ACCOUNTS
of chemical research

Room-Temperature Ionic Liquids and Composite Materials: Platform Technologies for CO_2 Capture

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RECEIVED ON JUNE 16, 2009

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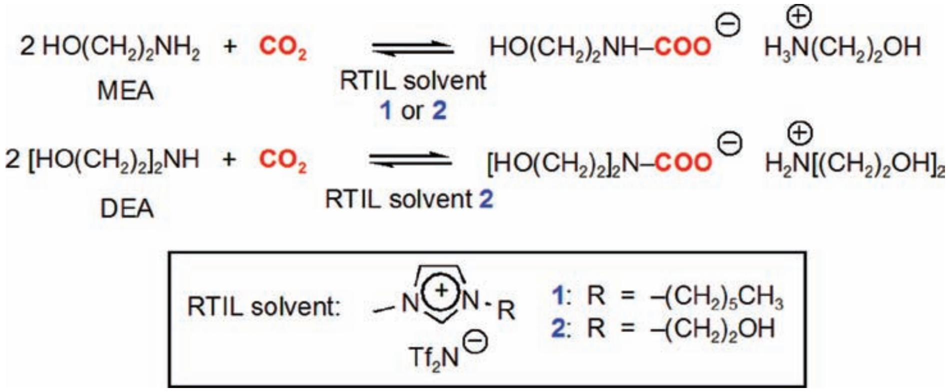

Clean energy production has become one of the most prominent global issues of the early 21st century, prompting social, economic, and scientific debates regarding energy usage, energy sources, and sustainable energy strategies. The reduction of greenhouse gas emissions, specifically carbon dioxide (CO_2), figures prominently in the discussions on the future of global energy policy. Billions of tons of annual CO_2 emissions are the direct result of fossil fuel combustion to generate electricity. Producing clean energy from abundant sources such as coal will require a massive infrastructure and highly efficient capture technologies to curb CO_2 emissions.

Current technologies for CO_2 removal from other gases, such as those used in natural gas sweetening, are also capable of capturing CO_2 from power plant emissions. Aqueous amine processes are found in the vast majority of natural gas sweetening operations in the United States. However, conventional aqueous amine processes are highly energy intensive; their implementation for postcombustion CO_2 capture from power plant emissions would drastically cut plant output and efficiency. Membranes, another technology used in natural gas sweetening, have been proposed as an alternative mechanism for CO_2 capture from flue gas. Although membranes offer a potentially less energy-intensive approach, their development and industrial implementation lags far behind that of amine processes. Thus, to minimize the impact of postcombustion CO_2 capture on the economics of energy production, advances are needed in both of these areas. In this Account, we review our recent research devoted to absorptive processes and membranes.

Specifically, we have explored the use of room-temperature ionic liquids (RTILs) in absorptive and membrane technologies for CO_2 capture. RTILs present a highly versatile and tunable platform for the development of new processes and materials aimed at the capture of CO_2 from power plant flue gas and in natural gas sweetening. The desirable properties of RTIL solvents, such as negligible vapor pressures, thermal stability, and a large liquid range, make them interesting candidates as new materials in well-known CO_2 capture processes. Here, we focus on the use of RTILs (1) as absorbents, including in combination with amines, and (2) in the design of polymer membranes. RTIL amine solvents have many potential advantages over aqueous amines, and the versatile chemistry of imidazolium-based RTILs also allows for the generation of new types of CO_2-selective polymer membranes.

RTIL and RTIL-based composites can compete with, or improve upon, current technologies. Moreover, owing to our experience in this area, we are developing new imidazolium-based polymer architectures and thermotropic and lyotropic liquid crystals as highly tailorable materials based on and capable of interacting with RTILs.

10.1021/ar9001747

Integration of Room-Temperature Ionic Liquids into Industrial Processes

The global-scale engineering challenges associated with realizing clean energy production (from fossil or renewable sources), implementing large scale carbon capture and sequestration (CCS),[1] and developing "green" industrial processes are unprecedented. While the magnitude of these tasks will drive the discovery and development of many unforeseen technologies in the long term, new ways of thinking about existing technologies are the most effective mechanisms to most rapidly begin tackling these critical issues.

Room-temperature ionic liquids (RTILs) present many opportunities to reassess and optimize existing technologies and processes. RTILs are classified as (largely) organic salts that are molten at ambient conditions. Three intrinsic properties of RTILs that differentiate them from common organic solvents and water are nonvolatility, thermal stability, and tunable chemistry.[2] Additionally, RTILs provide a unique solvent environment for carrying out chemical reactions.[3] These properties can impart significant advantages to RTILs for chemical engineering applications, especially in gas separations.[4,5] While RTILs are certainly much more expensive than common organic solvents and water, detailed engineering designs taking into account the unique properties of RTILs could reveal unforeseen process benefits and improvements that offset RTIL costs.

In order to integrate RTILs into existing industrial processes, there must first be a thorough understanding of their true capabilities and limitations. While the unique properties of RTILs make them undoubtedly amazing materials, their performances should not be expected to exceed conventional methodologies in every application. Often, the combination of RTILs with one or more non-RTIL components may be required to produce an optimal, RTIL-based "hybrid" solution amenable to use within an existing process. Such an approach may prove much more attractive than attempting to incorporate the desired functionality into the RTIL itself.

We find that imidazolium systems, which comprise the vast majority of RTIL-related research, are an especially attractive platform for chemical engineering applications. This Account focuses on our efforts in utilizing and understanding the properties of imidazolium-based RTIL solvents with respect to CO_2 capture,[4,6−12,16−19] as well as designing new polymers[13−15] and composites[21−23] for use as CO_2-selective membranes.

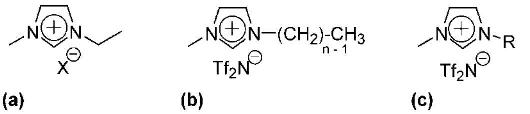

FIGURE 1. Families of imidazolium-based RTILs: (a) $[C_2mim][X]$; (b) $[C_nmim][Tf_2N]$; (c) $[Rmim][Tf_2N]$.

RTIL-Based Solvents for Postcombustion CO_2 Capture and Natural Gas Sweetening

Aqueous amine processes are currently used to remove CO_2 in more than 95% of U.S. natural gas sweetening operations.[24,25] While aqueous amine solutions are effective to remove CO_2 from natural gas under a variety of conditions, aqueous amine processes often suffer from issues with corrosion, amine degradation, and solvent losses.[26] Furthermore, the use of aqueous amine processes is highly energy intensive, largely as a consequence of the thermodynamic properties of water.[26] Were conventional aqueous monoethanolamine (MEA) technologies to be applied to postcombustion CCS processes at coal-fired power plants, it is estimated that output would likely drop by 30% or more, driving down efficiencies while significantly increasing the cost of energy (COE).[27] Improved CO_2 capture technologies are highly desirable to improve the economics of both natural gas sweetening and CCS.

A great deal of effort has been focused on the potential of RTILs as physical solvents (i.e., without chemical reaction with CO_2) for natural gas sweetening (CO_2/CH_4) and CCS from the power plant flue gas (CO_2/N_2).[4] To address the potential viability of RTILs in industrial CO_2 separation applications, we undertook fundamental studies aimed at determining the solubility of CO_2, N_2, and CH_4 in common RTILs.[4,6,7,9−12,16−19] We initially focused on the family of RTILs composed of a 1-ethyl-3-methylimidazolium cation paired with various anions (herein referred to as $[C_2mim][X]$ RTILs) (Figure 1a) and related 1-*n*-alkyl-3-methylimidazolium cations with Tf_2N anions (herein referred to as $[C_nmim][Tf_2N]$ RTILs) (Figure 1b). The large amounts of gas solubility and selectivity data generated from these studies enabled us to use regular solution theory (RST) to formulate predictive models for both CO_2 solubility and selectivity in RTILs.[7,9,10,16,17] The RST-based models that we employed required molar volume as the sole input needed to predict gas solubility and separation performance. These models enable the rapid selection of an RTIL with particular properties and also serve to predict performance trends in RTILs of interest if no experimental data exists.[10]

While the early $[C_2mim][X]$ and $[C_nmim][Tf_2N]$ RTILs were convenient to synthesize, they did not appear to us to be the ideal candidates for use as physical solvents in CO_2 separations. The vast amounts of research in gas separations with organic solvents and polymers illustrate that alkyl chains are most often not the functional group of choice for separating CO_2 from N_2 and CH_4.[28] Materials containing polar groups such as ethers and nitriles exhibit larger CO_2 solubility levels and are much more selective for CO_2 relative to their hydrocarbon analogues.[28] We thus synthesized two series of functionalized 1-*R*-3-methylimidazolium cations with Tf_2N anions (herein referred to as [Rmim][Tf_2N]) RTILs (Figure 1c), where R is various lengths of a methyl-terminated oligo(ethylene glycol) unit[12] or a nitrile-terminated alkyl chain.[18]

[Rmim][Tf_2N] RTILs containing ether and nitrile groups were found to exhibit selectivities for CO_2/N_2 and CO_2/CH_4 that were 25−75% greater than their [$C_n$mim][Tf_2N] analogues.[12,18] Functionalization had little effect on CO_2 solubility levels in the [Rmim][Tf_2N] RTILs relative to [$C_n$mim][Tf_2N] analogues.[12,18] Because the original RST models did not predict the enhanced CO_2 selectivity in the functionalized systems,[10] we employed a group contribution approach to assign solubility parameters to [$C_n$mim][Tf_2N] and [Rmim][Tf_2N] RTILs.[18] By breaking down RTILs into their constituent parts, we were able to correlate higher solubility parameters with increasing CO_2 selectivity.[18] The success of the group contribution approach in predicting CO_2 selectivity trends based on chemical structure motivated us to further apply this methodology to [Rmim][Tf_2N] RTILs to a variety of other functional groups including benzyl,[4] fluoroalkyl,[19] and silicon-based[4] units. The group contribution approach was again accurate in predicting that [Rmim][Tf_2N] RTILs with lower calculated solubility parameters relative to [$C_n$mim][Tf_2N] RTILs correlated with reduced CO_2 selectivity.[4,19] Thus, the use of RST and group contributions provides two powerful tools to rapidly design and select imidazolium-based RTILs as physical (i.e., nonreactive) solvents for CO_2 separations.

During the course of our systematic studies on the influence of chemical structure on CO_2 separations in imidazolium-based RTILs, it became apparent that the physical solubility of CO_2 in RTILs (moles gas/volume RTIL) remained on the lower end of the levels observed in common organic solvents.[4] Given their performance levels, industrial applications of RTILs for CO_2 separations would appear limited to situations where CO_2 was present at high concentrations and high pressures.[26] Industrial processes employing physical solvents for selective CO_2 removal include Rectisol and Selexol, which employ MeOH[29] and poly(ethylene glycol),[30] respectively. Further efforts to increase physical solubility of CO_2 in [Rmim][Tf_2N] RTILs did not appear to be a viable research path, yet improvements in CO_2 uptake could most likely be made through chemical complexation of CO_2 through addition of various amines to the RTIL solvent.[20]

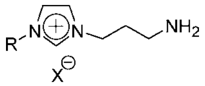

FIGURE 2. General representation of amine-functionalized "task-specific" ionic liquids.

In 2002, Davis and co-workers published the first report of a "task-specific" ionic liquid (TSIL) featuring a primary amine tethered to an imidazolium cation (Figure 2, where R = *n*-Bu, X = BF_4).[31] This TSIL was reported to be capable of reversibly capturing up to 1 mol of CO_2 per 2 mol of TSIL, a level more than 100 times greater than the physical CO_2 uptake in [Rmim][Tf_2N] solvents at similar temperature and pressure conditions.[31] This example of a functionalized RTIL as a nonvolatile chemical (reactive) solvent for CO_2 separations was certainly of great interest to many research groups, including our own. As we began working with an analogue of this TSIL (Figure 2, R = Me, X = Tf_2N), several major limitations of the amine-functionalized TSIL approach to CO_2 capture rapidly became apparent. The synthesis of amine-functionalized TSILs requires more steps than a typical [Rmim][Tf_2N] RTIL, including the removal of a protecting group.[31] The resultant TSIL is quite viscous at ambient temperature and becomes almost intractable after reaction with CO_2.[31,32] While we certainly appreciated the novelty of amine-functionalized TSILs, we sought ways by which to improve upon the concept of combining the capture performance of amines with the desirable properties of RTILs.

Our initial, but short-lived, efforts centered on dissolving the TSIL in a common RTIL, [C_6mim][Tf_2N], to reduce the overall viscosity associated with the TSIL and create a solution that could be processed in conventional gas sweetening equipment. While the solution was capable of absorbing 1 mol of CO_2 per 2 mol of amine-functionalized TSIL at pressures below 1 atm (as well as additional uptake of CO_2 in the physical RTIL solvent), the viscosity was still much greater than that of [C_6mim][Tf_2N] alone, and the intensive synthesis of the TSIL still presented issues for an industrially viable CO_2 capture solvent.

The concept of tethering amines to cations (or anions) places constraints on the types of amines that may be used as well as on amine concentration in solution. We began to view the combination of [Rmim][Tf_2N] RTILs with commodity alkanolamines as a much more viable approach to achieve high levels of reversible CO_2 capture in RTIL solvents.[20] Through straightforward mixing experiments, we found that MEA was soluble in [Rmim][Tf_2N] RTILs.[20] MEA is a highly

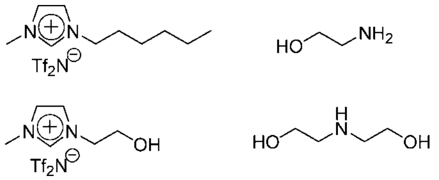

FIGURE 3. [Rmim][Tf_2N] RTILs and alkanolamines of interest for CO_2 capture.

effective agent to capture CO_2 as a carbamate salt, even at very low partial pressures of CO_2.[20,26,27] In order to assess the performances of RTIL−amine solutions relative to amine-functionalized TSILs, we examined low pressure (1 atm) CO_2 capture in equimolar solutions containing RTILs and alkanolamines (Figure 3).[20]

RTIL−MEA solutions were able to rapidly reduce the concentration of CO_2 in the feed gas to concentrations of parts per million (ppm), even at low CO_2 partial pressure (<1 mmHg).[20] Interestingly, MEA−carbamate was found to precipitate from the RTIL solution,[20] which is a behavior not observed in aqueous solution.[26] We have since found that the precipitation of MEA−carbamate does not occur in other [$C_n$mim][X] RTILs, such as [C_2mim][dca], suggesting that this behavior may be a consequence of the Tf_2N anion. Through inclusion of a primary alcohol on the imidazolium cation of the [Rmim][Tf_2N] RTIL, we were also able to dissolve diethanolamine (DEA) to capture CO_2.[20] DEA, a secondary amine, can be employed to capture CO_2 at moderate partial pressures.[26] While the capture of CO_2 by a RTIL−DEA solution does not proceed to the levels observed in RTIL−MEA solutions, the capture is also more readily reversible.[20]

Because RTIL−amine solutions are highly tunable systems for CO_2 capture, we are continually exploring aspects of this technology relating to CCS and natural gas sweetening. One pursuit is the selective separation of H_2S from CO_2, which are often found together in natural gas wells.[26] The combination of RTILs with tertiary or hindered secondary amines may hold promise for addressing this important separation.

Designing Polymer Gas Separation Membranes around RTILs

Membranes represent an alternative mechanism by which CO_2 may be separated from N_2 and CH_4 in industrial processes.[25,33−35] High-throughput, highly selective polymer membranes may represent a long-term alternative to amine-based processes for certain CO_2 separation applications.[25,35] Natural gas processing with polymer membranes is a small but growing component of commercial sweetening applications, applicable at high CO_2 concentrations and low gas throughput.[25,35] Combined amine−membrane processes are favorable at high CO_2 concentrations and high natural gas throughput.[25] Baker has recently published an excellent review on this topic that may be consulted for a more in depth discussion.[25]

The utility of polymer membranes in various roles for CO_2 capture from fossil fuel burning power plants is also under consideration.[36] In postcombustion CO_2 capture, a membrane would be used to separate CO_2 from flue gas, largely composed of N_2.[36] Membranes might also be used for an oxy-combustion configuration, with the membrane used to separate O_2 from N_2 (i.e., air separation).[36] By combustion of fossil fuels in an O_2-rich environment, ideally the only gases present in the exhaust stream products would be CO_2 and H_2O, the latter of which would be condensed and the former compressed and introduced into a pipeline for sequestration or beneficial reuse.[36] A thorough discussion and modeling of the potential advantages and limitations of membranes for CCS can be found in a work by Favre.[36]

Given their CO_2-selective properties, there has also been a great deal of interest in using RTILs as the selective component in membranes.[4,8,10,13−15,19,21,22,37] A straightforward approach to use RTILs in a membrane configuration is to employ supported ionic liquid membranes (SILMs).[4,8,10,19] In general, supported liquid membranes (SLMs) are composed of a liquid immobilized within a polymer or inorganic support.[38] SLMs typically provide larger gas permeabilities than conventional polymer membranes, because gas diffusion through a dense liquid film is often much more rapid than that through a rubbery or glassy polymer.[38] However, traditional SLMs suffer from issues relating to evaporative losses of the liquid phase into the gas stream, resulting in degradation of membrane integrity and loss of selectivity.[39] SILMs circumvent this limitation, because the RTIL component cannot evaporate.[4,8,10,19] Our group was among the first to publish on the potential of SILMs in CO_2 separations.[8] Evaluation of several different imidazolium-based RTILs revealed that SILMs possessed permeability and selectivity properties for CO_2/N_2 that were superior to most conventional polymer membranes when viewed in the context of a "Robeson Plot".[4,8,10,33,34] CO_2/CH_4 separation appeared to be a less promising application for SILMs when analyzed via an analogous "Robeson Plot" for that gas pair.[4,8,10,33,34]

One limitation of SILMs (and SLMs in general) is that the liquid component is subject to "blow out" through the pores of the support should the pressure drop across the membrane exceed the capillary forces stabilizing the liquid within the matrix.[39] Additionally, polymer membranes are much more amenable than SLMs to being produced as high flux ultrathin

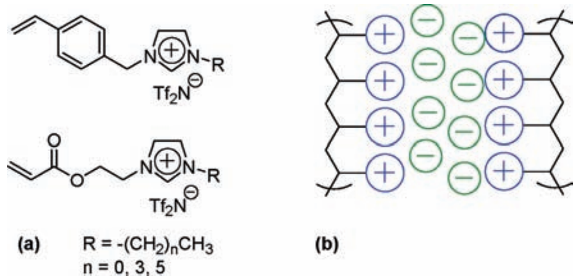

FIGURE 4. (a) First generation RTIL monomers and (b) general representation of a poly(RTIL) formed from these monomers.

(<500 nm) films for industrial applications. We proposed that RTIL-based membranes with a greater degree of stability under pressure might be formed through polymerization of an RTIL-based monomer to create a polymerized RTIL or "poly(RTIL)".[10]

Because solution diffusion (SD) is the dominant mode of transport through a dense liquid or polymer film, the permeability (*P*) of a molecule is defined as the product of its solubility (*S*) and diffusivity (*D*) (eq 1).[40] Barrers (1 barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} (cm Hg)$^{-1}$) are the common unit used to express gas permeabilities in polymer membranes.

$$P = SD \tag{1}$$

Selectivity ($\alpha_{i,j}$) is taken as the ratio of permeabilities for a given gas pair and, based on eq 1, can be attributed to both solubility and diffusion contributions (eq 2).

$$\alpha_{i,j} = \frac{P_i}{P_j} = \frac{S_i}{S_j}\frac{D_i}{D_j} \tag{2}$$

Using RST-based gas solubility models and assuming that gas diffusion coefficients would be reduced by up to several orders of magnitude upon polymerization, there still existed a wide performance window for poly(RTIL)-based membranes to exceed the "upper bound" of the Robeson Plot for CO_2/N_2, while a much more narrow scenario presented itself for CO_2/CH_4.[10] Thus, the pursuit of poly(RTIL) membranes as a platform for CO_2 separation from power plant flue gas appeared to be warranted.

The early poly(RTIL) materials presented by Ohno for ion conductivity[41] and Radosz for CO_2 sorption[42] were used as the basis for our initial poly(RTIL) membranes studies.[13] We chose to evaluate a series of imidazolium-based RTILs bearing various length alkyl substituents and polymerizable units composed of a styrene or acrylate group (Figure 4a).[13] By coating these monomers (mixed with a small amount of photoinitiator and cross-linker) on a porous support and through subsequent photopolymerization, we were able to form poly(RTIL) materials as thin (~150 μm) films and study their properties and performances relating to CO_2, N_2, and CH_4.[13] A general representation of a poly(RTIL) with polymer-bound cations is presented in Figure 4b.

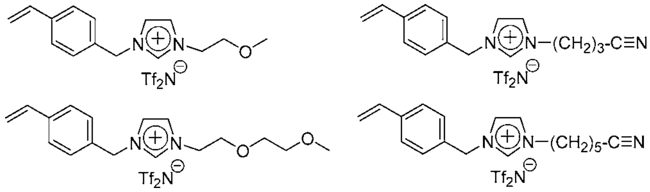

FIGURE 5. RTIL monomers with ether and nitrile groups.

In our first study, we found that CO_2 permeability and selectivity was largely a function of the length of the alkyl chain attached to the imidazolium cation, while the type of polymer backbone formed from the radical polymerization had little effect on performance.[13] We also determined that poly(RTIL) membranes behaved similarly to conventional polymer membranes, rather than SILMs, as a distinct "flux-selectivity trade-off" was observed.[13,33,34] While increasing the length of the alkyl substituent increased CO_2 permeability (within a range of 9−39 barrers), it also resulted in reduced CO_2/N_2 (from 32 to 28) and CO_2/CH_4 (from 39 to 17) selectivity. However, as the performances of these initial poly(RTIL) membranes appeared to closely approximate the upper bound of a Robeson Plot for CO_2/N_2,[13] we were motivated to find mechanisms to improve their performance.

Through an approach similar to that employed to improve CO_2 selectivity in bulk RTIL fluids, we found that replacing the alkyl groups on the RTIL monomers with oligo(ethylene glycol) and nitrile-terminated alkyl substituents (Figure 5) also improved CO_2/N_2 and CO_2/CH_4 selectivities in the resultant poly(RTIL) membranes (39 to 44 and 29 to 37, respectively).[14] For poly(RTILs) containing pendant nitrile units, gas permeability was greatly reduced (4−8 barrers) relative to the alkyl-functionalized analogues, a property typically associated with polymers containing nitrile side groups.[13,14] However, poly(RTIL) membranes containing oligo(ethylene glycol) units exhibited CO_2 permeabilities (16−22 barrers) that were on par with the alkyl analogues.[13,14]

A less successful approach was to create polymer membranes fabricated from self-cross-linkable gemini RTILs (GRTILs) (Figure 6a,b). As a result of their highly cross-linked structures, CO_2 permeability (4 barrers) and selectivity (CO_2/N_2 = 22−28, CO_2/CH_4 = 27−32) were significantly reduced relative to the side chain poly(RTIL) membranes produced from monomers shown in Figures 4 and 5. While the properties of poly(GRTILs) suggest they may be useful as barrier films (materials that greatly restrict the transport of one or more gas species), we chose not to pursue this route further.

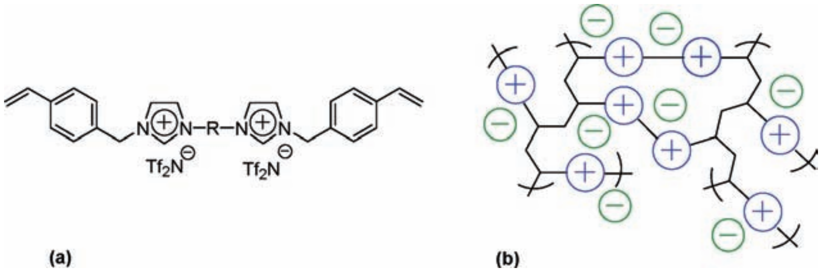

FIGURE 6. General structures of (a) self-cross-linking GRTILs and (b) poly(GRTIL) networks.

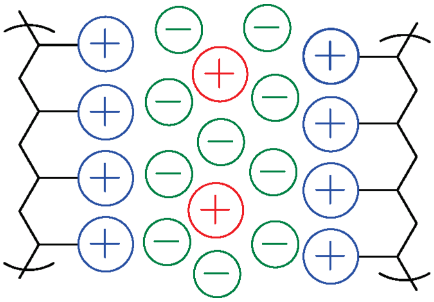

FIGURE 7. Representation of a poly(RTIL)−RTIL composite containing 20 mol % "free" cations (red).

At this stage, it became apparent that functionalization of the RTIL monomer alone could not produce the large gains in gas permeability required for poly(RTIL) membranes to be competitive with more common polymers such as poly(ethylene glycol) (PEG) in CO_2/N_2 membrane separations. We began to view the concept of a poly(RTIL)−RTIL composite membrane as a way to achieve greater gas permeability while maintaining CO_2 selectivity and retaining material stability.[21]

Poly(RTIL)−RTIL composites are formed from the polymerization of an RTIL-based monomer in the presence of nonpolymerizable RTIL.[21−23] For an imidazolium-based RTIL monomer, the resultant composite contains polymer-bound cations, "free" anions, and "free" cations, represented in Figure 7.

Poly(RTIL)−RTIL composites are unique materials where the polymer has been tailored for maximum compatibility with the RTIL component. Thus, the large degree of ionic interactions between the poly(RTIL) and RTILs is much stronger than any interactions between conventional polymers and RTILs.[21−23,43] This is where poly(RTIL)-RTIL composite membranes fundamentally differ from SILMs: the electrostatic forces that hold the RTIL within the poly(RTIL) matrix should not be overcome by applied pressure alone.[21−23,43] Indeed, in our experiences, it appears that the "free" RTIL component must be screened from interacting with the poly(RTIL) through solvation by molecules such as MeOH in order to be removed from the poly(RTIL)−RTIL composite.

Our initial proof-of-concept work in this area demonstrated that polymerization of a an RTIL monomer in the presence of 20 mol % [C_2mim][Tf_2N] formed a poly(RTIL)−RTIL composite that exhibited CO_2 permeability of 44 barrers, a gain of ~400% relative to the analogous neat poly(RTIL). Selectivities in the composite were 39 for CO_2/N_2 and 27 for CO_2/CH_4, respective differences of 33% and −25% compared with the neat poly(RTIL).

Our following work focused on changing the anion species associated with the free RTIL component and using an RTIL monomer with a pendant monoether functionality (Figure 5) to form the poly(RTIL) component. We found that both of these parameters can influence gas permeability and CO_2 selectivity. Poly(RTIL)−RTIL composites containing free [C_2mim] cations and only Tf_2N anions exhibited the greatest CO_2 permeability at 60 barrers, or an increase of 275% relative to the neat poly(RTIL). Slight reductions in CO_2/N_2 and CO_2/CH_4 selectivities were observed relative to composites containing [C_2mim] cations with mixtures of Tf_2N and other anion species such as dicyanamide (dca), triflate (OTf), and hexafluoroantimonate (SbF_6). It was proposed that as Tf_2N is the largest anion (in terms of its contribution to the molar volume of the parent [C_2mim]-based RTIL), it created a material with more free volume and thus allows for more rapid gas transport.

After assessing the effects of anion type on membrane performance, we continued this research direction by examining the effects of [Rmim][Tf_2N] RTILs in poly(RTIL)−RTIL composite membranes, again using a monoether-functionalized RTIL monomer (Figure 5) to form the poly(RTIL) scaffold. The RTIL monomer was polymerized in the presence of [Rmim][Tf_2N] RTILs containing alkyl, ether, nitrile, fluoroalkyl, and siloxane groups. These groups were chosen based on analogy to functional groups found in organic solvents and polymers whose behaviors with respect to CO_2 separations have been well-documented. We found that the nature of the functional group impacts both gas permeability and CO_2 selectivity. While composites containing alkyl, ether, and fluoroalkyl groups experienced very similar CO_2 permeabilities (~50 barrers) and selectivities ($CO_2/N_2 \approx 37$, $CO_2/CH_4 \approx 26$), the composites containing nitrile and siloxane functionalities produced strikingly different results. The poly(RTIL)−RTIL composites containing free cations with a nitrile group displayed the smallest CO_2 permeability in the study (33 barrers) but the largest separation selectivities ($CO_2/N_2 = 40$ and $CO_2/CH_4 = 28$). In contrast, the composite containing a siloxane functionality produced the most permeable membrane, with a CO_2 permeability of 55 barrers, but the smallest separation selecitivities ($CO_2/N_2 = 33$; $CO_2/CH_4 = 20$). Our previous work with this RTIL showed that when used in the SILM configuration, the siloxane functionality displayed large CO_2 permeability (770 barrers) but strikingly low CO_2/N_2 and CO_2/CH_4 separation selectivities among [Rmim][Tf_2N] RTILs (19 and 10, respectively). Because siloxane-based polymers are known to be highly permeable but less selective than polymers such as poly(ethylene glycol) (PEG), this behavior is not unexpected when this functional group is present.

Our current work in this area includes increasing the amount of "free" RTIL within the composite so as to further increase gas permeability. We have already formed stable composites containing as much as 50 mol % "free" cations. Additionally, we are examining the use of polymerizable groups other than styrenes and acrylates so as to reduce the bulkiness of polymer backbone. Reducing the volume of the polymer chain in poly(RTIL)−RTIL composites should increase gas diffusion and permeability and increase overall ionic character.

A promising future pursuit with poly(RTIL)−RTIL composite membranes may be to explore facilitated transport by including a nonvolatile, gas-specific agent. Recently, we were able to successfully form a poly(RTIL)−RTIL composite containing 20 mol % of an amine-functionalized "task-specific" ionic liquid (Figure 2). Our initial results indicate that, at ambient temperature and a CO_2 pressure of 2 atm, facilitated transport does not occur and CO_2 permeability is slightly less than other analogous poly(RTIL)−RTIL composite membranes. Based on results presented by Myers, there is likely a strong temperature dependence on CO_2 transport in this system, with temperatures well above ambient required to achieve facilitated transport of CO_2.[44] Other metal ion-based gas carriers such as Co^{2+} for O_2 and Ag^+ for olefins (i.e., ethylene, propylene) also appear as interesting opportunities for inclusion within poly(RTIL)−RTIL composites.

Outlook

CO_2 separations are just one area where RTILs and RTIL-based composites can be competitive with, or improve upon, current technologies. As more chemical engineers and chemists come to appreciate the capabilities of RTILs, we foresee that the utility of RTILs and related materials as platform technologies with broad industrial applicability will continue to grow. We are confident that a great number of process improvements can be developed around solvents that have no vapor pressure and are thermally stable and liquid over large temperature ranges. The ability to systematically vary the composition of the RTIL or composite material provides many opportunities continuous improvement.

While we expect the use of RTIL-based solvents and polymers for CO_2 capture to produce many more exciting results, the techniques and materials we have developed in those areas are enabling us to begin pursuing new research directions. We are currently examining new imidazolium-based polymer architectures and gemini thermotropic and lyotropic liquid crystals as the next generations of highly tailorable materials that are based on and capable of interfacing with RTILs.

BIOGRAPHICAL INFORMATION

Jason E. Bara was born in 1980 in Elizabeth, NJ. He received degrees in Chemical Engineering from Virginia Commonwealth University (B.S., 2002) and the University of Colorado (Ph.D., 2007). His ongoing work with ionic liquids for engineering applications focuses on energy-efficient CO_2 capture and industrial gas separations. He has used ionic liquids to develop new polymer and liquid crystal architectures and is also active in the areas of functionalized ionic liquids and the chemistry of imidazoles. He has authored more than 25 research publications to date and is named as an inventor on multiple patent applications.

Dean E. Camper received degrees in Chemical Engineering from Mississippi University (B.S., 2002) and the University of Colorado (Ph.D., 2006). He has been involved with ionic liquids for over 6 years, where his early worked focused on understanding thermodynamic properties and developing models to predict these properties. His ongoing work focuses on moving ionic liquid applications from the laboratory to the field. These applications are primarily based on energy-efficient CO_2 and H_2S capture from industrial processes.

Douglas L. Gin received his B.Sc. in Chemistry from the University of British Columbia (1988) and his Ph.D. in Chemistry from Caltech (1993) working with Robert H. Grubbs. After postdoctoral work with Alan G. MacDiarmid at the University of Pennsylvania, he began his independent research career in the Department of Chemistry at the University of California at Berkeley in 1994. In 2001, he moved to the University of Colorado, where he is currently a joint Professor in the Deparment of Chemistry & Biochemistry and the Department of Chemical & Biological Engineering.

Richard D. Noble is the Alfred T. and Betty E. Look Professor of Chemical Engineering at the University of Colorado. His research interests involve experimental and theoretical studies of processes that can attain highly selective chemical separations. He is interested in the use of specific interactions that can enhance the selectivity of a separation process. This specific interaction can involve unique solvents such as ionic liquids, reversible chemical complexation, use of external fields (light or electrical), or nanoporous structures (such as zeolites or lyotropic liquid crystals) to provide the selectivity. He is named as an inventor on over 20 patents and has authored more than 260 research publications, including 11 textbooks and monographs.

FOOTNOTES

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REFERENCES

1 NETL, CO_2 Capture. www.netl.doe.gov/technologies/carbon_seq/core_rd/co2capture.html. Accessed June 2009.

2 Holbrey, J. D.; Rogers, R. D. In *Ionic Liquids in Synthesis*, 2nd ed.; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2007.

3 Chiappe, C. In *Ionic Liquids in Synthesis*, 2nd ed.; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2007.

4 Bara, J. E.; Carlisle, T. K.; Gabriel, C. J.; Camper, D.; Finotello, A.; Gin, D. L.; Noble, R. D. Guide to CO_2 separations in imidazolium-based room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **2009**, *48*, 2739–2751.

5 Anderson, J. L.; Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. In *Ionic Liquids in Synthesis*, 2nd ed.; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2007.

6 Camper, D.; Scovazzo, P.; Koval, C.; Noble, R. Gas solubilities in room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 3049–3054.

7 Scovazzo, P.; Camper, D.; Kieft, J.; Poshusta, J.; Koval, C.; Noble, R. Regular solution theory and CO_2 gas solubility in room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 6855–6860.

8 Scovazzo, P.; Kieft, J.; Finan, D. A.; Koval, C.; DuBois, D.; Noble, R. Gas separations using non-hexafluorophosphate $[PF_6]^-$ anion supported ionic liquid membranes. *J. Membr. Sci.* **2004**, *238* (1−2), 57–63.

9 Camper, D.; Becker, C.; Koval, C.; Noble, R. Low pressure hydrocarbon solubility in room temperature ionic liquids containing imidazolium rings interpreted using regular solution theory. *Ind. Eng. Chem. Res.* **2005**, *44*, 1928–1933.

10 Camper, D.; Bara, J.; Koval, C.; Noble, R. Bulk-fluid solubility and membrane feasibility of Rmim-based room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **2006**, *45*, 6279–6283.

11 Camper, D.; Becker, C.; Koval, C.; Noble, R. Diffusion and solubility measurements in room temperature ionic liquids. *Ind. Eng. Chem. Res.* **2006**, *45*, 445–450.

12 Bara, J. E.; Gabriel, C. J.; Lessmann, S.; Carlisle, T. K.; Finotello, A.; Gin, D. L.; Noble, R. D. Enhanced CO_2 separation selectivity in oligo(ethylene glycol) functionalized room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **2007**, *46*, 5380–5386.

13 Bara, J. E.; Lessmann, S.; Gabriel, C. J.; Hatakeyama, E. S.; Noble, R. D.; Gin, D. L. Synthesis and performance of polymerizable room-temperature ionic liquids as gas separation membranes. *Ind. Eng. Chem. Res.* **2007**, *46*, 5397–5404.

14 Bara, J. E.; Gabriel, C. J.; Hatakeyama, E. S.; Carlisle, T. K.; Lessmann, S.; Noble, R. D.; Gin, D. L. Improving CO_2 selectivity in polymerized room-temperature ionic liquid gas separation membranes through incorporation of polar substituents. *J. Membr. Sci.* **2008**, *321*, 3–7.

15 Bara, J. E.; Hatakeyama, E. S.; Gabriel, C. J.; Zeng, X.; Lessmann, S.; Gin, D. L.; Noble, R. D. Synthesis and light gas separations in cross-linked gemini room temperature ionic liquid polymer membranes. *J. Membr. Sci.* **2008**, *316*, 186–191.

16 Finotello, A.; Bara, J. E.; Narayan, S.; Camper, D.; Noble, R. D. Ideal gas solubilities and solubility selectivities in a binary mixture of room-temperature ionic liquids. *J. Phys. Chem. B.* **2008**, *112*, 2335–2339.

17 Finotello, A.; Bara, J. E.; Camper, D.; Noble, R. D. Room-temperature ionic liquids: Temperature dependence of gas solubility selectivity. *Ind. Eng. Chem. Res.* **2008**, *47*, 3453–3459.

18 Carlisle, T. K.; Bara, J. E.; Gabriel, C. J.; Noble, R. D.; Gin, D. L. Interpretation of CO_2 solubility and selectivity in nitrile-functionalized room-temperature ionic liquids using a group contribution approach. *Ind. Eng. Chem. Res.* **2008**, *47*, 7005–7012.

19 Bara, J. E.; Gabriel, C. J.; Carlisle, T. K.; Camper, D. E.; Finotello, A.; Gin, D. L.; Noble, R. D. Gas separations in fluoroalkyl-functionalized room-temperature ionic liquids using supported liquid membranes. *Chem. Eng. J.* **2009**, *147*, 43–50.

20 Camper, D.; Bara, J. E.; Gin, D. L.; Noble, R. D. Room-temperature ionic liquid - amine solutions: tunable solvents for efficient and reversible capture of CO_2. *Ind. Eng. Chem. Res.* **2008**, *47*, 8496–8498.

21 Bara, J. E.; Hatakeyama, E. S.; Gin, D. L.; Noble, R. D. Improving CO_2 permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid. *Polym. Adv. Technol.* **2008**, *19*, 1415–1420.

22 Bara, J. E.; Gin, D. L.; Noble, R. D. Effect of anion on gas separation performance of polymer−room-temperature ionic liquid composite membranes. *Ind. Eng. Chem. Res.* **2008**, *47*, 9919–9924.

23 Bara, J. E.; Gin, D. L.; Noble, R. D. Effect of “free” cation substituent on gas separation performance of polymer−room-temperature ionic liquid composite membranes. *Ind. Eng. Chem. Res.* **2009**, *48*, 4607–4610.

24 NaturalGas.org, Processing Natural Gas. www.naturalgas.org/naturalgas/processing_ng.asp (Accessed June 2009).

25 Baker, R. W.; Lokhandwala, K. Natural gas processing with membranes: An overview. *Ind. Eng. Chem. Res.* **2008**, *47*, 2109–2121.

26 Astarita, G.; Savage, D. W.; Bisio, A. *Gas treating with Chemical Solvents*; John Wiley & Sons: New York, 1983.

27 Ciferno, J. P.; Fout, T. E.; Jones, A. P.; Murphey, J. T. Capturing carbon from existing coal-fired power plants. *Chem. Eng. Prog.* **2009**, *105*, 33–41.

28 Lin, H.; Freeman, B. D. Materials selection guidelines for membranes that remove CO_2 from gas mixtures. *J. Mol. Struct.* **2005**, *739*, 57–74.

29 Selexol Process. www.uop.com/objects/97%20Selexol.pdf. Accessed June 2009.

30 Rectisol Wash. www.linde-le.com/process_plants/hydrogen_syngas_plants/gas_processing/rectisol_wash.php. Accessed June 2009.

31 Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. CO_2 capture by a task-specific ionic liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926–927.

32 Gutowski, K. E.; Maginn, E. J. Amine-functionalized task-specific ionic liquids: a mechanistic explanation for the dramatic increase in viscosity upon complexation with CO_2 from molecular simulation. *J. Am. Chem. Soc.* **2008**, *130*, 14690–14704.

33 Robeson, L. M. The upper bound revisited. *J. Membr. Sci.* **2008**, *320*, 390–400.

34 Robeson, L. M. Correlation of separation factor versus permeability for polymeric membranes. *J. Membr. Sci.* **1991**, *62*, 165–185.

35 Baker, R. W. Future directions of membrane gas separation technology. *Ind. Eng. Chem. Res.* **2002**, *41*, 1393–1411.

36 Favre, E. Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption? *J. Membr. Sci.* **2007**, *294*, 50–59.

37 Han, X.; Armstrong, D. W. Ionic liquids in separations. *Acc. Chem. Res.* **2007**, *40*, 1079–1086.

38 Kocherginsky, N. M.; Yang, Q.; Seelam, L. Recent advances in supported liquid membrane technology. *Sep. Purif. Technol.* **2007**, *53*, 171–177.

39 Kemperman, A. J. B.; Bargeman, D.; Van Den Boomgaard, Th.; Strathmann, H. Stability of supported liquid membranes: State of the art. *Sep. Sci. Technol.* **1996**, *31*, 2733–2762.

40 Wijmans, J. G.; Baker, R. W. The solution-diffusion model: A review. *J. Membr. Sci.* **1995**, *107*, 1–21.

41 Ohno, H.; Yoshizawa, M.; Ogihara, W. Development of new class of ion conductive polymers based on ionic liquids. *Electrochim. Acta* **2004**, *50*, 255–261.

42 Tang, J.; Tang, H.; Sun, W.; Radosz, M.; Shen, Y. Poly(ionic liquid)s as new materials for CO_2 absorption. *J. Polym. Sci.: Polym. Chem.* **2005**, *43*, 5477–5489.

43 Lodge, T. P. A unique platform for materials design. *Science* **2008**, *321*, 50–51.

44 Myers, C.; Pennline, H.; Luebke, D.; Ilconich, J.; Dixon, J. K.; Maginn, E. J.; Brennecke, J. F. High temperature separation of carbon dioxide/hydrogen mixtures using facilitated supported ionic liquid membranes. *J. Membr. Sci.* **2008**, *322*, 28–31.