Use of Ionic Liquids for Membrane-based and Electrochemically-driven Gas Separations

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Ionic compounds that are liquids near room temperature (RTILs) have a number of properties (e.g. low volatility and high conductivity) which make them attractive as solvents, electrolytes and membrane materials [1]. This presentation will discuss the use of RTILs for gas separations.

Supported liquid membranes (SLMs) offer the potential for gas separations that are both highly selective and productive (high flux). SLMs prepared from conventional solvents are impractical for gas separations because of evaporation; therefore, the low volatility of RTILs make them an attractive class of materials for SLMs. Recently, we reported carbon dioxide, methane and nitrogen permeabilities for SLMs prepared from [emim][$(CF_3SO_2)_2N$], [emim][CF_3SO_3], [emim][$(CN)_2N$] (where emim is 1-ethyl-3-methylimidazolium) and [trihexyltetradecylphosphonium][Cl] [2]. The values can be used to calculate ideal selectivities for CO_2/CH_4 and CO_2/N_2 separations. For certain RTILs, the selectivity/permeability values are above the so-called upper-bound determined for dense polymer membranes (Robeson plot).

A key factor in determining which RTILs will be useful for a given gas separation is solubility. It would be useful to have a model that allows solubility for gases in RTILs to be predicted from easily determined physical properties. We have been exploring the use of Regular Solution Theory (RST) in this regard [3]. By estimating solubility parameters for a series of RTILs and combining them with known solubility parameters for gases such as CO_2 and light hydrocarbons, relative gas solubility can be accurately predicted. The RST model can also be used to predict gas solubility at elevated temperatures and pressures.

The utility of RTILs for gas separation can be enhanced by adding selective complexing agents. Under certain conditions, the complexing agent can result in facilitated transport in SLMs which enhances both selectivity and permeability. If the binding constant for the complexing agent can be modulated through a redox reaction, gases can be selectively separated and concentrated in an electrochemical process. We have shown that di-tert-butyl-benzoquinone can be used in such a process to separate/concentrate CO_2 from N_2 using either propylene carbonate or [bmim][PF_6] [4].

One difficulty with using complexing agents to enhance RTIL-based gas separations is achieving high concentrations of the complexing agents. In principle, this difficulty can be overcome by incorporating the complexing agent into the structure of the RTIL. Attempts to synthesize and characterize RTILs with covalently-bound quinone and ferrocene functionality will be discussed.

References:

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