RTILs needs to consider the changes to the dominant solvent/solvent interactions and not just the solute/solvent interactions.

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1. Introduction

Supported liquid membranes (SLMs) [1] are porous membranes with the pores saturated with a solvent mixture. Unfortunately, SLMs experience significant solvent loss due to volatilization. On the other hand, room temperature ionic liquids (RTILs) have no measurable solvent loss due to volatilization since RTILs are salts with negligible vapor pressures. Previous testing of RTIL-membranes or supported ionic liquid membranes (SILMs) showed promising results with permeabilities/selectivities that were consistently above the Robeson plot upper bound [2,3]. Recently, our report on mixed gas permeances and selectivities for the gas pairs CO_2/CH_4 and CO_2/N_2 using continuous flows of the mixed gases at various carbon dioxide concentrations (up to 2 bars of CO_2 partial pressure) showed no reduction in mixed gas selectivities vs. ideal selectivities for imidazolium-RTILs. The report also indicated that SILMs may have the potential for industrial applications [3]; specifically, low pressure systems such as the treatment of bio-methane from anaerobic digesters and CO_2 capture from flue gases. In reference to CO_2 capture from flue gases, economic studies on CO_2 capture using membranes operating under vacuum conditions vs. compression of the feed gases [4,5] indicate that membranes that operate with cross-membrane pressures of less than 2 bars and with CO_2/N_2 selectivities greater than 50 can be more efficient than existing systems for CO_2 capture. SILMs can potentially meet this 2 bar and selectivity >50 specification for CO_2 capture.

Because of these potential applications, much effort and many resources have been expended on developing new RTILs to enhance the already advantageous combination of permeability and selectivity of SILMs. Before the expenditure of more resources, this manuscript proposes that it is time to consider the following questions:

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1. What benchmarks for SILM performance exist?
2. Can we project upper limitations on SILM performance based on the physical chemistry of room temperature ionic liquids?
3. Are current research efforts properly focused, based on the successes and failures in the literature?

Due to the extent of data needed for analysis in the context of these three questions, this manuscript will focus on carbon dioxide separations from nitrogen and methane. The manuscript will also discuss, to a lesser extent, organic vapor permeabilities, olefin/paraffin, and oxygen/nitrogen separations. While some researchers have published SILM related material on sulfur dioxide [6], carbon monoxide [7], or hydrogen [8] separations, this manuscript will not discuss them since the literature database is not yet extensive enough for the chosen type of analysis. To be clear, this manuscript focuses on membrane separations and does not comment on the optimization of RTILs for absorption or adsorption separations.

2. Theory

Research on using SILMs for gas separations dates back to at least 1995 [9]. Over the years a number of groups have contributed to the fundamental and systematical understanding of gas separation and transport in RTILs. These contributions have resulted in predictive correlations for gas solubilities in RTILs [10–16], gas diffusivities in RTILs [17–21], RTIL and SILM gas pair selectivity dependence on RTIL molecular structure [22], temperature [23], and mixed gas feeds [3].

Robeson [24] and Freedman [25] qualitatively and quantitatively studied the separation performance of polymer membranes. Their research proves that, based on the physical chemistry of polymers, a trade-off exist between rate of separation (permeability) and the quality of separation (selectivity) [24]. Furthermore, polymer physical chemistry sets an upper limitation of selectivity vs. permeability for any gas pair irrelevant of the polymer structure [24,25]. While researchers have discovered means to exceed this upper bound, the “Robeson Plot” has benefitted membranologist by directing resources away from non-fruitful pathways.

To begin the determination of upper bounds for SILMs, we will start with the assumption that transport through a SILM follows a solution/diffusion mechanism [1,17]

$$P = S \times D \tag{1}$$

where P is permeability, S is solubility (in moles per volume per partial pressure), and D is diffusivity. We will first look at the literature models for the components, S and D, in RTILs before comparing the literature models against SILM data later in this manuscript.

2.1. Solubility and solubility selectivity models

A number of proposed models (such as COSMO-RS [13], UNIFAC, [14], Group Contribution Methods [15], and LFER/Abraham [16]) give accurate predictions of gas solubilities in RTILs. However, for permeability upper bound prediction in SILMs, the most useful models are those based on the regular solution behavior of RTILs [26], specifically the Camper Molar Volume Model [5,22] and the Kilaru Viscosity Model [7]. Even though limited to imidazolium-RTILs, the Camper Molar Volume Model gives useful predictions for gas solubility, maximum gas solubility, and solubility selectivity [22]. In solubility form, the Camper Model is

$$S\left(\frac{\text{mol}}{\text{L}}\right) = \left\{\left[\exp\left(\alpha + \frac{\beta}{(V_{\text{RTIL}})^{4/3}}\right) - 1\right] V_{\text{RTIL}}\right\}^{-1} \tag{2}$$

where α and β are gas specific parameters, S is the gas solubility, and V_{RTIL} is the RTIL molar volume. The maximum gas solubility occurs at the RTIL molar volume calculated from setting the derivative of Eq. (2), with respect to molar volume, equal to zero [22]

$$V_{\text{RTIL}}\,(\text{for max } S) \cong \left(\frac{4\beta}{3}\right)^{3/4} \tag{3}$$

The Camper Model’s predicted solubility selectivity results from forming a ratio of Eq. (2) solved for each gas of interest in the gas pair. The result is a prediction of an exponential increase in selectivity as the RTIL molar volume decreases [22]. We will show in the following manuscript that these predictions from the Camper Model are relevant in developing an upper bound for potential performance in all SILMs, not just imidazolium-SILMs. There are two key points of the Camper Model for separations dominated by gas solubility: first, the smaller the RTIL molar volume the better the selectivity; and second, as the molar volume increases the amount of gas absorbed per volume of fluid initially increases and then starts to decrease.

The Kilaru Viscosity Model is not limited to imidazolium-RTILs. However, it is a two parameter model, RTIL molar volume and RTIL viscosity. Following a development similar to that in Camper et al. [22], the solubility form of the Kilaru Viscosity Model [7] is

$$\ln\ S \cong B + C(\delta_{\text{RTIL}})^2 \tag{4}$$

and

$$\delta_{\text{RTIL}} = \left\{\frac{K_v RT}{V_{\text{RTIL}}} \ln\left(\frac{1\times10^{-9}\mu V_{\text{RTIL}}}{hN_A}\right)\right\}^{1/2} \tag{5}$$

where B and C are gas specific parameters, S is solubility, δ_{RTIL} is the RTIL solubility parameter, μ is the dynamic viscosity of RTIL in cP, V_{RTIL} is the RTIL molar volume in cm^3/mol, h is Plank’s constant in J s, N_{A} is Avogadro’s number, K_v is a proportionality constant, R is ideal gas constant, and T is system temperature. Therefore, the Kilaru model states that if the objective is a solubility model applicable to all RTILs then viscosity needs to be considered in addition to RTIL molar volume.

2.2. Diffusivity models and diffusivity selectivity

Other groups have studied diffusivity in RTILs [18,19]; but have focused mainly on imidazolium-RTILs. Our group has developed correlations for ammonium- [21] and phosphonium-RTILs [20] in addition to imidazolium [17] with the following form:

$$D_{1,\text{RTIL}} = A\frac{V_{\text{RTIL}}^{a}}{\mu_{\text{RTIL}}^{b} V_1^{c}} \tag{6}$$

where A, a, b, and c are RTIL-Class specific parameters, $D_{1,\text{RTIL}}$ is the diffusivity of solute, 1, in the RTIL, V_{RTIL} is the RTIL molar volume, V_1 is the solute molar volume, and μ_{RTIL} is the RTIL viscosity. While we do not recommend a diffusivity correlation covering all RTILs, we have noted certain “universal” trends that are useful for developing an upper bound for SILM performance [21]. Specifically, diffusivity scales inversely with the square-root of viscosity, $b \approx 0.5$, and inversely to the solute molar volume to the power of 1–1.3. This means that diffusivity in RTILs is less dependent on viscosity, and more dependent on solute size, than predicted by the conventional Stokes–Einstein model. Furthermore, for RTILs with cations having long flexible alkyl chains ($R \geq 4$), diffusivity may have a void space dependence. For this reason the power of “a” changes with RTIL classification, ranging from 0 for imidazolium-RTILs (R generally <4) to 1.57 for ammonium-RTILs (R generally >4).

The ratio of Eq. (6) for two different diffusing solutes will give insights into the role of diffusion selectivity in SILMs

$$\alpha_{1,2}(\text{diffusivity}) \approx \left(\frac{V_2}{V_1}\right)^{1.15} \tag{7}$$

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