Gas separations in fluoroalkyl-functionalized room-temperature ionic liquids using supported liquid membranes

Jason E. Bara [a,b], Christopher J. Gabriel [b], Trevor K. Carlisle [a], Dean E. Camper [a], Alexia Finotello [a], Douglas L. Gin [a,b,*], Richard D. Noble [a,**]

[a] Department of Chemical & Biological Engineering, University of Colorado, Boulder, CO 80309-0424, United States
[b] Department of Chemistry & Biochemistry, University of Colorado, Boulder, CO 80309-0215, United States

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ABSTRACT

A series of four imidazolium salts containing increasing lengths of fluoroalkyl substituents was synthesized. The three that exist as molten salts at 296 K were tested for their gas separation properties relating to CO_2, O_2, N_2 and CH_4 using a supported ionic liquid membrane (SILM) configuration. These fluoroalkyl-functionalized room-temperature ionic liquids (RTILs) were found to exhibit ideal selectivities for CO_2/N_2 separation that were lower than their alkyl-functionalized analogues, but higher ideal selectivity for CO_2/CH_4 separation. The differences in performance of fluoroalkyl-functionalized RTILs relative to their alkyl-functionalized counterparts are explained through the use of solubility parameters, group contributions and in context of the classically observed deviations of fluorocarbons from "regular" solution behavior.

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1. Introduction

Perhaps the most advantageous feature of room-temperature ionic liquids (RTILs), especially those containing imidazolium cations, is that they can be readily tailored with a variety of organic appendages [1–10]. These unique solvents provide scientists and engineers with unprecedented opportunities to incorporate specific functionalities into solvents and working fluids. As RTILs are non-volatile [11], thermally stable [12], largely inflammable [13], and many are of relatively low viscosity [14], they have gained attention as potential replacement media for volatile organic compounds (VOCs) in a variety of applications, especially gas separations [2,3,5,7,15–30].

A great deal of work has been devoted to understanding the behavior of CO_2, and to a lesser extent, light gases (N_2, CH_4, O_2, H_2), acid gases (SO_2, H_2S) and small organics (C_2H_6, C_3H_8, etc.) in imidazolium-based RTILs [2,3,5,7,15–30]. Fig. 1a contains a depiction of imidazolium-based RTILs, where R_1, R_2 and X are chosen from a virtually endless matrix of possibilities capable of producing molten salts at ambient conditions. Fig. 1b displays the structure

of widely used RTILs, the family of 1-*n*-alkyl-3-methylimidazolium bis(trifluoromethane)sulfonimide salts, herein collectively referred to as [$C_n$mim][Tf_2N] RTILs.

The study of imidazolium-based RTILs for gas separations has proceeded with three distinct approaches: direct solubility measurements, modeling and supported ionic liquid membranes (SILMs) [2,5,7,15–30]. The most direct route for obtaining information on the behavior of gases in RTILs has been to measure the ideal (single) gas solubility of a particular species in an RTIL [2,5,7,15–17,19–23,27–30]. These data have been obtained at low and high pressures and varying temperatures using pressure-decay techniques, microbalances and other equipment. Methods such as these have proven reliable for consistently obtaining accurate solubility values for gases in RTILs, especially for those species with high solubility (i.e. CO_2, SO_2). However, as there are perhaps trillions of RTILs that can be synthesized, the experimental determination of gas solubility in each possible fluid represents an impossible task. As such, several groups have presented models using thermodynamic principles such as regular solution theory (RST), equations of state, molecular dynamics or group contributions as predictive guides [16,17,19,20,22,23,28]. By determining just a few physical properties of the RTIL, and accounting for the chemical groups within the structure of the molecule, researchers can obtain predictive information on solubility, diffusivity and gas pair solubility selectivity. However, these methods have currently been applied to only a few gases of interest (primarily CO_2, N_2 and CH_4) and temperatures at or near ambient. Thus, there is still much room to expand the data sets used to formulate the models for the behaviors of gases in RTILs.

* Corresponding author at: Department of Chemical & Biological Engineering, University of Colorado, Boulder, CO 80309-0424, United States. Tel.: +1 303 492 7640; fax: +1 303 492 4341.
** Corresponding author.
E-mail addresses: gin@spot.colorado.edu (D.L. Gin), nobler@colorado.edu (R.D. Noble).
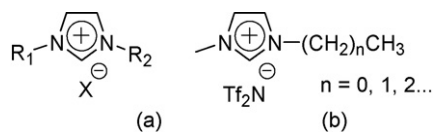
Fig. 1. Generalized structure of imidazolium-based RTILs (a) and representative structure of 1-*n*-alkyl-3-methylimidazolium bis(trifluoromethane)sulfonimide [C$_n$mim][Tf$_2$N] RTILs (b).

Table 2
Tabulated group contributions to solubility parameter for chemical functionalities of interest to this work.

Functional group	F_j (MPa$^{1/2}$ cm^3 mol^{-1})
–CH$_2$–	272
–CH$_3$	473
–CF$_2$–	307
–CF$_3$	561

The third approach to determining the properties of gases in RTILs has been to employ an SILM configuration [15,24–26,29]. By impregnating an RTIL of interest into a porous polymer or inorganic support, information can be readily and rapidly obtained regarding the gas permeability and gas pair selectivity of the RTIL. There has been interest in the use of SILMs for acid gas separations, as certain RTILs are highly permeable and selective for CO$_2$ and SO$_2$ [15,24–26,29]. The ability of RTILs to be stabilized in a highly permeable thin film may prove valuable for industrial natural gas "sweetening" and carbon capture applications. In the long-term, SILMs are perhaps more attractive than bulk-fluid RTILs and pressure swings for the separation of CO$_2$ or SO$_2$. SILMs can be formed with much smaller amounts of RTILs than it would take to process the same volume of gas using absorptive methods. However, the stability of current materials under the conditions of industrial processes (high temperatures and pressures) is of concern [24–26,29]. Regardless of whether they are eventually adopted for large-scale processes, SILM techniques will remain valuable research tools for understanding gas separations in RTILs.

We have previously demonstrated that polar groups such as ethers and nitriles [2,16], when tethered to imidazolium cations, can increase CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivity relative to analogous, imidazolium-based RTILs with alkyl chains tethered to the cation. Examination of the gas separation properties of imidazolium-based RTILs through calculation of solubility parameters (δ) has aided in our understanding of the gas pair selectivity trends associated with functionalization of the imidazolium cation with various chemical substituents [16]. The difference in values of δ for any solvent–solute pair serves as an indication of their mutual miscibility [16,20,21,27,31–34]. In general, the solubility (S) of a gas in a particular solvent is inversely proportional to the square of this difference (Eq. (1)), where 1 is the solvent and 2 is the gas [16,20,21,27,31–34].

$$S_{2,1} \propto \frac{1}{(\delta_1 - \delta_2)^2} \tag{1}$$

Widely accepted values of δ for many gases and organic solvents have been tabulated over several decades [31–35]. Values for the gases of interest to this work are presented in Table 1. We are choosing to use a value of 21.8 MPa$^{1/2}$ for CO$_2$, which has been convincingly demonstrated to better capture the trend of CO$_2$ solubility in a wide variety of organic solvents. Solubility of CO$_2$ in these solvents was demonstrated to be at a maximum when δ = 21.8 ± 0.2 MPa$^{1/2}$ [34] and differs from the traditionally used value of 12.2 MPa$^{1/2}$ [35].

As RTILs are relatively novel compounds and can feature a multitude of interchangeable chemistries, values of δ are not available for the large majority of even the more common of these ionic solvents. Furthermore, δ is traditionally calculated using the enthalpy of vaporization for liquids [31]. This is much more difficult to do with RTILs, as they have a real, but extremely small vapor pressure. Only a few papers thus far have focused on determining these constants for a limited set of RTILs [16,36–38]. We sought to find a method to approximate reasonable values of δ for imidazolium-based RTILs that currently exist as well as those that have not yet been synthesized [16]. To this end, we employed group contribution methods, such as those that have long been used to calculate solubility parameters for polymers and liquid solvents [16,33,39]. The solubility parameter of a molecule is a function of the sum of the various chemical group contributions (F_j) existing within the molecule divided by the molar volume of the molecule (Eq. (2)) [16,33,39].

$$\delta_i = \frac{\sum_j F_j}{V_m} \tag{2}$$

Values of F_j for a large number of chemical groups have been tabulated by Hoy and Small and are available in reference manuals [39]. Group contributions relative to molecules analyzed in this study are presented in Table 2.

Tabulated group contributions such as those above, and literature data relating to experimentally determined values of δ for several RTILs of the family [C$_n$mim][Tf$_2$N], were used to arrive at a value for the group contribution of the ionic pair, which was defined as that of five-membered cation ring, its protons, and its anion partner [16]. The average value obtained for the cationic ring-anion pair was 6330 MPa$^{1/2}$ cm^3 mol^{-1} [16]. While this value appears much larger than a typical value of F_j, it is also a far more complex system than is typically examined [16,33,34,39]. Furthermore, as our work focuses on the effects of substituents on gas separations in imidazolium-based systems, we feel it is appropriate to lump the cationic ring and anion together, as their chemical structures have remained unchanged as various functionalities have been systematically appended [2,16]. Furthermore, tabulated F_j values for ionic groups are not available, and determining the specific F_j-values for an imidazolium cation and various anions is beyond the scope of this or our previous work [16].

In each of the RTIL compounds to which we have applied group contributions, there is consistently a methyl group bound to one nitrogen atom in the ring and a methylene (–CH$_2$–) linkage to the other. Only the chemistry beyond this methylene linkage has been changed. However, the nature of the chemical groups beyond the methylene group can have significant impact on solubility parameter of the RTIL, and in turn, gas separation properties. Tethering of polar groups such as terminal nitriles (–C≡N, F = 725 MPa$^{1/2}$ cm^3 mol^{-1}) [16,39] and ethers (–O–, F = 235 MPa$^{1/2}$ cm^3 mol^{-1}) [2,16,39] to the imidazolium ring resulted in RTILs with higher densities, smaller molar volumes and in turn, larger solubility parameters than their alkyl-functionalized counterparts. These two classes of RTILs with polar appendages exhibited CO$_2$/N$_2$ and CO$_2$/CH$_4$ solubility selectivities (at 40 °C) significantly greater than predicted by our previous simple RST models [2,16,17,19,20,27]. Those RST models employ the molar volume of the RTIL as the sole predictor of gas solubility and gas pair solubility selectivity at a given temperature [17,19,20,27].

Table 1
Solubility parameters (δ) at 298 K for gases of interest to this work.

Gas	δ (MPa$^{1/2}$)
CO$_2$	21.8
N$_2$	5.3
O$_2$	8.2
CH$_4$	11.6